# Towards the use of Adaptive Feedback Control Pulse Shaping to Probe and Control Reactivity of the Metal-to-Ligand Charge Transfer Excited State in Ruthenium(II) Bis-Terpyridine Complexes

by

Joshua Thomas Hewitt

B.S., University of New Mexico, 2006

A thesis submitted to the Faculty of the Graduate School of the University of Colorado in partial fulfillment of the requirements for the degree of Doctor of Philosophy Department of Chemistry and Biochemistry

2013

This thesis entitled: Towards the use of Adaptive Feedback Control Pulse Shaping to Probe and Control Reactivity of the Metal-to-Ligand Charge Transfer Excited State in Ruthenium(II) Bis-Terpyridine Complexes written by Joshua Thomas Hewitt has been approved for the Department of Chemistry and Biochemistry

Niels Damrauer

Garry Rumbles

Date \_\_\_\_\_

The final copy of this thesis has been examined by the signatories, and we find that both the content and the form meet acceptable presentation standards of scholarly work in the above mentioned discipline.

Hewitt, Joshua Thomas (Ph.D., Physical Chemistry)

Towards the use of Adaptive Feedback Control Pulse Shaping to Probe and Control Reactivity of the Metalto-Ligand Charge Transfer Excited State in Ruthenium(II) Bis-Terpyridine Complexes

Thesis directed by Associate Prof. Niels Damrauer

A novel ruthenium (II) polypyridyl complex  $\left[\mathrm{Ru}(\mathrm{bpy}-\mathrm{An})(\mathrm{tpy}-\phi-\mathrm{MV})\right]^{4+}$  (where tpy-An = 4'- $(9-anthrcenyl)-2,2':6',2''-terpyridine and tpy-\phi-MV^{2+} = 4'-(1-(1'-methyl-4,4-bipyridinium-1-yl)-phenyl)-2,2':6',2''-terpyridine and tpy-\phi-MV^{2+} = 4'-(1-(1'-methyl-4,4-bipyridinium-1-yl)-phenyl)-2,2':6',2''-terpyridine and tpy-\phi-MV^{2+} = 4'-(1-(1'-methyl-4,4-bipyridinium-1-yl)-phenyl)-2,2':6',2''-terpyridine and tpy-\phi-MV^{2+} = 4'-(1-(1'-methyl-4,4-bipyridinium-1-yl)-phenyl)-2,2''-1,2''$ 2,2':6',2"-terpyridine) capable of undergoing energy transfer (EnT) or electron transfer (ET) following photo excitation to the metal-to-ligand charge transfer (MLCT) state is investigated. Adaptive feedback control (AFC) pulse shaping, which has proven to be a versatile experimental tool for probing photoinduced dynamics in a variety of chemical systems, is used try and control the EnT and ET reactivity in this complex with the goal of informing the underlying EnT and ET dynamics. To allow for interpretation of the aforementioned AFC experiments the photophysics of  $[Ru(bpy-An)(tpy-\phi-MV)]^{4+}$  and a family of six closely related bis-terpyridine Ru(II) complexes are characterized using static absorption, electochemical, and ultrafast pump-probe techniques. These experiments reveal previously unreported dynamics such as equilibration between the  ${}^{3}MLCT$  and  ${}^{3}MC$  (where MC = metal centered excited state) and interligand electron transfer. Furthermore, the EnT and ET reactions in  $[Ru(bpy-An)(tpy-\phi-MV)]^{4+}$  (and the associated model complexes) are found to occur on a sub-picosecond and picosecond timescale, respectively. These are the fastest EnT and ET timescales reported for any Ru(II) bis-terpyridine based complexes. As an addendum, photophysics of the mononuclear water oxidation catalysts  $[Ru(bpy)(tpy)(OH_2)]^{2+}$  and  $[Ru(bpy)(tpy)(OD_2)]^{2+}$  in neat H<sub>2</sub>O and D<sub>2</sub>O solvent, respectively, are reported. Ultrafast pump-probe experiments reveal an inverse kinetic isotope effect with the excited state lifetime being shorter for the  $D_2O$  complex than the  $H_2O$  complex. This is attributed to interactions between the coordinated aqua (or  $D_2O$ ) and solvent in the MLCT excited state and suggests design principles applicable to synthesis of photo-driven water oxidation assemblies.

## Dedication

"I don't know why I started writing. I don't know why anybody does it. Maybe they're bored, or failures at something else."

-Cormac McCarthy

### Contents

1	Intro	oduction	and Motivation	1
	1.1	Introdu	actory Remarks	1
	1.2	Designi	ing a Ru(II) Based Dual Acceptor System	7
	1.3	Target	Dual Acceptor and Concluding Remarks	10
	Cha	pter 1 B	Bibliography	13
2	Deve	eloping a	a Foundation: Photophysical Characterization of The ${}^{3}MLCT$ Excited State in Three	
	Ru(]	II) Terpy	yridyl Complexes Using Steady State Absorption, Electrochemistry and Ultrafast Pump-	
	Proł	be Techr	niques	19
	2.1	Introdu	action and Background	19
	2.2	Experi	mental Section	22
		2.2.1	General Information.	22
		2.2.2	Electrochemistry and Spectroelectrochemistry	22
		2.2.3	Transient Pump-Probe Kinetics and Spectra	23
	2.3	Results	s and Discussion	25
		2.3.1	Absorption Properties	25
		2.3.2	Spectroelectrochemical Properties	26
	2.4	Pump-	Probe Spectroscopy of $[\operatorname{Ru}(\operatorname{tpy})_2]^{2+}$	32
		2.4.1	Pump-Probe Spectroscopy of $[Ru(ttpy)_2]^{2+}$	37
		2.4.2	Pump-Probe Spectroscopy of $[Ru(tpy)(ttpy)]^{2+}$	41

	2.5	Concl	usion	46
	Cha	pter 2 ]	Bibliography	49
3	Pho	tophysi	cal Characterization of $[Ru(tpy-An)(tpy)]^{2+}$ using Ultrafast and Nanosecond Pump-	-
	Proł	be Tech	niques: Observation of Ultrafast Triplet-Triplet Energy Transfer.	56
	3.1	Overv	iew	56
	3.2	Exper	imental	57
		3.2.1	General	57
		3.2.2	Nanosecond Transient Pump-Probe	58
		3.2.3	Linear Absorption and Electrochemical Properties	59
	3.3	Ultraf	ast Pump-Probe Results	61
		3.3.1	Nanosecond Pump-Probe Results	67
	3.4	Concl	usion	68
	Cha	pter 3 ]	Bibliography	70
4	Pho	tophysi	cal Characterization of $[Ru(tpy)(tpy-\phi-MV]^{4+}$ and $[Ru(ttpy)(tpy-\phi-MV]^{4+}$ : Ultrafast	5
	Forv	vard an	d Back Electron Transfer Resulting in Formation of a Vibrationally Hot Ground State.	74
	4.1	Overv	iew	74
	4.2	Exper	imental	76
		4.2.1	General	76
		4.2.2	Electrochemistry and Spectroelectrochemistry	77
		4.2.3	Ultrafast Transient Pump-Probe Kinetics and Spectra	77
	4.3	Result	s and Discussion	77
		4.3.1	Ground State Absorption Properties	77
		4.3.2	Electrochemistry	79
		4.3.3	Spectroelectrochemisty	81
		4.3.4	Ultrafast Pump-Probe Spectroscopy	85

vi

<ul> <li>4.4 Concluding Remarks</li></ul>	
Chapter 4 Bibliography	96
5 Photophysics of $[Ru(tpy-An)(tpy-\phi-MV]^{4+}$ : Observation of Both Photoinduced Energy	
	and Elec-
tron Transfer Following MLCT Photoexcitation.	101
5.1 Introduction	101
5.2 Experimental	101
5.2.1 General	101
5.2.2 Ultrafast Pump-Probe Measurements	103
5.2.3 Nanosecond Pump-Probe Measurements	103
5.3 Results and Discussion	103
5.3.1 Ground State Absorption Properties	103
5.3.2 Ultrafast Pump-Probe Spectroscopy	104
5.3.3 Nanosecond Pump-Probe Characterization	112
5.4 Concluding Remarks	113
Chapter 5 Bibliography	115
6 Adaptive Feedback Control Pulse Shaping Experiments to Modulate The Yield of Electron	ı Transfer
and Energy Transfer in $[Ru(tpy-An)(tpy-\phi-MV)]^{4+}$	117
6.1 Introductory Comments	117
	118
6.2 Experimental	
6.2 Experimental	118
<ul> <li>6.2 Experimental</li></ul>	· · · · · 118 · · · · · 119
<ul> <li>6.2 Experimental</li></ul>	118 119 120
<ul> <li>6.2 Experimental</li></ul>	118 119 120 124

vii

7	Add	endum: Photophysics Of The Aqua-Coordinated $\operatorname{Ru}(\operatorname{II})$ Species $[\operatorname{Ru}(\operatorname{bpy})(\operatorname{tpy})(\operatorname{OH}_2)]^{2+}$ in $\operatorname{H}_2\operatorname{O}$	
	and	D <sub>2</sub> O. 1	.28
	7.1	Introduction	128
	7.2	Experimental	129
		7.2.1 General	129
		7.2.2 Transient pump-probe spectra and kinetics	129
	7.3	Results and Discussion	130
		7.3.1 Ground State Absorption Properties	130
		7.3.2 Ultrafast Pump-Probe Spectroscopy	131
	7.4	Conclusion	141
	Cha	pter 7 Addendum Bibliography	143
$\mathbf{A}$	Sup	porting Information for Chapter 2	.73
	A.1	Additional Information about the Ultrafast Spectrometer	173
	A.2	Details of Data Collection Procedures, Chirp Correction, and Fitting Practices Used For	
		Collection of the Ultrafast Data	173
	A.3	Deriving the <sup>3</sup> MLCT <sup>-3</sup> MC $K_{eq}$ and associated rate constants in $[Ru(tpy)_2]^{2+}$ using a pre-	
		equilibrium assumption	175
	A.4	Estimating the Molar Absorptivity of $[Ru^{III}(tpy^{-})(ttpy)]^{2+}$ and $[Ru^{III}(tpy)(ttpy^{-})]^{2+}$ using	
		the Isoabsorptive Transient Absorption Spectra	176
	App	endix A	179
в	Sup	porting Information for $[Ru(tpy-An)(tpy)]^{2+}$ 1	.80
	B.1	Calculating the redox potentials for the two steps in the Dexter energy transfer process	180
	B.2	<sup>1</sup> H-NMR spectrum of $[Ru(tpy-An)(tpy)]^{2+}$	181
$\mathbf{C}$	Sup	porting Information for Chapter 4	.82
	C.1	<sup>1</sup> H-NMR spectra	182

	C.2	$A \rightarrow B \rightarrow C \text{ Kinetics Model} \dots \dots$	182
	C.3	Assigning the ET and BET timescale based on Analysis of the Pre-Exponential Values	185
D	Sup	porting Information for Photophysical Characterization of $[Ru(tpy-An)(tpy-\phi-MV)]^{4+}$ Pulse	9
	Shap	ping Experiments	187
$\mathbf{E}$	Sup	porting Information for AFC Pulse Shaping Experiments	188
	E.1	Power Dependent Study	188
	E.2	Experimental Signal Simulations for Single Versus Pulse Train Excitation	188
$\mathbf{F}$	Sup	porting Information for $[Ru(bpy)(tpy)(OH_2)]^{2+}$	19 <b>2</b>
	F.1	<sup>1</sup> H-NMR spectra of $[Ru(bpy)(tpy)(OH_2)]^{2+}$ and $[Ru(bpy)(tpy)(OD_2)]^{2+}$ species	192
	F.2	Bleach recovery dyanimes of $\left[{\rm Ru(tpy)_2}\right]^{2+}$ in ${\rm H_2O}$ and ${\rm D_2O}$	193
	F.3	Magic angle transient spectra of the ${}^{3}MLCT$ excited state of $[Ru(bpy)_{3}]^{2+}$ in room tempera-	
		ture acetonitrile and $[Ru(bpy)(tpy)(OD_2)]^{2+}$ in $D_2O$	196

### List of Tables

2.1	$ Electrochemical data for \left[\mathrm{Ru}(\mathrm{tpy})_2\right]^{2+}, \left[\mathrm{Ru}(\mathrm{tpy})(\mathrm{ttpy})\right]^{2+}, \text{ and } \left[\mathrm{Ru}(\mathrm{ttpy})_2\right]^{2+} \text{ collected in CH}_3\mathrm{CN} $	27
2.2	Global fitting results for ${\rm [Ru(tpy)_2]}^{2+}$ kinetics data collected in room temperature ${\rm CH_3CN}$	34
2.3	Global fitting results for $[Ru(ttpy)_2]^{2+}$ kinetics data collected in room temperature $CH_3CN$ .	40
2.4	Global fitting results for $[Ru(tpy)(ttpy)]^{2+}$ kinetics data collected in room temperature $CH_3CN$	42
3.1	Electrochemical data for $[Ru(tpy-An)(tpy)]^{2+}$ and related complexes collected in room tem-	
	perature $CH_3CN$	60
3.2	Global fitting results for $[Ru(tpy-An)(tpy)]^{2+}$ kinetics data collected in room temperature	
	$CH_3CN$	64
4.1	$ Electrochemical data for \left[\mathrm{Ru}(\mathrm{tpy})(\mathrm{tpy}-\phi-\mathrm{MV})\right]^{4+},  \left[\mathrm{Ru}(\mathrm{ttpy})(\mathrm{tpy}-\phi-\mathrm{MV})\right]^{4+},  \mathrm{and}  \mathrm{And} $	
	(tpy– $\phi-{\rm MV}^{2+})$ collected in room temperature ${\rm CH}_3{\rm CN}$	80
4.2	Calculated Driving Forces for Photoinduced Forward and Back Electron Transfer in	
	$[\operatorname{Ru}(\operatorname{tpy})(\operatorname{tpy}-\phi-\operatorname{MV})]^{4+}$ and $[\operatorname{Ru}(\operatorname{ttpy})(\operatorname{tpy}-\phi-\operatorname{MV})]^{4+}$	81
4.3	Global fitting results for $[Ru(tpy)(tpy-\phi-MV)]^{4+}$ kinetics data collected in room temperature	
	$CH_3CN$	89
4.4	Global fitting results for $[Ru(ttpy)(tpy-\phi-MV)]^{4+}$ kinetics data collected in room tempera-	
	ture $CH_3CN$	94
5.1	Global fitting results for $[Ru(tpy-An)(tpy-\phi-MV)]^{4+}$ kinetics data collected in room tem-	
	perature $CH_3CN$	109
7.1	Global fitting results for $[Ru(bpy)(tpy)(OH_2)]^{2+}$ kinetics collected in room temperature $H_2O_{-}$	134

- 7.2 Global fitting results for  $[Ru(bpy)(tpy)(OD_2)]^{2+}$  kinetics collected in room temperature D<sub>2</sub>O 137
- C.1 A and B coefficients from fitting the kinetics collected 415 nm for  $[Ru(tpy)(tpy-p-MV)]^{4+}$ to either case 1 ( $\tau_1$ = ET and  $\tau_2$ =BET) or case 2 ( $\tau_1$ = BET and  $\tau_2$ =ET) ..... 185

# List of Figures

1.1	Approximate timescales for a variety of physical, chemical and biological processes. $\ldots$ .	2
1.2	A generic pump-dump control scenario. Here the first laser pulse (blue line) creates a	
	wavepacket on the excited state surface while a second laser pulse (red line) returns pop-	
	ulation to the ground state potential energy surface. By varying the time delay between the	
	two pulses population can be preferentially deposited back into the initial ground state well	
	or beyond a potential energy barrier (dashed grey line)	3
1.3	A demonstration of rational pulse shaping in our lab. Given are the intensity auto-correlations	
	of near a bandwidth limited 47 fs laser pulse (black) and two user defied pulse trains with	
	intra-pulse temporal spacing of 100 fs (red) and 200 fs (geen). Note: the two photon response	
	of the pulse trains has been scaled to allow for easier comparison	4
1.4	Cartoon representation of the adaptive feedback control approach for generation of optimal	
	pulses proposed by Rabitz.	5
1.5	The central question of this thesis: can shaped light pulses be used to control the yield of	
	either electron transfer (ET) or energy transfer (EnT) product following $^{1}MLCT$ excitation	
	of a Ru(II) polypyridyl chromophore? In the cartoon (D) represents the Ru(II) chromophore	
	while (A) and (A') are electron and energy accepting moieties, respectively. $\ldots$	6
1.6	Two of the possible geometric isomers arising from functionalizating the 4-position of a pair	
	of bipyridine ligands in $[Ru(bpy)_3]^{2+}$ .	8

1.7	Steady state absorption spectrum of $[Ru(tpy)_2]^{2+}$ , the chosen central chromophore, in room	
	temperature acetonitrile. The lowest energy $^1\mathrm{MLCT}$ $\leftarrow$ $^1\mathrm{GS}$ absorption corresponds to the	
	peak centered at 472 nm. The peaks in the UV region correspond to $\pi \leftarrow \pi^*$ and higher energy	
	<sup>1</sup> MLCT excitations. Inset: $[Ru(tpy)_2]^{2+}$	9
1.8	The EnT dyad used in this study $[Ru(tpy-An)(tpy)]^{2+}$ . The EnT accepting moiety (an-	
	thracene) is highlighted by the red, dashed circle.	10
1.9	The ET dyad $[Ru(tpy)(tpy-\phi-MV)]^{4+}$ used in this study. The ET acceptor moiety is high-	
	lighted by the blue, dashed circle	11
1.10	The dual acceptor species $[Ru(tpy-An)(tpy-\phi-MV)]^{4+}$ synthesized for this study	11
2.1	The three complexes characterized in this chapter	20
2.2	The generic excited state picture for $[Ru(L)_2]^{2+}$ type complexes where (L) is a tpy-like ligand.	21
2.3	Steady state absorption spectrum of $[Ru(ttpy)_2]^{2+}$ (dark blue), $[Ru(tpy)(ttpy)]^{2+}$ (light blue),	
	and $[\operatorname{Ru}(\operatorname{tpy})_2]^{2+}$ (green) in room temperature acetonitrile. The MLCT absorption maxima	
	are 490 nm ( $\epsilon = 28,900~{\rm M}^{\text{-1}}~{\rm cm}^{\text{-1}}),482~{\rm nm}~(\epsilon = 15,600~{\rm M}^{\text{-1}}~{\rm cm}^{\text{-1}}),\text{and}~475~{\rm nm}~(\epsilon = 10,400~{\rm M}^{\text{-1}})$	
	${\rm cm}^{\text{-}1})$ respectively. Inset: Overlay of the absorption spectrum of $\left[{\rm Ru}({\rm tpy})({\rm ttpy})\right]^{2+}$ and that	
	calculated from an average of the $[Ru(tpy)_2]^{2+}$ and $[Ru(ttpy)_2]^{2+}$ absorption spectra (dashed	
	purple)	25
2.4	$Oxidative \ spectroelectrochemistry \ of \ \left[\mathrm{Ru}(\mathrm{ttpy})_2\right]^{2+} \ (\mathrm{top}), \ \left[\mathrm{Ru}(\mathrm{tpy})(\mathrm{ttpy})\right]^{2+} \ (\mathrm{middle}), \ \mathrm{and}$	
	$\left[\mathrm{Ru}(\mathrm{tpy})_2\right]^{2+}$ (bottom) collected in room temperature acetonitrile with 0.1 M TBAP as the	
	supporting electrolyte. The extent of sample oxidation in each of these panels has not been	
	quantified	29
2.5	Reductive spectroelectrochemistry of $[Ru(ttpy)_2]^{2+}$ (top), $[Ru(tpy)(ttpy)]^{2+}$ (middle), and	
	${\rm [Ru(tpy)_2]}^{2+}$ (bottom) collected in room temperature acetonitrile with 0.1 M TBAP as	
	the supporting electrolyte. The jagged lines, most prominent in the data collected for	
	$[Ru(tpy)(ttpy)]^{2+}$ are a result of imperfect blanking of the light transmitted through the	
	Pt mesh. The extent of sample reduction in each of these panels has not been quantified	30

Chirp corrected magic angle transient absorption spectrum of  $[Ru(tpy)_2]^{2+}$  (green) collected 2.610 ps after excitation. The transient spectra of  $[Ru(ttpy)_2]^{2+}$  (dark blue, transparent) and  $[Ru(tpy)(ttpy)]^{2+}$  (light blue, transparent) have been included for reference. Data points were collected every 5 nm and are represented by the filled circles. Each sample was isoabsoprive at the 514 nm excitation frequency. Data contained between the two dashed lines has been omitted due to contamination by pump beam scatter. Inset: chirp corrected magic angle transient absorption spectra of each complex using a pump beam centered at 495 nm. These spectra have been included to show the bleach-to-absorbance transition on the red side of the spectrum. Note: for these data the absorbance of each sample at the pump central frequency was variable. 33 Magic angle transient kinetics of  $[Ru(tpy)_2]^{2+}$  collected in acetonitrile at  $\lambda_{probe} = 380$  nm 2.7(top),  $\lambda_{\text{probe}} = 475 \text{ nm}$  (middle), and  $\lambda_{\text{probe}} = 620 \text{ nm}$  (bottom). The solid red lines represent global fits to the data. 35Chirp corrected magic angle transient spectra of  $[Ru(tpy)_2]^{2+}$  collected over the first 10 ps 2.8following photoexcitation. Data points were collected every 5 nm and are represented by the 36Chirp corrected magic angle transient absorption spectrum of  $[Ru(ttpy)_2]^{2+}$  (dark blue) col-2.9lected 10 ps after excitation. The transient spectra of  $[Ru(tpy)_2]^{2+}$  (green, transparent) and  $[Ru(tpv)(ttpv)]^{2+}$  (light blue, transparent) have been included for reference. Data points were collected every 5 nm and are represented by the filled circles. Each sample was isoabsoprive at the 514 nm excitation frequency. Data contained between the two dashed lines has been omitted due to contamination by pump beam scatter. Inset: chirp corrected magic angle transient absorption spectra of each complex using a pump beam centered at 495 nm. These spectra have been included to show the bleach-to-absorbance transition on the red side of the spectrum. Note: for these data the absorbance of each sample at the pump central frequency was variable. 38

2.10	Magic angle transient kinetics of $[Ru(ttpy)_2]^{2+}$ collected in acetonitrile at $\lambda_{probe} = 380$ nm	
	(top), $\lambda_{probe} = 475$ nm (middle), and $\lambda_{probe} = 620$ nm (bottom). The solid red lines represent	
	global fits to the data.	

## 

39

3.3	Chirp corrected magic angle transient spectra of $[Ru(tpy-An)(tpy)]^{2+}]$ in room temperature	
	acetonitrile collected at a variety of time points after excitation. Spectral points were collected	
	every 5 nm and are represented by the filled circles. Arrows have been added to highlight the	
	temporal evolution of the features. The portion of each spectrum between the dashed lines	
	has been omitted due to contamination by pump scatter.	62
3.4	Normalized transient spectra of $[Ru(tpy-An)(tpy)]^{2+}$ collected at 10 ps and 100 ns after	
	excitation.	63
3.5	Magic angle transient kinetics of $[Ru(tpy-An)(tpy)]^{2+}$ in room temperature acetonitrile col-	
	lected at $\lambda_{\rm probe} = 420$ nm (top), 490 nm (middle), and 620 nm (bottom). The red open circles	
	represent the raw data with global fits to a tri-exponential model shown in black. Taus of $0.5$	
	$\pm$ 0.1 ps, 2.2 $\pm$ 0.9 ps and 6 $\pm$ 1 ps were found to be present at each wavelength with the 0.5	
	and 2.2 ps component contributing most strongly at 420 and 490 nm and the 6 ps component	
	contributing most strongly at 620 nm (see Table 3.2). $\ldots$ $\ldots$ $\ldots$ $\ldots$ $\ldots$	65
3.6	Energy level diagram and photoinduced dynamics of $[Ru(tpy-An)(tpy)]^{2+}$ based on the ul-	
	trafast pump-probe spectra and kinetics	67
3.7	Nanosecond transient kinetics of $[Ru(tpy-An)(tpy)]^{2+}$ collected in room temperature acetoni-	
	trile at a variety of probe wavelengths. The raw data is represented by open circles. Global	
	fits to the data using a single exponential model are represented by the solid black lines. $\ .$ .	68
4.1	The novel electroactive ligand tpy $-\phi-\mathrm{MV}^{2+}$ synthesized in our lab. The blue, dashed ellipse	
	denotes the $(\phi - MV^{2+})$ electron acceptor portion of the ligand	75
4.2	The two complexes investigated in this chapter	76
4.3	Steady state absorption spectra of $[Ru(tpy)(tpy-\phi-MV)]^{4+}$ (sea foam) and	
	$[Ru(ttpy)(tpy-\phi-MV)]^{4+}$ (ash blue). The MLCT absorption maxima are 486 nm	
	(16,400 ${\rm M}^{\text{-1}}~{\rm cm}^{\text{-1}})$ and 493 nm (30,000 ${\rm M}^{\text{-1}}~{\rm cm}^{\text{-1}}),$ respectively. The absorption spectrum of	
	$[Ru(tpy)(ttpy)]^{2+}$ (sea foam, dashed) and $[Ru(ttpy)_2]^{2+}$ (ash blue, dashed) are included for	
	reference.	78

- 4.5 Reductive spectroelectrochemistry of  $[Ru(tpy)(tpy-\phi-MV)]^{4+}$  (top) and  $[Ru(ttpy)(tpy-\phi-MV)]^{4+}$  (bottom) collected at -0.80 V vs. 0.01 Ag/AgNO<sub>3</sub> (-0.51 V vs. SCE) with 0.1 M TBAP as the supporting electrolyte. The jagged lines, most prominent in data collected for  $[Ru(tpy)(tpy-\phi-MV)]^{4+}$ , are a result of imperfect blanking of the spectrometer with light transmitted through the Pt wire mesh. The dotted lines have been added to allow for facile comparison of the new absorptive features in both complexes. . . . 84

- room temperature acetonitrile at a variety of time points after excitation. Data points were collected every 5 nm and are represented by the filled circles. The data between the vertical dashed lines has been omitted due to contamination by scatter from the pump beam centered near 525 nm.
  5.4 Normalized and overlaid magic angle transient spectra of [Ru(tpy-An)(tpy)]<sup>2+</sup> and

5.5	Magic angle single wavelength transient kinetics of $[Ru(tpy-An)(tpy-\phi-MV)]^{4+}$ in room
	temperature acetonitrile collected at $\lambda_{\rm probe}$ = 420 nm (top), 480 nm (middle) and 620 nm
	(bottom). The red solid lines represent global fits to the data. The data collected at 420 and
	620 nm were found to contain two common tau values of 1.1 $\pm$ 0.1 ps and 5.5 $\pm$ 0.2 ps. The
	bleach data collected at 480 nm was fit using a tri-exponential model yielding taus of 0.32 $\pm$
	0.05 ps and $4.8 \pm 0.3$ ps $27 \pm 8$ ps
5.6	Population simulations using Equations $5.1$ and $5.2$ along with the timescales and initial
	conditions detailed in the text
5.7	Nanosecond transient pump probe kinetics of $[Ru(tpy-An)(tpy-\phi-MV)]^{4+}$ collected in de-
	gassed room temperature acetonitrile at $\lambda_{\rm probe}$ = 420 nm. The pump beam was centered at
	532 nm and found to have a temporal FWHM of $\approx 3$ ns (superimposed on the plot in grey).
	The solid red line represents a single exponential fit to the data
6.1	Representative intensity auto-correlation of the excitation pulse pre (red) and post (blue)
	compression. The intensity of the compressed and uncompressed pulses have been normalized
	to aide comparison. This data was collected by Paul Vallett
6.2	Diagram of the pulse shaper used for the experiments detailed in this chapter. G1 and G2 are
	gratings. CM1 and CM2 are cylindrical mirrors. The SLM is placed at the Fourier plane to
	allow for the highest spectral resolution. The left side of the compressor (CM1 and G1) Fourier
	transform the pulse from the time to the frequency domain while the right side performs the
	inverse
6.3	Cartoon representation of the optimization experiments undertaken in this chapter (repro-
	duced from Chapter 1)
6.4	Simulated population dynamics of $[Ru(tpy-An)(tpy-\phi-MV)]^{4+}$ following MLCT photoex-
	citation. This a reproduction of a figure presented in Chapter 5

7.3 Magic angle transient kinetics of  $[Ru(bpy)(tpy)(OH_2)]^{2+}$  in room temperature H<sub>2</sub>O collected at  $\lambda_{\text{probe}} = 400 \text{ nm} (top), \lambda_{\text{probe}} = 470 \text{ nm} (middle), \text{ and } \lambda_{\text{probe}} = 650 \text{ nm} (bottom)$ . The solid red line represent global fits to the data. A common decay component of  $270 \pm 18$  ps was found at each probe wavelength with a weak early time dynamic of  $2 \pm 1$  ps present at Early time chirp corrected magic angle transient spectra of  $[Ru(bpy)(tpy)(OH_2)]^{2+}$  collected 7.4in room temperature H<sub>2</sub>O. Data points were collected every 5 nm and are represented by the filled circles. Scaled and overlaid chirp corrected magic angle transient spectra of  $\left[\mathrm{Ru}(\mathrm{bpy})(\mathrm{tpy})(\mathrm{OH}_2)\right]^{2+}$  in 7.5room temperature  $H_2O$  (blue) and  $[Ru(bpy)(tpy)(OD_2)]^{2+}$  in room temperature  $D_2O$  (green) collected 100 ps after excitation. Data points were collected every 5 nm and are represented by the filled circles. The portion of the spectrum contained between the dashed line has been Magic angle transient kinetics of  $[Ru(bpy)(tpy)(OD_2)]^{2+}$  in room temperature  $D_2O$  collected 7.6at  $\lambda_{\text{probe}} = 400 \text{ nm} (top), \lambda_{\text{probe}} = 470 \text{ nm} (middle), \text{ and } \lambda_{\text{probe}} = 650 \text{ nm} (bottom).$  The solid black line represent global fits to the data. A common decay component of  $220 \pm 12$  ps was found at each probe wavelength with a weak early time dynamic of  $1.4 \pm 0.5$  ps present at Single wavelength kinetics of  $[Ru(bpy)(tpy)(OH_2)]^{2+}$  collected in room temperature  $H_2O$ 7.7(blue) and  $[Ru(bpy)(tpy)(OD_2)]^{2+}$  in room temperature  $D_2O$  (green) at 470 nm. The global A.1 Top: Magic angle TA of neat  $CHCl_3$  collected using a pump pulse centered at 525 nm and probing at 600 nm. The inset shows an enlarged picture of the observed beat pattern. Bottom: FFT of the data presented in the inset. The peaks at 260 cm<sup>-1</sup> (period = 127 fs), 366 cm<sup>-1</sup> (period = 91 fs), and 667 cm<sup>-1</sup> (period = 50 fs) all correspond to known modes of  $CHCl_3$ . . . 174 

C.1	<sup>1</sup> H-NMR spectra of $[Ru(tpy)(tpy-p-MV)]^{4+}$ in d-acetonitrile	2
C.2	<sup>1</sup> H-NMR spectra of $[Ru(ttpy)(tpy-p-MV)]^{4+}$ in d-acetonitrile	3
C.3	The three state picture used to derive the fitting model employed for fitting the kinetics data	
	collected at 420 and 620 nm for $[Ru(tpy)(tpy-p-MV)]^{4+}$ and $[Ru(tpy)(tpy-p-MV)]^{4+}$ . The	
	initial intersystem crossing (ISC) has been omitted because it occurs on a sub-100 fs timescale,	
	which is shorter than the time resolution of the spectrometer. The two processes shown in	
	black, $k_o$ and $k_{REV}$ have also been ignored as they are orders of magnitude smaller than $k_{ET}$	
	and $k_{BET}$	4
D.1	<sup>1</sup> H-NMR of $[Ru(tpy-An)(tpy-p-MV)]^{4+}$ in d-acetonitrile. Residual DMF solvent from the	
	synthesis is indicated with the red arrow	7
E.1	Normalized magic angle transient kinetics of $\left[\mathrm{Ru}(\mathrm{tpy}-\mathrm{An})(\mathrm{tpy}-\phi-\mathrm{MV})\right]^{4+}$ collected at a	
	variety of excitation pulse energies	9
E.2	MLCT population created by each pulse in the pulse train	0
E.3	Simulated transient signal measured at 607 nm for $[Ru(tpy-An)(tpy-\phi-MV)]^{4+}$ when ex-	
	cited with a single pulse (red) and a train of pulses (blue) with inter-pulse spacing of $0.5$	
	ps	1
F.1	$^1\mathrm{H}\text{-}\mathrm{NMR}$ of $[\mathrm{Ru}(\mathrm{bpy})(\mathrm{OH}_2)](\mathrm{OTf})_2$ dissolved in d-DMSO. This spectrum was collected	
	immediately after dissolution because the bound $\mathrm{OH}_2$ is completely replaced by DMSO after	
	about 8 hours	2

F.2 <sup>1</sup>H-NMR of [Ru(bpy)(tpy)(OH<sub>2</sub>)](OTf)<sub>2</sub> collected 5 minuets (blue) and 8 hours (red) after being dissolved in d-DMSO. The resonance near 5.89 ppm, corresponding to a bound water, is clearly lost after prolonged exposure to the weakly coordinating DMSO solvent. The resonance at 10 ppm, corresponding to the bpy proton pointing at the ligated water, also undergoes a considerable shift during this time period further supporting loss of the ligated OH<sub>2</sub>. The resulting complex is presumably [Ru(bpy)(tpy)(DMSO)]<sup>2+</sup>. This assignment is supported by the marked shift in UV-vis spectrum also accompanying prolonged time in DMSO. . . . . . . 193

- F.5 Chirp corrected magic angle transient spectra of  $[Ru(bpy)_3]^{2+}$  collected 10 ps after excitation. Spectral data points were collected every 5 nm and represented by the filled circles. The data contained between the dashed grey lines has been omitted due to contamination by pump scatter. The dip in the absorptive intensity near 620 nm is due to detected emission from the <sup>3</sup>MLCT as determined by collecting spectra at a variety of negative time points. . . . . 196

# Chapter 1

### Introduction and Motivation

### 1.1 Introductory Remarks

For more than 40 years the primary step in vision<sup>\*</sup> has been known to involve photoinduced isomerization of 11-*cis*-rhodopsin into all *trans*-rhodpsin.[1] The timescale of this isomerization process has, however, only recently been resolved. Using ultrashort pulses of light (tens of femtoseconds temporal duration) Shank, Mathies and co-workers were able to directly monitor the photoinduced dynamics and determined the cisto-trans isomerization is essentially complete in 200 fs.[2, 3] In the experiment one ultrashort laser pulse is used to excite an ensemble of molecules, triggering the isomerization process, while at some time delay later a second laser pulse is used to measure the change in absorption. By probing the change in absorbance at a variety of different pump-probe time delays the experimenters were able to track the isomerization process in a manner akin to a photographer taking rapid sequence of photographs. As a number of relevant processes have been observed to occur on an ultrafast timescale (Figure 1.1<sup>†</sup>) the development of experimental techniques utilizing ultrashort laser pulses (pulses with a femtosecond temporal duration) has revolutionized our understanding in the fields of biology, chemistry and physics.[4] In recognition of this point the 1999 Nobel Prize in chemistry was awarded to Ahmed Zewail for

"... showing that it is possible with rapid laser technique(s) to see how atoms in a molecule move during a chemical reaction"  $^{\ddagger}$ 

<sup>\*</sup> which is allowing you to read the words typed here (assuming it is not printed in braille)

<sup>&</sup>lt;sup>†</sup> Adapted from[4]

<sup>&</sup>lt;sup>‡</sup> http://www.nobelprize.org/nobel prizes/chemistry/laureates/1999/press.html



Figure 1.1: Approximate timescales for a variety of physical, chemical and biological processes.

Beyond their use as interrogators of molecular dynamics, some also wondered if ultrashort optical pulses could be used to *control* chemical reactions.<sup>[5]</sup> Theoretical work by Tannor, Koslov and Rice<sup>[6, 7]</sup> showed that, indeed, non-trivial control of molecular reactivity is possible using a series of ultrashort laser pulses (Figure 1.2). Briefly, an initial ultrashort laser pulse (pump) is used to create a nuclear wavepacket on an electronic excited state surface. This wavepacket is allowed to evolve for some amount of time after which a second laser pulse (dump) is used to couple the excited state population back down to the ground state. The interaction with the second laser pulse creates a nuclear wavepacket on the ground state potential energy surface that is displaced from the equilibrium geometry. By varying the time delay between the pump and dump pulses the location of the wavepacket created on the ground state potential energy surface can be controlled giving an experimental "control knob" for directing reactivity. As shown in the cartoon given in Figure 1.2, by waiting an appropriate amount of time population can either be deposited back in the initial ground state well or beyond a potential energy barrier. This approach is also equally relevant when the second laser pulse is instead used to couple population to an additional excited state(s). The first experimental verification of this idea came in work by Gerber and co-workers on ionization of sodium dimers<sup>[8, 9]</sup> and Zewail and co-workers on the photoinduced reactivity of molecular iodine and xenon.<sup>[10]</sup> Additional theoretical work by Tannor, Koslov and Rice showed that by shaping the pump pulse one could direct the motion of the wavepacket created [11] thereby driving molecules toward (or away from) nuclear configurations corresponding to a given reaction channel. For example, using chirped excitation pulses



Figure 1.2: A generic pump-dump control scenario. Here the first laser pulse (blue line) creates a wavepacket on the excited state surface while a second laser pulse (red line) returns population to the ground state potential energy surface. By varying the time delay between the two pulses population can be preferentially deposited back into the initial ground state well or beyond a potential energy barrier (dashed grey line).

vibrational wavepacket can be selectively created in either the ground or the excited state which,[12] for example, can be used to control the yield of photoinduced dissociation reactions.[13] At this point it is worth noting that an alternate control scenario employing continuous wave (CW) laser excitation sources has been proposed by Brumer and Shapiro.[14–17] At first blush these two approaches for controlling chemical reactivity, pulsed laser vs. CW excitation, may seem distinctly different, however, if all the colors contained in an ultrashort laser pulse are accounted for the two approaches can be viewed as equivalent.[18]

Experiments utilizing shaped laser fields were not wide spread until the advent of robust pulse shapers such as acousto-optic modulators (AOM) and spatial light modulators (SLM). In their current form automated pulse shapers allow almost arbitrary control of the ultrafast laser pulse waveform.[19–22] For example, the SLM based pulse shaper in our lab is able to generate approximately 10<sup>200</sup>- 10<sup>400</sup> distinct pulse shapes.<sup>§</sup>



Figure 1.3: A demonstration of rational pulse shaping in our lab. Given are the intensity auto-correlations of near a bandwidth limited 47 fs laser pulse (black) and two user defied pulse trains with intra-pulse temporal spacing of 100 fs (red) and 200 fs (geen). Note: the two photon response of the pulse trains has been scaled to allow for easier comparison.

Rational pulse synthesis using current pulse shaping methodologies is also facile. As an illustration, using a simple sinusoidal phase function (see Chapter 6) a single input pulse can be converted into a train of output pulses with the inter-pulse temporal spacing controllable via a click of the mouse (Figure 1.3). Despite the ease with which shaped pulses can be synthesized, *a priori* design of pulse shapes able to drive chemical reactions toward a desired outcome is computationally demanding and experimentally difficult to implement.[23–26] To surmount this obstacle, Rabitz proposed a novel approach to optimal pulse design wherein the molecular response is used to iteratively improve the laser pulse shape until the optimal solution is generated.[27] Called adaptive feedback control (AFC) this approach requires only that the molecule response be coupled to an adaptive learning algorithm and an automated pulse shaper (Figure 1.4). The beauty of this methodology is that detailed knowledge of the molecular system being investigated *is not* needed. The molecule knows its' own Hamiltonian and is actively relaying this information to the adaptive algorithm to refine the pulse shape. Even with the vast parameter space afforded by modern pulse shapers (vide supra), the learning algorithms used in AFC experiments are able to quickly and efficiently uncovered

<sup>§</sup> Calculated using the number of pixels in a typical experiment and distinct drive voltages that can be applied to each.



Figure 1.4: Cartoon representation of the adaptive feedback control approach for generation of optimal pulses proposed by Rabitz.

optimal pulse shapes for a variety of photo-driven reaction such as bond cleavage, [28] electronic excited-state population transfer, [29] and excited state energy transfer. [30] For a comprehensive review of AFC, and laser based control in general, the interested reader is directed to the recent review by Rabitz and Chakabarti. [31]

Because the optimal pulse shapes discovered over the course of an AFC experiment necessarily contain detailed information about the process being studied, this experimental technique can be an incisive tool for investigating light-coupled reactions. For example, pulse shapes discovered via AFC pulse shaping have allowed for insight into the role of vibrational coherences in biological light harvesting systems,[30, 32–35] the mechanism of singlet fission in tetracene thin film,[36] and rate of charge injection in Ru(II) sensitized TiO<sub>2</sub>.[37] Accordingly, in this thesis we seek to use AFC pulse shaping techniques to gain insight into the photoinduced dynamics of the metal-to-ligand charge transfer (MLCT) excited state of Ru(II) polypyridyls. Specifically, we are interested in using AFC pulse shaping methodologies to probe electron transfer (ET) and energy transfer (EnT) reactivity coupled to the photo-generated MLCT excited state (Figure 1.5). To accomplish this we propose a "dual-acceptor" system capable of undergoing both ET and EnT from the MLCT excited state (Figure 1.5). Because Ru(II) polypyridyl complexes have diverse solar energy conversion applications, such as sensitization of solar cells[38, 39] and photo-driven oxidation/reduction,[40–44] our hope is development of AFC pulse shaping as an experimental tool will lead to insight that can inform future applications and/or synthetic schemes directed at solar energy conversion. Given the complexity of



Figure 1.5: The central question of this thesis: can shaped light pulses be used to control the yield of either electron transfer (ET) or energy transfer (EnT) product following <sup>1</sup>MLCT excitation of a Ru(II) polypyridyl chromophore? In the cartoon (D) represents the Ru(II) chromophore while (A) and (A') are electron and energy accepting moieties, respectively.

the early time dynamics in these types of complexes, which include intersystem crossing, [45-48] vibrational cooling, [49, 50] electron localization [50, 51] and interligand electron hopping dynamics, [50, 52-54] AFC pulse shaping experiments could be considered an ideal experiment for teasing apart information pertaining only to solvation and vibrational modes coupled to the EnT and ET processes. In principle iterative refinement of the pulse shape in an AFC experiment results in an optimal pulse shape that is a distillate of the processes coupled to the chosen observable. Transformation of the optimal pulse shape into physically meaningful information can, however, prove difficult. [24, 55, 56] The "knobs" available in a pulse shaping experiment–e.g. the phase function applied to the laser pulse–are not easily projected onto physically meaningful coordinates. Nonetheless, in many experiments meaningful information has been extracted from the optimal pulse shapes. [30, 32, 33, 36, 57-59] One pertinent example is the work of Yartsev and co-workers where the optimal pulse shapes discovered via AFC allowed for correlation of the rate of electron injection in Ru(II) sensitized TiO<sub>2</sub> with vibrational modes of the sensitizer dye. [37]

It should be said that interpretation of the results of weak field AFC experiments<sup>¶</sup> have often been debated, [18, 60–62] especially those [33, 34, 58, 63] invoking "one-photon" type control scenarios. Experimental results, however, demonstrated that control is possible in the linear excitation regime [12, 30, 33, 34, 36, 58, 59, 64–66] and, in regards to "one-photon" type control, recent theoretical work suggests such control is possible given the system is coupled to a dissipative bath. [67–69] We also note here that the EnT and ET reactions posed for study are similar in make-up to that of Katz, Ratner, and Kosloff [67] where the initial excited state population bifurcates into a spectroscopically dark states (i.e. ET and EnT reactivity following population of the optically "bright" MLCT photoexcitation). Therefore, "one-photon" type control scenarios may be accessible. [67–69]

Having laid out why AFC methodologies are a reasonable experimental technique for exploring the photoinduced reactivity of Ru(II) polypyridyl complexes the remainder of this introduction is dedicated to discussion of the specific Ru(II) based dual acceptor (DAA') species synthesized and how both EnT and ET reactivity are incorporated. Much thought has been devoted to the design of this system and what follows is a brief introduction to some of the main ideas that guided our choice.

### 1.2 Designing a Ru(II) Based Dual Acceptor System

The photophysics of Ru(II) polypyridyl complexes have been the subject of research for more than 30 years.[70] These types of coordination complexes are typically intensely colored owing to the presence of visible spectral region metal-to-ligand charge transfer transitions (MLCT) which, as the name implies, involve excitation of an electron from the Ru(II) metal center to one of the coordinating ligands. One of the most well studied complexes is  $[Ru(bpy)_3]^{2+}[71]$  (where bpy equals 2,2'-bipyrdine), therefore, we felt it would seem prudent to utilize  $[Ru(bpy)_3]^{2+}$  or some other well studied derivative as the central chromophoric unit in our dual-acceptor system. Unfortunately,  $[Ru(bpy)_3]^{2+\parallel}$  is helically chiral consisting of a  $\Delta$  and  $\Lambda$  propellers. Separation of these isomers is non-trivial[72, 73] and as a result any dual acceptor system derivatives built upon such a chromophoric center will likely be racemic in nature. Although this heterogeneity is unlikely

<sup>¶</sup> Here weak field refers to AFC experiments conducted in the linear excitation regime (where the transient absorption signal scales linearly with the power of the excitation pulse)

 $<sup>\</sup>parallel$  and tris-bidentate complexes with a  $c_2$  axis of rotation

to result in different EnT and ET rates, additional complications arise when the EnT and ET reactive moieties are included. As shown in Figure 1.6, additional geometric isomers are possible when the EnT and ET reactive moieties are incorporated into the bpy ligands. Although it may not be readily apparent, the distance between the two acceptors in the complex on the left is significantly longer than in the complex on the right; for the complex on the left, the EnT and ET acceptors are attached to pyridine rings which are another 180° apart while in the complex on the right the pyridine rings containing the EnT and ET acceptors are only 90°. This variable inter-acceptor distances could result in differing rates of excited state EnT and ET for the two species, therefore, additional effort to separate these isomers would be required prior to photophysical investigations. Furthermore, synthesis of mono-substituted bipyridine ligands is not a facile process.[74, 75] To avoid these complications the bis-tridentate complex [Ru(tpy)<sub>2</sub>]<sup>2+</sup> (where tpy = 2,



Figure 1.6: Two of the possible geometric isomers arising from functionalizating the 4-position of a pair of bipyridine ligands in  $[Ru(bpy)_3]^{2+}$ .

2':6', 2''-terpyridine) was chosen as the central chromophoric building block for our dual-acceptor species. This complex is non-chiral, belonging to the  $D_{2d}$  point group, and can be easily functionalized at the 4' position of the terpyridne ligand[76] (para to the nitrogen on the central terpyridine ring). This allows for incorporation of ET and EnT reactive moieties at a fixed inter-acceptor distance and without generation of geometric isomers.[77] However, unlike  $[Ru(bpy)_3]^{2+}$ , the photophysics of  $[Ru(tpy)_2]^{2+}$  have not been extensively studied, especially on ultrafast timescales.[78, 79] Therefore, a portion of this thesis (Chapter 2)

has been devoted to photophysical characterization of these types of complexes.



Figure 1.7: Steady state absorption spectrum of  $[\text{Ru}(\text{tpy})_2]^{2+}$ , the chosen central chromophore, in room temperature acetonitrile. The lowest energy <sup>1</sup>MLCT  $\leftarrow$  <sup>1</sup>GS absorption corresponds to the peak centered at 472 nm. The peaks in the UV region correspond to  $\pi \leftarrow \pi^*$  and higher energy <sup>1</sup>MLCT excitations. *Inset*:  $[\text{Ru}(\text{tpy})_2]^{2+}$ .

Having chosen the central chromophoric unit we turn now to a discussion of the EnT and ET acceptors. Considering that we are interested in using AFC pulse shaping to try and control EnT and ET it is important that these reactions occur quickly–i.e. on an ultrafast timescale–such that information encoded in the system by the shaped laser pulse is still present when the reaction occurs.[67] Therefore, choice of an appropriate EnT and ET acceptor is paramount. Addressing first the EnT acceptor, the initially prepared <sup>1</sup>MLCT excited state undergoes sub-100 fs intersystem crossing to <sup>3</sup>MLCT.[45–48] As a result the EnT reactive moiety must be amenable to triplet-triplet energy transfer and *not* Förster-type singlet-singlet resonance EnT.[80] No reports of ultrafast EnT using  $[\text{Ru}(\text{tpy})_2]^{2+}$  as the sensitizer exist in the literature, however, results from a number of research groups[81–83] show incorporation of an anthracene moiety at the 4'-position of a coordinating terpyridine ligand results in near unit efficiency quenching of the <sup>3</sup>MLCT excited state. Given the short lifetime of  $[\text{Ru}(\text{tpy})_2]^{2+}$  (~ 120 ps, see Chapter 2) a sub-five picosecond EnT timescale is expected. In a related Ru(II) tris-polypyridyl complex, where the anthracene is appended via an ethylene spacer,



Figure 1.8: The EnT dyad used in this study  $[Ru(tpy-An)(tpy)]^{2+}$ . The EnT accepting moiety (anthracene) is highlighted by the red, dashed circle.

triplet-triple energy transfer from the <sup>3</sup>MLCT to the lowest energy anthracene triplet (T<sub>1</sub>) was observed to occur on a picosecond timescale.[84] In light of these observations we chose to use the tpy-An ligand (where tpy-An = 4'-(9-anthracenyl)-2,2':6',2''-terpyridine) as the energy transfer portion of the target dual acceptor species. This ligand incorporated into the central chromophore is shown in Figure 1.8.

In regards to possible ET reactive ligands to utilize in the dual acceptor species, many examples of  $[\text{Ru}(\text{tpy})_2]^{2+}$  based ET dyads have been published in the literature. Almost without exception[85] these complexes exhibit very slow rates of excited state ET and negligible yield of the electron transfer product.[86–89] Given our need for ultrafast ET from the MLCT excited state none of the previously synthesized system are suitable. Therefore, we undertook development of a novel terpyridine based ET dyad. Based on recent work in our lab probing the conformational dependence of ET in Ru(II) tris-bidentate complexes[75], we suspected direct connection of a methylviologen-like acceptor to the 4' position of the terpyridine ligand would result in ultrafast ET following MLCT photoexcitation. The proposed ligand and its incorporation into the  $[\text{Ru}(\text{tpy})_2]^{2+}$  chromophore is shown in Figure 1.9. As expected, ultrafast forward electron transfer is observed and is detailed in Chapter 4.

### **1.3** Target Dual Acceptor and Concluding Remarks

Combining the EnT and ET reactive ligands into a single chromophoric unit yields the target dual acceptor species  $[Ru(tpy-An)(tpy-\phi-MV)]^{4+}$  (Figure 1.10). In this novel complex we have engineered a



Figure 1.9: The ET dyad  $[Ru(tpy)(tpy-\phi-MV)]^{4+}$  used in this study. The ET acceptor moiety is highlighted by the blue, dashed circle.



Figure 1.10: The dual acceptor species  $[Ru(tpy-An)(tpy-\phi-MV)]^{4+}$  synthesized for this study.

system where the initial prepared optically-bright MLCT state has a choice of decaying via two pathways, namely energy transfer (EnT) or electron transfer (ET). This system, it would seem, is ideally poised for application of weak-field adaptive feedback control (AFC) pulse shaping experiments trying to interrogate the solvent and/or nuclear modes coupled to ET and/or EnT. However, before AFC experiments can be undertaken in a meaningful way, a firm understanding of the photophysics of each constituent part of the dual acceptor species is necessary. As a consequence, the bulk of this thesis is devoted to characterization of the substituent parts, namely the central chromophoric unit  $[Ru(tpy)_2]^{2+}$ , the EnT dyad  $[Ru(tpy-An)(tpy)]^{2+}$ ,

the ET dyad  $[Ru(tpy)(tpy-\phi-MV)]^{4+}$ , and dual acceptor species  $[Ru(tpy-An)(tpy-\phi-MV)]^{4+}$ , in the absence of shaped pulse excitation. The general structure of the thesis is as follows; the next chapter, Chapter 2, details the photophysics of the central chromophore,  $[Ru(tpy)_2]^{2+}$ , and two related bis-tridentate complexes thereby establishing a framework for understanding later experimental results. Chapter 3 details the photophysics of  $[Ru(tpy-An)(tpy)]^{2+}$  on the ultrafast and nanosecond time scale. Chapter 4 details synthesis and photophysics of the ET dyad  $[Ru(tpy)(tpy-\phi-MV)]^{4+}$  and one closely related analog. Synthesis and characterization of the dual acceptor species  $[Ru(tpy-An)(tpy-\phi-MV)]^{4+}$  is give in Chapter 5. The final chapter, Chapter 6, is devoted to discussion and interpretation of the pulse shaping experiments conducted on the total dual acceptor complex and comments about future work.

#### Chapter 1 Bibliography

- (1) G. Wald, *Science*, 1968, **162**, 230.
- (2) R. W. Schoenlein, L. A. Peteanu, R. A. Mathies, and C. V. Shank, *Science*, 1991, 254, 412.
- (3) L. A. Peteanu, R. W. Schoenlein, Q. Wang, R. A. Mathies, and C. V. Shank, Proceedings of the National Academy of Sciences of the United States of America, 1993, 90, 11762.
- (4) A. H. Zewail, Pure and Applied Chemistry, 2000, 72, 2219–2232.
- (5) A. H. Zewail, *Physics Today*, 1980, **33**, 27–33.
- (6) D. J. Tannor and S. A. Rice, Journal of Chemical Physics, 1985, 83, 5013–5018.
- (7) D. J. Tannor, R. Kosloff, and S. A. Rice, Journal of Chemical Physics, 1986, 85, 5805–5820.
- (8) T. Baumert, M. Grosser, R. Thalweiser, and G. Gerber, *Physical Review Letters*, 1991, 67, 3753–3756.
- (9) T. Baumert, B. Bühler, M. Grosser, R. Thalweiser, V. Weiss, E. Wiedenmann, and G. Gerber, Journal Of Physical Chemistry, 1991, 95, 8103–8110.
- (10) E. D. Potter, J. L. Herek, S. Pedersen, Q. Liu, and A. H. Zewail, *Nature*, 1992, 355, 66–68.
- R. Kosloff, S. A. Rice, P. Gaspard, S. Tersigni, and D. J. Tannor, *Chemical Physics*, 1989, 139, 201–220.
- (12) C. J. Bardeen, Q. Wang, and C. V. Shank, Physical Review Letters, 1995, 75, 3410–3413.
- (13) C. J. Bardeen, J. Che, K. R. Wilson, V. V. Yakovlev, P. Cong, B. Kohler, J. L. Krause, and M. Messina, *The Journal of Physical Chemistry A*, 1997, **101**, 3815–3822.
- (14) P. Brumer and M. Shapiro, *Chemical Physics*, 1986, **126**, 541–564.
- (15) P. Brumer and M. Shapiro, Accounts of Chemical Research, 1989, 22, 407–413.
- (16) M. Shapiro, J. W. Hepburn, and P. Brumer, *Chemical Physics*, 1988, 149, 451–454.
- M. Shapiro and P. Brumer, Principles of the Quantum Control of Molecular Processes, Wiley, Hoboken, 2003.
- (18) M. Shapiro and P. Brumer, Journal of Physical Chemistry A, 2001, 105, 2897–2902.
- (19) A. M. Weiner, D. E. Leaird, J. S. Patel, and J. R. Wullert, *Optics Letters*, 1990, 15, 326–328.
- (20) A. M. Weiner, Progress in Quantum Electronics, 1995, 19, 161–237.
- (21) A. M. Weiner and A. M. Kan'an, IEEE Journal of Selected Topics in Quantum Electronics, 1998, 4, 317–331.
- (22) A. M. Weiner, Optical Communications, 2011, 284, 3669–3692.
- (23) S. Shi, A. Woody, and H. Rabitz, Journal of Chemical Physics, 1988, 88, 6870–6883.
- (24) H. Rabitz and W. Zhu, Accounts of Chemical Research, 2000, 33, 572–578.
- (25) H. Rabitz, R. de Vivie-Riedle, M. Motzkus, and K. Kompa, *Science*, 2000, **288**, 824–828.
- (26) Q. Ren and G. G. Balint-Kurti, The Journal of Physical Chemistry A, 2009, 113, 14255–14260.
- (27) R. S. Judson and H. Rabitz, *Physical Review Letters*, 1992, 68, 1500–1503.
- (28) R. J. Levis, G. M. Menkir, and H. Rabitz, Science, 2001, 292, 709–713.
- (29) C. J. Bardeen, V. V. Yakovlev, K. R. Wilson, S. D. Carpenter, P. M. Weber, and W. S. Warren, *Chemical Physics Letters*, 1997, 280, 151–158.
- (30) J. L. Herek, W. Wohlleben, R. J. Cogdell, D. Zeidler, and M. Motzkus, *Nature*, 2002, 417, 533–535.
- (31) C. Brif, R. Chakrabarti, and H. Rabitz, New Journal of Physics, 2010, 12, 075008.
- (32) W. Wohlleben, T. Buckup, J. L. Herek, and M. Motzkus, *ChemPhysChem*, 2005, 6, 850–857.
- (33) V. I. Prokhorenko, A. M. Nagy, S. A. Waschuk, L. S. Brown, R. R. Birge, and R. J. D. Miller, *Science*, 2006, **313**, 1257–1261.
- (34) V. I. Prokhorenko, A. M. Nagy, L. S. Brown, and R. J. Dwayne Miller, *Chemical Physics*, 2007, 341, 296–309.
- (35) T. Buckup, J. Hauer, J. Voll, R. Vivie-Riedle, and M. Motzkus, *Faraday Discussions*, 2011, 153, 213–225.
- (36) E. M. Grumstrup, J. C. Johnson, and N. H. Damrauer, *Physical Review Letters*, 2010, 105, 257403.

- (37) B. Brüggemann, J. Organero, T. Pascher, T. Pullerits, and A. Yartsev, *Physical Review Letters*, 2006, 97, 208301.
- (38) D. Kuciauskas, J. E. Monat, R. Villahermosa, H. B. Gray, N. S. Lewis, and J. K. McCusker, Journal of Physical Chemistry B, 2002, 106, 9347–9358.
- (39) B. O'Regan and M. Grätzel, Nature, 1991, 353, 737–740.
- (40) V. Balzani, L. Moggi, M. F. Manfrin, F. Bolletta, and M. Gleria, *Science*, 1975, 189, 852–856.
- (41) M. Grätzel, in *Energy Resources through Photochemistry and Catalysis*, Academic Press Inc., New York, 1983, 71 and references therein.
- (42) M. Grätzel and K. Kalyanasundaram, in Photosensitization and Photocatalysis Using Inorganic and Organometallic Compounds, Kluwer Academic Publishers, Dordrecht, 1993, 247 and references therein.
- (43) J. J. Concepcion, J. W. Jurss, M. K. Brennaman, P. G. Hoertz, A. O. T. Patrocinio, N. Y. Murakami Iha, J. L. Templeton, and T. J. Meyer, Accounts of Chemical Research, 2009, 42, 1954–1965.
- (44) J. W. Tucker and C. R. J. Stephenson, Journal of Organic Chemistry, 2012, 77, 1617–1622.
- (45) N. H. Damrauer, G. Cerullo, A. Yeh, T. R. Boussie, C. V. Shank, and J. K. McCusker, *Science*, 1997, 275, 54–57.
- (46) A. C. Bhasikuttan, M. Suzuki, S. Nakashima, and T. Okada, *Journal of the American Chemical Society*, 2002, **124**, 8398–8405.
- (47) S. Yoon, P. Kukura, C. M. Stuart, and R. A. Mathies, *Molecular Physics*, 2006, **104**, 1275–1282.
- (48) A. Cannizzo, F. van Mourik, W. Gawelda, G. Zgrablic, C. Bressler, and M. Chergui, Angewandte Chemie-International Edition, 2006, 45, 3174–3176.
- (49) W. Henry et al., Journal of Physical Chemistry A, 2008, 112, 4537–4544.
- (50) S. Wallin, J. Davidsson, J. Modin, and L. Hammarström, Journal of Physical Chemistry A, 2005, 109, 4697–4704.
- (51) A. Yeh, C. V. Shank, and J. K. McCusker, Science, 2000, 289, 935–938.

- (52) G. B. Shaw, C. L. Brown, and J. M. Papanikolas, Journal of Physical Chemistry A, 2002, 106, 1483–1495.
- (53) G. B. Shaw, D. J. Styers-Barnett, E. Z. Gannon, J. C. Granger, and J. M. Papanikolas, Journal of Physical Chemistry A, 2004, 108, 4998–5006.
- (54) S. A. Miller and A. M. Moran, Journal of Physical Chemistry A, 2010, 114, 2117–2126.
- M. A. Montgomery, R. R. Meglen, and N. H. Damrauer, Journal of Physical Chemistry A, 2006, 110, 6391–6394.
- (56) M. A. Montgomery, R. R. Meglen, and N. H. Damrauer, Journal of Physical Chemistry A, 2007, 111, 5126–5129.
- (57) G. Vogt, G. Krampert, P. Niklaus, P. Nuernberger, and G. Gerber, *Physical Review Letters*, 2005, 94, 068305.
- (58) V. I. Prokhorenko, A. M. Nagy, and R. J. D. Miller, Journal of Chemical Physics, 2005, 122, 184502.
- (59) J. Savolainen, R. Fanciulli, N. Dijkhuizen, A. L. Moore, J. Hauer, T. Buckup, M. Motzkus, and J. L. Herek, Proceedings of the National Academy of Sciences of the United States of America, 2008, 105, 7641–7646.
- (60) M. Joffre, *Science*, 2007, **317**, 453b–453b.
- (61) A. C. Han and M. Shapiro, *Physical Review Letters*, 2012, **108**, 183002.
- (62) P. Brumer and M. Shapiro, *Chemical Physics*, 1989, **139**, 221.
- (63) V. I. Prokhorenko, A. M. Nagy, S. A. Waschuk, L. S. Brown, R. R. Birge, and R. J. Dwayne Miller, Science, 2007, 317, 453c–453c.
- (64) T. Buckup, J. Hauer, C. Serrat, and M. Motzkus, Journal of Physics B: Atomic, Molecular and Optical Physics, 2008, 41, 074024.
- (65) P. van der Walle, M. T. W. Milder, L. Kuipers, and J. L. Herek, Proceedings of the National Academy of Sciences of the United States of America, 2009, 106, 7714–7717.

- (66) J. Roslund, M. Roth, L. Guyon, V. Boutou, F. Courvoisier, J.-P. Wolf, and H. Rabitz, Journal of Chemical Physics, 2011, 134, pages.
- (67) G. Katz, M. A. Ratner, and R. Kosloff, New Journal of Physics, 2010, 12, 015003.
- (68) M. Spanner, C. A. Arango, and P. Brumer, The Journal of Chemical Physics, 2010, 133, 151101.
- (69) C. A. Arango and P. Brumer, The Journal of Chemical Physics, 2013, 138, 071104.
- (70) S. Campagna, F. Puntoriero, F. Nastasi, G. Bergamini, and V. Balzani, Photochemistry and Photophysics of Coordination Compounds I, 2007, 280, 117–214.
- (71) R. J. Watts, Journal of Chemical Education, 1983, 60, 834–842.
- (72) N. C. Fletcher, M. Nieuwenhuyzen, and S. Rainey, Journal of the Chemical Society-Dalton Transactions, 2001, 2641–2648.
- E. Holder, G. Trapp, J. C. Grimm, V. Schurig, and E. Lindner, *Tetrahedron: Asymmetry*, 2002, 13, 2673–2678.
- (74) H. A. Meylemans, Ph.D. Thesis, 2010.
- (75) M. Abdelhaq, Physical Chemistry, University of Colorado at Boulder, 2012.
- (76) M. Heller and U. S. Schubert, European Journal of Organic Chemistry, 2003, 2003, 947–961.
- (77) J. P. Sauvage, J. P. Collin, J. C. Chambron, S. Guillerez, C. Coudret, V. Balzani, F. Barigelletti, L. Decola, and L. Flamigni, *Chemical Reviews*, 1994, 94, 993–1019.
- J. Winkler, T. L. Netzel, and N. Sutin, Journal Of The American Chemical Society, 1987, 109, 2381–2392.
- (79) U. Siemeling et al., Chemistry A European Journal, 2003, 9, 2819–2833.
- (80) G. D. Scholes, Annual Review of Physical Chemistry, 2003, 54, 57–87.
- (81) G. Albano, V. Balzani, E. C. Constable, M. Maestri, and D. R. Smith, *Inorganica Chimica Acta*, 1998, 277, 225–231.
- (82) R. Passalacqua, F. Loiseau, S. Campagna, Y. Q. Fang, and G. S. Hanan, Angewandte Chemie-International Edition, 2003, 42, 1608–1611.

- (83) H. Y. Ding, X. S. Wang, L. Q. Song, J. R. Chen, J. H. Yu, Chao-Li, and B. W. Zhang, Journal of Photochemistry and Photobiology A: Chemistry, 2006, 177, 286–294.
- (84) J. R. Schoonover, D. M. Dattelbaum, A. Malko, V. I. Klimov, T. J. Meyer, D. J. Styers-Barnett, E. Z. Gannon, J. C. Granger, W. S. Aldridge, and J. M. Papanikolas, *Journal of Physical Chemistry A*, 2005, **109**, 2472–2475.
- (85) K. Hutchison, J. C. Morris, T. A. Nile, J. L. Walsh, D. W. Thompson, J. D. Petersen, and J. R. Schoonover, *Inorganic Chemistry*, 1999, **38**, 2516–2523.
- (86) J. P. Collin, S. Guillerez, J. P. Sauvage, F. Barigelletti, L. Decola, L. Flamigni, and V. Balzani, *Inorganic Chemistry*, 1991, **30**, 4230–4238.
- (87) O. Johansson, M. Borgström, R. Lomoth, M. Palmblad, J. Bergquist, L. Hammarström, L. C. Sun, and B. Åkermark, *Inorganic Chemistry*, 2003, 42, 2908–2918.
- (88) P. P. Laine, F. Bedioui, F. Loiseau, C. Chiorboli, and S. Campagna, Journal of the American Chemical Society, 2006, 128, 7510–7521.
- (89) E. A. Alemán, C. D. Shreiner, C. S. Rajesh, T. Smith, S. A. Garrison, and D. A. Modarelli, *Dalton Transactions*, 2009, 6562–6577.

# Chapter 2

Developing a Foundation: Photophysical Characterization of The <sup>3</sup>MLCT Excited State in Three Ru(II) Terpyridyl Complexes Using Steady State Absorption, Electrochemistry and Ultrafast Pump-Probe Techniques

# 2.1 Introduction and Background

As outlined in the previous chapter, shaped electric fields derived from broadband laser pulses can be used to manipulate dynamics in chemical and material systems.[1–4] In this context we have been interested in polypyridyl complexes of d<sup>6</sup> transition metals and whether adaptive feedback control (AFC) pulse shaping experiments can be used as an experimental tool to probe photoinduced energy and electron transfer. The studies discussed in this chapter concern characterization of the MLCT excited-state in three chromophoric building blocks,  $[Ru(tpy)_2]^{2+}$ ,  $[Ru(tpy)(ttpy)]^{2+}$ , and  $[Ru(ttpy)_2]^{2+}$  (where tpy = 2,2':6',2''-terpyridine and ttpy = 4'-(4-methylphenyl)-2,2':6',2''-terpyridine). The understanding developed in this chapter lays the ground work for interpretation of the photoinduced dynamics of the target dual acceptor complex,  $[Ru(tpy-An)(tpy-\phi-MV)]^{4+}$ , as well as the energy transfer (EnT) and electron transfer (ET) dyads also investigated.



Figure 2.1: The three complexes characterized in this chapter

We have undertaken a systematic exploration of the bis-tridentate complexes shown in Figure 2.1 using linear absorption, electrochemical, spectroelectrochemical, and ultrafast pump-probe techniques. The photophysics of these types of complexes have been investigated previously by a number of research groups 5-17] and the consensus excited state picture is summarized schematically in Figure 2.2. Here MLCT is the metal-to-ligand charge transfer excited state and <sup>3</sup>MC is the metal center, or ligand field, excited state. In the <sup>3</sup>MC, the ruthenium metal center has an electronic configuration of  $d\pi^5\sigma^*$  whereas in the <sup>1</sup>GS its  $d\pi^6$  (assuming an octahedral ligand field). The decay pathways  $k_r$  and  $k_{nr}$  correspond to radiative and non-radiative decay from the <sup>3</sup>MLCT while  $k_{\rm mc}$  is activated crossing to the <sup>3</sup>MC and  $k_{\rm mc_g}$  non-radiative decay to the <sup>1</sup>GS. The hindered bite angle of the tpy ligand,  $158^{\circ}$  vs the ideal  $180^{\circ}$ , [18] significantly lowers the <sup>3</sup>MC relative to the <sup>3</sup>MLCT such that in room temperature solution essentially all of the excited state population decays via population of the  ${}^{3}MC.[12]$  This distorted ligand field is the root cause of the short MLCT lifetime of  $[Ru(tpy)_{2}]^{2+}$ -like complexes, typically on the order of hundreds of picoseconds(vide infra) as compared to the  $\sim 1 \,\mu s$  lifetime observed  $[Ru(bpy)_3]^{2+}$  in degassed room temperature solvent.[19]

Despite the aforementioned previous investigations, the early time dynamics of  $[Ru(tpy)_2]^{2+}$  as well as  $[Ru(tpy)(ttpy)]^{2+}$  and  $[Ru(ttpy)_2]^{2+}$  have not been thoroughly characterized. The two previous pumpprobe experiments concerning  $[Ru(tpy)_2]^{2+}$  had temporal resolution on the order of tens of picoseconds.[7,



Figure 2.2: The generic excited state picture for  $[Ru(L)_2]^{2+}$  type complexes where (L) is a tpy-like ligand.

15] The improved temporal resolution of our pump-probe spectrometer (see Experimental Section) allows us to resolve dynamics not previously reported. In  $[Ru(tpy)_2]^{2+}$ , equilibration between the <sup>3</sup>MLCT and the triplet metal-centered excited-state <sup>3</sup>MC, which had been previously inferred from studies of crystalline samples of  $[Ru(tpy)_2]^{2+}$ , [20] is directly observed and the timescale quantified. Comparison of the dynamics observed in  $[Ru(tpy)_2]^{2+}$  with those of the homoleptic arylated species  $[Ru(ttpy)_2]^{2+}$  also allows us to discern the consequences of stabilizing the <sup>3</sup>MLCT relative to the <sup>3</sup>MLCT on the excited state dynamics. Finally, the bis-heteroleptic species  $[Ru(tpy)(ttpy)]^{2+}$  allowed us to study the interligand electron transfer (ILET) dynamics in these complexes because of distinct spectroscopic signatures of the excited electron localized on either the tpy-ligand  $[Ru(tpy<sup>--</sup>)(ttpy)]^{2+}$  or the ttpy-ligand  $[Ru(tpy)(ttpy<sup>--</sup>)]^{2+}$ .

## 2.2 Experimental Section

#### 2.2.1 General Information.

All photophysical measurements were made at 294 K (the temperature of our laser lab) using Burdick & Jackson UV-grade acetonitrile. Steady-state electronic absorption spectra were recorded on a Hewlett-Packard HP8452A diode array UV-Vis spectrometer. The ligand 4'-(4-methylphenyl)-2,2':6',2''-terpyridine (ttpy),[21] precursor metal complexes  $Ru(tpy)Cl_3$ ,  $Ru(ttpy)Cl_3$ , and target complexes  $[Ru(tpy)_2](PF_6)_2$ ,  $[Ru(ttpy)_2](PF_6)_2$ , and  $[Ru(tpy)(ttpy)](PF_6)_2$ , where tpy = 2,2':6',2''-terpyridine, were prepared in a manner similar to previously published procedures[22–24] with triethylamine used as the reductant and  $Ag(CF_3SO_3)$  as a chloride scavenger. All samples synthesized were purified via silica gel column chromatography with 8:1:1 acetonitrile, water, and saturated potassium nitrate used as the eluent. The identity and purity of each complex was confirmed by <sup>1</sup>H-NMR and mass spectrometry. <sup>1</sup>H-NMR spectra were recorded using either a Varian Inova 500 MHz spectrometer or a Bruker Avance-III 300 MHz spectrometer. All deuterated solvents were purchased from Cambridge Isotopes Laboratories Inc. Mass spectrometry and accurate mass analysis was preformed by the Central Analytical Laboratory at the University of Colorado at Boulder, Department of Chemistry and Biochemistry.

#### 2.2.2 Electrochemistry and Spectroelectrochemistry

The cyclic voltammetry measurements utilized a standard three-electrode set-up with a 3.0 mm diameter Pt working electrode, 0.5 mm Pt wire counter electrode and 0.01M Ag/AgNO<sub>3</sub> reference electrode constructed immediately before use. The latter involves dissolving the appropriate mass of AgNO<sub>3</sub> with fresh 0.1 M TBAP (tetrabutylammonium hexafluorophosphate; Aldrich) to make the 0.01 M AgNO<sub>3</sub> solution into which the silver wire is placed. Analyte concentrations were adjusted to approximately 2 mM in a supporting electrolyte of 0.1 M TBAP in anhydrous  $CH_3CN$ . Before each measurement, samples were deaerated with argon. For each measurement a scan rate of 200 mV/s was used. Adaptation of the potentials measured with our reference electrode to potentials vs. SCE were accomplished using the conversion factors of Pavlishchuk and Addison.[25] Spectroelectrochemistry measurements used a home-built OTTLE cell (Optically Transparent Thin-Layer Electrode) with a transparent platinum mesh working electrode, a platinum wire auxiliary electrode, and a  $0.01 \text{ M} \text{ Ag/AgNO}_3$  reference electrode that, as discussed above, is constructed immediately prior to use. The three-electrode set up is placed in a modified 2 mm path length cell that allows an atmosphere of argon to be maintained above the sample for the duration of the experiment. Both the oxidative and reductive spectroelectrochemistry where observed to be chemically reversible based on recovery of the initial sample absorption following a null voltage being applied to the platinum mesh.

#### 2.2.3 Transient Pump-Probe Kinetics and Spectra

Transient kinetics and spectra were collected using a home built pump-probe spectrometer derived from a commercially available amplified Ti:Sapphire laser system that has been used previously by our group. [26] The spectrometer has been modified and the details are listed here. The output of the regenerative amplifier (Clark MXR CPA1000,  $\approx 800 \text{ nm} \pm 10 \text{ nm}$ ,  $\approx 150 \text{ fs temporal FWHM}$ , 1kHz, 500  $\mu$ J/pulse) was split using a 70:30 beam splitter with  $\sim 350 \,\mu\text{J}$  being sent to a home built NOPA[27, 28] in order to generate pump pulses centered between 495 - 525 nm. Prism compression (Thorlabs; AFS-FS) resulted in pulses with a temporal FWHM of less than 50 fs. The remaining output of the regenerative amplifier,  $\sim 150 \,\mu J$ , was used to generate the probe pulse and traveled along a path containing two computer controlled linear delay stages (Newport MM3000 0.049 fs/step time resolution, 14 inches of travel; Velmex 169 fs/step time resolution, 48 inches of travel) which were used to control the relative time delay between the pump and probe pulses. The probe beam was generated by attenuating the fundamental to approximately 1  $\mu$ J with neutral density filters and then focusing it into a 3 mm thick disk of calcium fluoride (Thorlabs, WG50530, mounted on a constantly moving translational stage) resulting in a single filament continuum with a nearly Gaussian spatial profile. The probe pulse train was then split by a 50:50 beam splitter (Thor Labs; BSW26) with both beams directed towards the sample cell (2 mm quartz cuvette) and focused with a 50 mm achromatic lens to a measured spot diameter of 90  $\mu$ m inside the sample volume. One of the continuum beams is spatially overlapped with the pump while the other travels through an un-pumped portion of the sample cell and functions as a reference. The pump beam was focused into the sample cell with a 200 mm lens yielding an experimentally measured beam diameter of 200  $\mu$ m inside the sample volume. The angle between the pump and probe beams in this configuration is approximately 3°. For all experiments the power of the pump at the sample was attenuated to less than 260 nJ/pulse ( $\sim 1.7 \ge 10^{10} \text{ W/cm}^2$ ) with neutral density filters. The typical sample absorbance at the pump laser central frequency was adjusted to approximately 0.5. Analyte concentrations and pump powers were adjusted to maintain an excitation probability of less than 1 molecule in 100 per pump pulse. [29] One mirror bounce prior to the sample the pump beam polarization was cleaned by passage through a thin polarizer (Thorlabs; LPVISE100-A) set transmit to only horizontally polarized light. The probe beam polarization was also cleaned by passage through a thin polarizer placed directly after continuum generation set to transmit only horizontally polarized light. Both the beams conditioned this way showed a ratio of transmission to extinction through a cube polarizer placed at sample in excess of 1000:1. To ensure only population dynamics were being monitored, the relative electric-field polarization between the pump and the probe was set to the magic angle  $(54.7^{\circ})$  by rotating the pump beam polarization relative to the probe with an achromatic half-wave plate (Thorlabs; AHWP05M-600) just before entering the sample. After the probe and reference pulse trains had traveled through the sample they were coupled into a 220 mm scanning monochromator (Spex; 220M, 0.5 mm entrance and exit slits) and spectrally dispersed by a 1200 grooves/mm grating. Resolution measured at the exit slit was  $\pm 3$  nm. Both the probe and reference beams were monitored with a differential detector (ThorLabs, PDB210) placed after the exit slit of the monochromator with the output sent to a boxcar amplifier (Stanford Research, SRS250), an analog to digital converter digital (NI PCI-6036E), and a computer based lock-in program (LabVIEW 2010) synchronized to the frequency of a mechanical chopper wheel that was used to modulated the pump beam repetition rate. Additional information about the spectrometer, such as determination of temporal resolution, is provided in the Appendix A. Plotting and analysis of the experimental data was accomplished using the commercially available software Igor Pro 6.20B02 (WaveMetrics). The transient kinetics presented herein are plotted in terms of negative change in normalized transmittance of the probe beam,  $-\Delta T$ , while the transient spectra are plotted in terms of  $-\Delta T/T$ . Both can be interpreted in the same way as a  $\Delta A$  signal with positive features corresponding to a net transient absorption and negative signals corresponding to overall transient bleach.

### 2.3 Results and Discussion

#### 2.3.1 Absorption Properties

Like the well studied tris-bipyridyl  $[Ru(bpy)_3]^{2+}$ , [30, 31] the bis-terpyridyl complexes  $[Ru(tpy)_2]^{2+}$ ,  $[Ru(ttpy)_2]^{2+}$ , and  $[Ru(ttpy)_2]^{2+}$  (see Figure 2.1) studied herein are brightly colored with their visible light absorption spectra dominated by intense <sup>1</sup>MLCT  $\leftarrow$  <sup>1</sup>GS electronic transitions centered at 475 nm ( $\varepsilon = 10,400 \text{ M}^{-1} \text{ cm}^{-1}$ ), 482 nm ( $\varepsilon = 15,600 \text{ M}^{-1} \text{ cm}^{-1}$ ), and 490 nm ( $\varepsilon = 28,900 \text{ M}^{-1} \text{ cm}^{-1}$ ) respectively (Figure 2.3). As has been pointed out by Sauvage and coworkers, the introduction of a tolyl fragment at



Figure 2.3: Steady state absorption spectrum of  $[Ru(ttpy)_2]^{2+}$  (dark blue),  $[Ru(tpy)(ttpy)]^{2+}$  (light blue), and  $[Ru(tpy)_2]^{2+}$  (green) in room temperature acetonitrile. The MLCT absorption maxima are 490 nm ( $\varepsilon = 28,900 \text{ M}^{-1} \text{ cm}^{-1}$ ), 482 nm ( $\varepsilon = 15,600 \text{ M}^{-1} \text{ cm}^{-1}$ ), and 475 nm ( $\varepsilon = 10,400 \text{ M}^{-1} \text{ cm}^{-1}$ ) respectively. Inset: Overlay of the absorption spectrum of  $[Ru(tpy)(ttpy)]^{2+}$  and that calculated from an average of the  $[Ru(tpy)_2]^{2+}$  and  $[Ru(ttpy)_2]^{2+}$  absorption spectra (dashed purple).

the 4' position of the terpyridine ligand leads to both a red-shifted absorption maximum and increased MLCT oscillator strength.[32] The latter is a result of the appended tolyl groups elongation of the transition dipole length[33–35] while former is due to the lower energy  $\pi^*$  orbitals of the ttpy ligand (vide infra) and its slight electron donating nature relative to an un-substituted tpy ligand.[32] The nature of the MLCT state created in Ru(II) polypyridyls upon photo-excitation—i.e. whether the excited electron is localized on

one ligand vs. delocalized over all the ligands—has been the topic of some debated in the literature [36-41] For systems involving metal complexes in polar solvent, there is compelling evidence that the photoinduced charge-transferred electron is localized on a single ligand. [42–46] Based on the results of Stark spectroscopy, [39, 47, 48] resonance Raman, [49] and solvatochromism experiments, [50] the initial <sup>1</sup>MLCT  $\leftarrow$  <sup>1</sup>GS excitation process seems to involve promotion of an electron to a single ligand and not an excited state delocalized over all the ligands. More recent ultrafast experiments have been somewhat mixed, with some reports of the <sup>1</sup>MLCT  $\leftarrow$  <sup>1</sup>GS process involving a single ligand localized excitation[51] while others reported excitation to a delocalized excited state with localization occurring on a sub-100 fs timescale. [52] Nonetheless, on the timescales discussed in this chapter, greater than 300 fs after excitation (vide infra). the MLCT should be thought of as localized on a single ligand  $([Ru^{III}(L)(L^{-})]^{2+})$  in nature). For the two homoleptic species  $[\operatorname{Ru}(\operatorname{tpy})_2]^{2+}$  and  $[\operatorname{Ru}(\operatorname{ttpy})_2]^{2+}$ , this results in indistinguishable MLCT configurations while in the bis-heteroleptic species  $[Ru(tpy)(ttpy)]^{2+}$  it is possible to have both a tpy-localized (formally  $[\operatorname{Ru}^{\operatorname{III}}(\operatorname{tpy}^{-})(\operatorname{ttpy})]^{2+})$  or a ttpy-localized (formally  $[\operatorname{Ru}^{\operatorname{III}}(\operatorname{tpy})(\operatorname{ttpy}^{-})]^{2+})$  MLCT configuration. We have observed that a simple averaging of the molar absorption coefficients of  $[Ru(tpy)_2]^{2+}$  and  $[Ru(ttpy)_2]^{2+}$ approximately reproduces the visible region molar absorption spectrum of  $[Ru(tpy)(ttpy)]^{2+}$  (Figure 2.3 inset). Therefore, based on a ratio of the molar absorptivity of  $[Ru(tpy)_2]^{2+}$  and  $[Ru(ttpy)_2]^{2+}$  at 525 nm, the central wavelength of the excitation pulses used in the transient absorption data discussed later, the initial photoexcited population is expected to be made up of  $\sim 25\%$  tpy-localized and  $\sim 75\%$  is ttpy-localized MLCT species.

#### 2.3.2 Spectroelectrochemical Properties

To lay the ground work for interpretation of the ultrafast pump-probe experiments we have adopted an approach similar to that outlined by McCusker and coworkers[53] where "optical tags" of the MLCT excited-state are formulated from a superposition of the difference spectra obtained for one-electron oxidation and reduction of the complex. Accordingly, cyclic voltammetry has been employed to measure the oneelectron oxidation and reduction potentials for each complex with the relevant data listed in Table 2.1.  $E_{ox}$ corresponds to the average of the anodic and cathodic  $\frac{1}{2}$ -wave potentials for the Ru(III)/Ru(II) couple while

Complex	$E_{ox}(V)$	$E_{red(1)}(V)$	$E_{red(2)}(V)$
$\left[{\rm Ru(tpy)}_2\right]^{2+}$	$0.95^{\rm a}$ (0.089), $1.25^{\rm b}$	-1.61 <sup>a</sup> (0.095), -1.31 <sup>b</sup>	$-1.86^{\rm a}$ (0.106), $-1.56^{\rm b}$
$\left[\mathrm{Ru(tpy)(ttpy)} ight]^{2+}$	$0.92^{\rm a}\;(0.078),1.22^{\rm b}$	$1.59^{\rm a}$ (0.072), -1.29 <sup>b</sup>	-1.84 <sup>a</sup> (0.078), -1.54 <sup>b</sup>
$\left[{\rm Ru(ttpy)}_2\right]^{2+}$	$0.90^{\rm a}$ (0.069), $1.202^{\rm b}$	$1.59^{\rm a}$ (0.066), -1.29 <sup>b</sup>	$-1.83^{\rm a}$ (0.074), $-1.53^{\rm b}$

Table 2.1: Electrochemical data for  $[Ru(tpy)_2]^{2+}$ ,  $[Ru(tpy)(ttpy)]^{2+}$ , and  $[Ru(ttpy)_2]^{2+}$  collected in  $CH_3CN$ 

<sup>a</sup>All electrochemical measurements were recorded vs. a freshly prepared 0.01 M Ag/AgNO<sub>3</sub> reference electrode. The anodic and cathodic wave peak separation is given in parentheses. A scan rate of 200 mV/s and supporting electrolyte of 0.1 M TBAP was used.

<sup>b</sup>The values reported vs. SCE using the referenced conversion factors.<sup>[25]</sup>

 $E_{red(1)}$  and  $E_{red(2)}$  refer to the average of the anodic and cathodic  $\frac{1}{2}$ -wave potentials for the two sequential one-electron ligand reduction events. Across the series of complexes, the Ru(III)/Ru(II) couple shows a small but systematic decrease as the number of ttpy ligands is increased. While one tends to think of the tolyl-group as an electron acceptor because of its affect on MLCT energetics (vide supra) and reduction potentials (vide infra), it is nonetheless more electron rich than a hydrogen atom in an un-substituted terpyridine ligand. [32] This leads to an inductive increase in the basicity of the polypyridine moiety ( $\sigma$ -donation), which makes one-electron oxidation of the metal center, from an orbital that is primarily of metal d-orbital character, less energetically demanding. The potential measured for  $E_{red(1)}$ , which corresponds to the addition of an electron to the  $\pi^*$  system of one of the ligands, [8, 54] is essentially identical for  $[Ru(ttpy)_2]^{2+}$  and  $[Ru(tpy)(ttpy)]^{2+}$  while the potential measured for  $[Ru(tpy)_2]^{2+}$  is more negative. This is not surprising as the LUMO  $\pi^*$  of the ttpy is lower in energy than that of the tpy ligand due to delocalization onto the appended tolyl group.[11, 35] These electrochemical data imply that the lowest energy <sup>3</sup>MLCT excitedstate in the heteroleptic  $[Ru(tpy)(ttpy)]^{2+}$  will be ttpy-localized. Considering these results in the context of the electronic absorption, and our prediction that photo-excitation of  $[Ru(tpy)(ttpy)]^{2+}$  at 525 nm will produce both tpy-localized and ttpy-localized MLCT configurations, we anticipate that dynamics related to interligand electron transfer (ILET) of the type tpy-localized  $\rightarrow$  ttpy-localized may contribute to the transient population dynamics, assuming the two species are spectrally distinct.

The absorptive features of the one-electron oxidized species of each complex were recorded by way

of bulk electrolysis at a platinum mesh working electrode placed in the sample compartment of a UV-Vis spectrophotometer, as detailed in the experimental section, with the potential held at 1.10 V vs. 0.01 M Ag/AgNO<sub>3</sub> (1.40 V vs. SCE). As shown in Figure 2.4, the most prominent change in the spectra of all three complexes with increasing bulk electrolysis time is loss of the visible region  $^{1}MLCT \leftarrow ^{1}GS$  electronic transition, which is highlighted in the figure by the downward arrow. This is expected, as <sup>1</sup>MLCT excitation from a Ru(III) center is significantly more energetic. Flanking this loss of absorption, and characterized by two well-behaved isosbestic points, is the growth of new absorption features ranging from 350 to 420 nm and 600 to 800 nm. The redder of the two features, 600 to 800 nm, is attributed to ligand-to-metal charge transfer (LMCT) with the smaller oscillator strength and relatively broad and featureless absorption characteristic of this type of transition. [19, 55-58] The absorptive feature from 350 to 420 nm, which is notably more prominent in  $[Ru(tpy)(ttpy)]^{3+}$  and  $[Ru(ttpy)_2]^{3+}$  as compared to  $[Ru(tpy)_2]^{3+}$ , is thought to be intraligand charge transfer (ILCT) absorption of the ttpy ligand analogous to that observed in other 4'-aryl-substituted terpyridine complexes. [56, 59] These transitions involve excitation of electron density from the tolyl fragment to the total center. In the Ru(II) oxidation state these transitions are presumably buried under the intense  $\pi^* \leftarrow \pi$  ligand-based absorption in the UV. Oxidization of the metal center to Ru(III) lowers the energy of the tpy-localized  $\pi^*$  orbitals near the metal center, increasing their acceptor quality, and red-shifting these transitions into the near UV.

Generation of the one-electron reduced species of each complex was accomplished using the same experimental set-up with platinum mesh working electrode held at a reducing potential, -1.70 V vs. 0.01 M Ag/AgNO<sub>3</sub> (-1.40 V vs. SCE). Absorption scans collected as a function of bulk electrolysis time (Figure 2.5) shows a growth of new absorption features throughout the visible and UV regions with a decrease in the <sup>1</sup>MLCT  $\leftarrow$  <sup>1</sup>GS intensity. The new absorption feature centered near 380 nm and the broad, flat absorptions from 580 to 820 nm are ascribed to  $\pi^* \leftarrow \pi^*$  (IL) transitions of the reduced ligand[8, 60–62] while the absorptive feature peaked near 515 nm is thought to be a combination of IL transitions of the reduced ligand and red-shifted <sup>1</sup>MLCT  $\leftarrow$  <sup>1</sup>GS absorption due to the anionic ligands electron donating character which destabilize the metal center d $\pi$  orbitals thereby reducing the  $\pi^* \leftarrow d\pi$  energy gap.[32, 63]

Before embarking on a discussion of how the features observed in the spectroelectrochemical data likely



Figure 2.4: Oxidative spectroelectrochemistry of  $[Ru(ttpy)_2]^{2+}$  (top),  $[Ru(tpy)(ttpy)]^{2+}$  (middle), and  $[Ru(tpy)_2]^{2+}$  (bottom) collected in room temperature acetonitrile with 0.1 M TBAP as the supporting electrolyte. The extent of sample oxidation in each of these panels has not been quantified.



Figure 2.5: Reductive spectroelectrochemistry of  $[Ru(ttpy)_2]^{2+}$  (top),  $[Ru(tpy)(ttpy)]^{2+}$  (middle), and  $[Ru(tpy)_2]^{2+}$  (bottom) collected in room temperature acetonitrile with 0.1 M TBAP as the supporting electrolyte. The jagged lines, most prominent in the data collected for  $[Ru(tpy)(ttpy)]^{2+}$  are a result of imperfect blanking of the light transmitted through the Pt mesh. The extent of sample reduction in each of these panels has not been quantified.

relate to those seen in the <sup>3</sup>MLCT excited-state, it is important to take note of recent work by Chergui, Hartl, Vlček, and coworkers that explored how well the absorptive features observed in one-electron reduced  $\alpha$ -dimine Re(I) complexes correlate with those of the MLCT excited-state. [62] In this study the authors used computational techniques to correlate, in terms of their physical origin, the absorptive features observed in the one-electron reduced species with those observed in the transient absorption experiment. In the near UV region, similar IL transitions of the reduced  $\alpha$ -dimine ligand were found to dominate both the MLCT excited-state and one-electron reduced complex absorption; therefore, the reductive spectroelectrochemical data is reasonably predictive of the MLCT absorption in this region. Correlations of the absorptive features in the visible and near IR were, however, found to be much less robust. For the one-electron reduced species, absorption over this spectral region was found to be dominated by IL transitions of the reduced ligand while absorption of the <sup>3</sup>MLCT was found to primarily involve transitions that are LMCT in nature wherein an electron is transferred from the  $\pi$ -system of a ligand (not the  $\pi$ \*-system) to the formally oxidized Ru<sup>III</sup> center. Moreover, the visible and near infrared IL transitions that dominated the one-electron reduced species absorption were found to be completely absent in the MLCT excited-state. This implies correlation of the absorptive features observed in the visible and near infrared region in the reductive electrochemistry with those of the MLCT excited-state are likely to be, at best, coincidental. Therefore, caution must be exercised when trying to interpret the visible region absorption features of the MLCT using solely reductive spectroelectrochemistry. To more accurately predict the MLCT absorption in this region we have also included the results of the oxidative spectroelectrochemistry, which allows for inclusion of LMCT absorption and any additional neutral ligand absorption that may result from oxidation of the metal center.

With these caveats in mind we turn to a discussion of predicted MLCT absorption features based on the oxidative and reductive spectroelectrochemistry. We stress that because efforts were not made to correct for absolute concentrations of the reduced and oxidized species, these spectra should be viewed in a strictly qualitative sense. Beginning with the UV and near UV region, the transient absorption of all three complexes is expected to have significant reduced ligand IL character as evidenced by the peaked absorption centered near 365 nm in each complex. The similarity in absorptive shape of the reduced tpy and ttpy ligands in the reductive electrochemistry implies that differentiation between the two species based on the differences in the absorptive feature shape, in for example the bis-heteroleptic species  $[Ru(tpy)(ttpy)]^{2^+}$ , will likely not be possible. ILCT transitions, manifest in the oxidative spectroelectrochemical traces, are expected to provide additional absorptive character in this region provided a neutral ttpy ligand is coordinated to the metal center that will be formally oxidized following photoexcitation. This will always be the case in  $[Ru(ttpy)_2]^{2^+}$ , never the case in  $[Ru(tpy)_2]^{2^+}$ , and only sometimes the case for  $[Ru(tpy)(ttpy)]^{2^+}$ ; namely, when the chargetransferred electron resides on the higher energy tpy ligand in, for example, the tpy-localized configuration. From 440 to 600 nm, bleaching of the ground state absorption is expected to dominate in all three complexes with absorption beyond approximately 600 nm expected to be relatively weak and featureless due to the domination of LMCT transitions (vide supra). The distinct band centered near 535 nm in the reductive spectroelectrochemistry of all three complexes is not expected to be present in the transient spectra as it is thought to be red-shifted <sup>1</sup>MLCT  $\leftarrow$  <sup>1</sup>GS absorption of the one-electron reduced species (vide supra).

# 2.4 Pump-Probe Spectroscopy of $[Ru(tpy)_2]^{2+}$

With an understanding of the features likely to be present in the <sup>3</sup>MLCT difference spectra, we begin our discussion of the time-resolved UV-Vis pump-probe spectra and kinetics. At the outset we have assumed the absorptive features observed are <sup>3</sup>MLCT in character because ultrafast measurements of Group VIII polypyridyls have found that intersystem crossing of the initially excited <sup>1</sup>MLCT to the <sup>3</sup>MLCT state occurs on a sub-100 fs timescale.[34, 64–67] As detailed in the experimental section, the relative electric field polarization between the pump and probe beam was set to the magic angle (54.7°) to ensure only excited-state population dynamics were being monitored.[68, 69] Finally, all of the kinetics studies presented herein made use of an excitation pulse centered at 525 nm, which corresponds to the red edge of the <sup>1</sup>MLCT absorption band. This central excitation frequency was chosen in an effort to minimize the amount of energy used during the photoexcitation process and, therefore, the amplitude of vibrational cooling dynamics in the transient data.[70] For reference, the timescale of such vibrational cooling processes have been reported over a 5 to 20 ps range in related Ru(II) and Os(II) polypyridyl species.[51, 57, 70, 71] The transient spectrum of [Ru(tpy)<sub>2</sub>]<sup>2+</sup> collected 10 ps after <sup>1</sup>MLCT  $\leftarrow$  <sup>1</sup>GS excitation, Figure 2.6, qualitatively agrees with our predictions based on the spectroelectrochemical results and is dominated by three features, namely, a strong bleach centered near 475 nm and two absorption features from 360 to 425 nm and from 550 to 650 nm. The bleach is ascribed to loss of  ${}^{1}MLCT \leftarrow {}^{1}GS$  absorption while the absorptive feature from 360



Figure 2.6: Chirp corrected magic angle transient absorption spectrum of  $[\text{Ru}(\text{tpy})_2]^{2+}$  (green) collected 10 ps after excitation. The transient spectra of  $[\text{Ru}(\text{ttpy})_2]^{2+}$  (dark blue, transparent) and  $[\text{Ru}(\text{tpy})(\text{ttpy})]^{2+}$  (light blue, transparent) have been included for reference. Data points were collected every 5 nm and are represented by the filled circles. Each sample was isoabsoprtive at the 514 nm excitation frequency. Data contained between the two dashed lines has been omitted due to contamination by pump beam scatter. Inset: chirp corrected magic angle transient absorption spectra of each complex using a pump beam centered at 495 nm. These spectra have been included to show the bleach-to-absorbance transition on the red side of the spectrum. Note: for these data the absorbance of each sample at the pump central frequency was variable.

to 425 nm is attributed to IL transitions of the reduced tpy ligand. The latter assignment agrees with the spectroelectrochemistry characterization of other groups, [8, 61] previous transient absorption experiments on  $[\text{Ru}(\text{tpy})_2]^{2+}$  and related complexes, [7, 10, 11] as well as studies of the tris-polypyridyl analogue molecule  $[\text{Ru}(\text{bpy})_3]^{2+}$ . [15, 51, 72, 73] The weak, featureless absorption from 550 to 650 nm is assigned to LMCT transitions based on our oxidative spectroelectrochemistry and the previously discussed results of Chergui, Hartl, Vlček, and coworkers. [62] Temporal dynamics of the <sup>3</sup>MLCT in  $[\text{Ru}(\text{tpy})_2]^{2+}$  were monitored by collecting single wavelength kinetics at 380, 475 and 620 nm. These probe wavelengths allow us to monitor overall <sup>3</sup>MLCT dynamics as well as absorptive changes associated with the reduced ligand, the ground state recovery and LMCT absorption, respectively. Representative traces are shown in Figure 2.7. Global fitting of the data (see Appendix for details) revealed a dominant decay component of 124  $\pm$  3 ps present at all

probe wavelengths and a weak, early time decay of  $2.3 \pm 0.4$  ps present at 380 and 620 nm (Table 2.2). The 124 ps excited-state lifetime we measure closely agrees with the previously published 120 ps lifetime

Probe Wavelength/nm	Tau Values^b/ps ( $\pm 2\sigma)$	Averaged pre-exponential values b $(\pm 2\sigma)$
380	$ au_1 = 124 \; (3);   au_2 = 2.3 \; (0.4)$	$A_1 = 0.92 \ (0.01); \ A_2 = 0.16 \ (0.01)$
475	$\tau_1 = 124 \ (3); \ \tau_2 = NA^a$	$A_1 = -1.00 (0.004); A_2 = NA^a$
620	$\tau_1 = 124 \; (3);  \tau_2 = 2.3 \; (0.4)$	$A_1 = 0.98 \; (0.03);  A_2 = 0.07 \; (0.03)$

Table 2.2: Global fitting results for  $[Ru(tpy)_2]^{2+}$  kinetics data collected in room temperature  $CH_3CN$ 

<sup>a</sup>Component not present

<sup>b</sup>Average values resulting from global fitting three independent data sets. The values given in parenthesis represent  $\pm$  two times the standard deviation.

of  $[Ru(tpy)_2]^{2+}$  measured in room temperature 2:3 water/acetonitrile using picosecond transient absorption techniques.[15] This is much shorter than the often cited 250 ps lifetime of  $[Ru(tpy)_2]^{2+}$  in room temperature water recorded by Winkler and coworkers[7] and points to significant solvation effects in the excited-state decay. Preliminary experiments using neat water as the solvent system corroborate the solvent dependence of the excited-state lifetime (see Appendix A).

Considering only the data collected in acetonitrile, the early time loss of absorptive signal observed at 380 and 620 nm has not been previously reported in the literature and we initially hypothesized it to be a signature of vibrational cooling of the <sup>3</sup>MLCT. Despite our efforts to minimize the amount of excess energy used during the photoexcitation process, approximately 2000 cm<sup>-1</sup> of energy must be dissipated to thermalize the <sup>3</sup>MLCT (based on the <sup>3</sup>MLCT  $E_{oo}$  value[74] and the 525 nm excitation wavelength). Without the use of time-resolved infrared techniques such vibrational cooling assignments can prove difficult.[71] Papanikolas and coworkers, however, have shown in ultrafast studies of  $[Os(bpy)_3]^{2+}$  that vibrational cooling dynamics can be probed by monitoring the reduced ligand absorption feature in the near UV. Specifically, vibrational cooling dynamics manifest as an overall spectral narrowing of the reduced ligand absorption feature concomitant with an increase in absorbance at the absorptive maximum.[51, 70] To test for this in  $[Ru(tpy)_2]^{2+}$ , we collected additional chirp corrected spectra focusing on the wavelength region from 360 to 430 nm (Figure 2.8). In the first picoseconds following photo-excitation the entire UV absorption band



Figure 2.7: Magic angle transient kinetics of  $[Ru(tpy)_2]^{2+}$  collected in acetonitrile at  $\lambda_{probe} = 380$  nm (top),  $\lambda_{probe} = 475$  nm (middle), and  $\lambda_{probe} = 620$  nm (bottom). The solid red lines represent global fits to the data.

undergoes a quasi-monotonic decay with negligible spectral narrowing. This suggests another excited-state process, and not vibrational cooling, is responsible for the 2.3 ps dynamics observed in the kinetics at 380 and 620 nm. The UV absorption band is characteristic of the <sup>3</sup>MLCT state; therefore, the decrease in absorptive intensity of this feature at early times (Figure 2.8) suggests a loss of <sup>3</sup>MLCT population shortly after photoexcitation. The lost population, however, is not decaying directly to the ground state as



Figure 2.8: Chirp corrected magic angle transient spectra of  $[Ru(tpy)_2]^{2+}$  collected over the first 10 ps following photoexcitation. Data points were collected every 5 nm and are represented by the filled circles. The arrows highlight the temporal evolution of the spectra.

evidenced by the monoexponential bleach recovery at 475 nm and appears to be funneling into a non-MLCT type excited-state. A likely candidate is the triplet metal-centered excited state ( ${}^{3}MC$ ,  $d\pi^{5}\sigma^{*}$  metal-center electron configuration). Computational results have consistently found it to be energetically proximal to the  ${}^{3}MLCT$  state in  $[Ru(tpy)_{2}]^{2+}$ .[17, 75, 76] We believe the early time 2.3 ps dynamics are a result of excited-state population equilibrating between the  ${}^{3}MLCT$  and  ${}^{3}MC$ . During the equilibration process, excited-state absorptions indicative of  ${}^{3}MLCT$  population, such as the ligand-based radical anion character at 395 nm, can be expected to become less intense as population flows out of the  ${}^{3}MLCT$  and into the  ${}^{3}MLCT$  and  ${}^{3}MC$  metal-center in LMCT absorption observed in the data collected at 620 nm can also be attributed to  ${}^{3}MLCT$  and  ${}^{3}MC$  equilibration as population of an anti-bonding metal center orbital increases the Ru-N bond distances,[17]

thereby decreasing the metal-ligand orbital overlap and reducing the LMCT oscillator strength. Moving to the longer timescale dynamics we now consider the rate limiting steps for ground state recovery. Because equilibration between the <sup>3</sup>MLCT and <sup>3</sup>MC occurs much faster than the overall excited-state decay, 2.3 ps vs. 124 ps, the rate determining decay process must involve either decay directly from the <sup>3</sup>MLCT to the <sup>1</sup>GS or <sup>3</sup>MC to <sup>1</sup>GS intersystem crossing. The excited-state potential energy surface calculations of Persson and coworkers[17] prove informative in this context; they observed a low energy crossing of the <sup>3</sup>MC and <sup>1</sup>GS potential energy surface at more extended Ru-tpy bond lengths (approximately 2400 cm<sup>-1</sup> above the <sup>3</sup>MC minimum). In agreement with previous conclusions,[6, 17, 77] the presence of such a crossing would allow for efficient <sup>3</sup>MC  $\rightarrow$  <sup>1</sup>GS intersystem crossing, and can therefore rationalize the short <sup>3</sup>MC lifetime. Furthermore, based on temperature dependent emission measurements, direct <sup>3</sup>MLCT  $\rightarrow$  <sup>1</sup>GS decay occurs on a much longer microsecond timescale.[74] Therefore, we have assigned the rate limiting decay step to <sup>3</sup>MC  $\rightarrow$  <sup>1</sup>GS intersystem crossing, which agrees with the conclusion reached by Ohno and co-workers for crystalline [Ru(tpy)<sub>2</sub>]<sup>2+</sup>.[20] The overall kinetics scheme describing the photoexcited state in [Ru(tpy)<sub>2</sub>]<sup>2+</sup> is given in Eq 2.1

$${}^{3}\text{MLCT} \xrightarrow[k_{a}]{k_{b}} {}^{3}\text{MC} \xrightarrow{k_{c}} {}^{1}\text{GS}$$
 (2.1)

Equilibration between the <sup>3</sup>MLCT<sup>-3</sup>MC states causes the three processes characterized by  $k_a$ ,  $k_b$ ,  $k_c$ , to be convolved into the observed rate constant of decay. If one assumes that <sup>3</sup>MLCT<sup>-3</sup>MC equilibrium is fast relative to ground state recovery (pre-equilibrium approximation)[78] extracting the values of  $k_a$ ,  $k_b$ ,  $k_c$ , and the equilibrium constant ( $K_{eq} = k_a/k_b$ ) from the experimentally observed rates is straightforward. This is detailed in the Appendix A. We find that  $k_a = 6.4 \times 10^{10} \text{ s}^{-1}$  (~15 ps),  $k_b = 3.7 \times 10^{11} \text{ s}^{-1}$  (~2.7 ps),  $k_c =$  $5.4 \times 10^{10} \text{ s}^{-1}$  (~18 ps), and  $K_{eq} = 0.17$ . The equilibrium constant we measure is at odds with those predicted by theory, where the <sup>3</sup>MC is typically lower in energy than the <sup>3</sup>MLCT.[17, 75, 79] We suspect the lack of explicit solvation in the theoretical results may be leading to this discrepancy.

# 2.4.1 Pump-Probe Spectroscopy of $[Ru(ttpy)_2]^{2+}$

Turning now to characterization of the arylated homoleptic  $[Ru(ttpy)_2]^{2+}$ , the transient spectrum collected 10 ps after excitation (Figure 2.9) is, again, qualitatively similar to our predictions based on the

oxidative and reductive spectroelectrochemistry (Figures 2.4 and 2.5). The absorption feature from 360 to 435 nm is attributed to both IL transitions of the reduced ttpy ligand and ILCT transitions of the neutral ttpy ligand (vide supra). This results in the oscillator strength of this feature being significantly larger than that observed in  $[\text{Ru}(\text{tpy})_2]^{2+}$  and  $[\text{Ru}(\text{tpy})(\text{ttpy})]^{2+}$ . In contrast to  $[\text{Ru}(\text{tpy})_2]^{2+}$ , the region from 525 to 650 nm is dominated by an intense absorption feature peaked near 590 nm. Based on the similar oxidative spectroelectrochemical traces collected for  $[\text{Ru}(\text{ttpy})_2]^{2+}$  and  $[\text{Ru}(\text{tpy})_2]^{2+}$  in this spectral range, this new absorption is not thought to be LMCT in nature. Instead, it is assigned to reduced ttpy IL absorption. Strong, visible region absorption feature like this are characteristic of the <sup>3</sup>MLCT in phenyl-substituted Ru(II) polypyridyl complexes[11, 57, 80–83] while non-phenyl substituted analogs[7, 34, 51, 71, 73] typically show weak, featureless absorption similar to that of  $[\text{Ru}(\text{ttpy})_2]^{2+}$ . Temporal evolution of the <sup>3</sup>MLCT was



Figure 2.9: Chirp corrected magic angle transient absorption spectrum of  $[\operatorname{Ru}(\operatorname{ttpy})_2]^{2+}$  (dark blue) collected 10 ps after excitation. The transient spectra of  $[\operatorname{Ru}(\operatorname{tpy})_2]^{2+}$  (green, transparent) and  $[\operatorname{Ru}(\operatorname{tpy})(\operatorname{ttpy})]^{2+}$  (light blue, transparent) have been included for reference. Data points were collected every 5 nm and are represented by the filled circles. Each sample was isoabsoprtive at the 514 nm excitation frequency. Data contained between the two dashed lines has been omitted due to contamination by pump beam scatter. Inset: chirp corrected magic angle transient absorption spectra of each complex using a pump beam centered at 495 nm. These spectra have been included to show the bleach-to-absorbance transition on the red side of the spectrum. Note: for these data the absorbance of each sample at the pump central frequency was variable.

monitored by collecting single wavelength kinetics at 400, 480, and 620 nm and representative data are shown in Figure 2.10. Global fitting recovered a dominate exponential decay component of  $680 \pm 10$  ps present at



Figure 2.10: Magic angle transient kinetics of  $[Ru(ttpy)_2]^{2+}$  collected in acetonitrile at  $\lambda_{probe} = 380 \text{ nm}$  (top),  $\lambda_{probe} = 475 \text{ nm}$  (middle), and  $\lambda_{probe} = 620 \text{ nm}$  (bottom). The solid red lines represent global fits to the data.

all probe wavelengths (Table 2.3). The data collected at 620 nm were also found to contain an additional, poorly determined, growth component of  $30 \pm 40$  ps. We note that our kinetics differ from those reported by Laine and co-workers[82] where an approximate 2 ps rise dynamic in the transient data collected at 620 nm was observed. That we do not unambiguously observe similar timescale growth dynamics is likely a result of the different excitation frequencies used in the two experiments. Laine and co-workers employed a 400 nm excitation pulse, corresponding to the far blue edge of the <sup>1</sup>MLCT absorbance feature, and can be expected to preferentially excite molecules with high-energy ligand and solvation environments.[70] Largescale conformational relaxation dynamics are, therefore, expected during thermalization of the <sup>3</sup>MLCT excited-state and accordingly, the authors attributed the rising dynamic to delocalization of the excited electron onto the tolyl portion of the ttpy ligand (based on comparison to observations made in a phenylsubstituted Ru(II) tris-bipyridine analog).[57] On the other hand, our experiment employed excitation pulses

Table 2.3: Global fitting results for  $[Ru(ttpy)_2]^{2+}$  kinetics data collected in room temperature  $CH_3CN$ 

Probe Wavelength/nm	Tau Values^b/ps ( $\pm 2\sigma)$	Averaged pre-exponential values $^{\rm b}(\pm 2\sigma)$
400	$ au_1 = 680 \; (10)$	${\rm A}_1=1.00~(0.01)$
480	$ au_1 = 680 \; (10)$	$A_1 = -1.01 \ (0.01)$
620	$\tau_1=680~(10),\tau_2=30~(40)$	$A_1 = 1.09 \ (0.03); A_2 = -0.14 \ (0.06)$

<sup>a</sup>Component not present

centered at 525 nm, the red edge of the <sup>1</sup>MLCT absorption feature, and can be expected to preferentially excite molecules with ligand and solvation environments amenable to formation of the charge transfer excitedstate. Therefore, similar large-scale conformational relaxation dynamics are expected to be minimized in our transient data. The weak and poorly determined rise dynamics that we do observe at 620 nm ( $30 \pm 40$ ps) could be due to vibrational cooling of the photo-reduced ligand as this timescale roughly agrees with the results of transient IR experiments on related tris-bipyridyl complexes.[71] That similar vibrational cooling dynamics are not observed in the kinetics collected at 400 nm, where there is significant reduced ligand absorption, is likely a result of the neutral ttpy ILCT absorption and ground state bleaching contributing

<sup>&</sup>lt;sup>b</sup>Average values resulting from global fitting three independent data sets. The values given in parenthesis represent  $\pm$  two times the standard deviation.

significantly at this probe wavelength. The absence of early time decay dynamics in  $[Ru(ttpy)_2]^{2+}$  that would be similar to those observed in  $[Ru(tpy)_2]^{2+}$  suggests negligible equilibration of <sup>3</sup>MLCT and the <sup>3</sup>MC in the former. This is expected as the <sup>3</sup>MLCT in  $[Ru(ttpy)_2]^{2+}$  is stabilized by approximately 1,100 cm<sup>-1</sup> relative to the <sup>3</sup>MLCT in  $[Ru(tpy)_2]^{2+}$  (based on comparison of  $E_{oo}$  values[14, 74]) as a result of the ttpy ligand's lower energy  $\pi^*$  orbital and greater  $\sigma$ -donor character. Considering the kinetics scheme presented in Eq. 2.1, the rate of <sup>3</sup>MLCT  $\rightarrow$  <sup>3</sup>MC internal conversion can now be expected to be much slower while the <sup>3</sup>MC  $\rightarrow$  <sup>1</sup>GS internal conversion rate is likely comparable to the previously estimated rate of 5.4×10<sup>10</sup> s<sup>-1</sup> (~18 ps) as the identity of the tridentate ligand should have a limited effect on the <sup>3</sup>MC energy.[17, 79] Accordingly, we attribute the 680 ps timescale to the <sup>3</sup>MLCT  $\rightarrow$  <sup>3</sup>MC internal conversion process. As a final note, the 680 ps excited state lifetime we measure agrees well with an average of the previously published  $[Ru(ttpy)_2]^{2+}$  lifetimes measured by time correlated single photon counting.[14, 84, 85]

# 2.4.2 Pump-Probe Spectroscopy of $[Ru(tpy)(ttpy)]^{2+}$

We conclude with a discussion of the heteroleptic species  $[Ru(tpy)(ttpy)]^{2^+}$ . Again, the magic angle transient spectrum collected 10 ps after excitation, Figure 2.11, qualitatively agrees with the spectroelectrochemical predictions (Figures 2.4 and 2.5). In assigning the absorptive features one must be cognizant that both the ttpy-localized ( $[Ru^{III}(tpy)(ttpy^-)]^{2^+}$ ) and tpy-localized ( $[Ru^{III}(tpy^-)(ttpy)]_2^+$ ) <sup>3</sup>MLCT could be contributing to the overall absorptive signal. However, the strong, peaked absorption at 590 nm in the TA spectra (Figure 2.11), indicates that by 10 ps after photoexcitation essentially all of the photoexcited population resides in the low energy ttpy-localized <sup>3</sup>MLCT configuration – i.e. all  $[Ru^{III}(tpy)(ttpy^-)]^{2^+}$ . Accordingly, the absorptive feature from 360 to 425 nm is attributed solely to IL transitions of the reduced ttpy ligand as the neutral tpy ligand possesses negligible absorption at these wavelengths (vide supra). Temporal evolution of the <sup>3</sup>MLCT was monitored by collecting single wavelength kinetics at 400, 480, and 620 nm. Representative data are shown in Figure 2.12 Global fitting of the data returned two components, 3.3  $\pm 0.4$  ps and  $422 \pm 1$  ps (Table 2.4), that are present at each probe wavelength. The 3.3 ps component manifests as decay at 400 and 480 nm and as a growth at 620 nm. The longer 422 ps component was found to be the dominant decay at each probe wavelength. The data collected at 620 nm were also found to contain



Figure 2.11: Chirp corrected magic angle transient absorption spectrum of  $[Ru(tpy)(ttpy)]^{2+}$  (light blue) collected 10 ps after excitation. The transient spectra of  $[Ru(tpy)_2]^{2+}$  (green, transparent) and  $[Ru(ttpy)_2]^{2+}$  (dark blue, transparent) have been included for reference. Data points were collected every 5 nm and are represented by the filled circles. Each sample was isoabsoprtive at the 514 nm excitation frequency. Data contained between the two dashed lines has been omitted due to contamination by pump beam scatter. Inset: chirp corrected magic angle transient absorption spectra of each complex using a pump beam centered at 495 nm. These spectra have been included to show the bleach-to-absorbance transition on the red side of the spectrum. Note: for these data the absorbance of each sample at the pump central frequency was variable.

an additional, ill-defined growth component of  $40 \pm 20$  ps, which by analogy to  $[Ru(ttpy)_2]^{2+}$  is thought to reflect vibrational cooling of the reduced ttpy ligand. The spectral dependence of the 3.3 ps dynamic was Table 2.4: Global fitting results for  $[Ru(tpy)(ttpy)]^{2+}$  kinetics data collected in room temperature CH<sub>3</sub>CN

Probe Wavelength/nm	Tau Values <sup>b</sup> /ps ( $\pm 2\sigma$ )	Averaged pre-exponential values <sup>b</sup> $(\pm 2\sigma)$
400 480	$egin{array}{ll}  au_1=3.3 & (0.4); \  au_2=422 & (1) \  au_1=3.3 & (0.4); \  au_2=422 & (1) \end{array}$	$A_1 = 0.19 \ (0.01); A_2 = 0.79 \ (0.07)$ $A_1 = -0.04 \ (0.01); A_2 = -0.97$
620	$\tau_1 = 3.3 \ (0.4); \ \tau_2 = 422 \ (1); \ \tau_3 = 30 \ (40)$	$(0.03) = (0.03) = (0.03) = (0.03) = (0.03); A_2 = 1.37 = (0.03); A_3 = 1-0.09 = (0.04)$

<sup>a</sup>Component not present

<sup>b</sup>Average values resulting from global fitting three independent data sets. The values given in parenthesis represent  $\pm$  two times the standard deviation.

probed further by collection of additional chirp corrected transient spectra focusing on the first 10 ps after excitation (Figure 2.13). In agreement with the kinetic data, these spectra show an increase in absorptive



Figure 2.12: Magic angle transient kinetics of  $[Ru(tpy)(ttpy)]^{2+}$  collected in acetonitrile at  $\lambda_{probe} = 380$  nm (top),  $\lambda_{probe} = 475$  nm (middle), and  $\lambda_{probe} = 620$  nm (bottom). The solid red lines represent global fits to the data.

character from 445 to 650 nm with a simultaneous loss of absorptive character from 360 to 445 nm. Addressing first the 422 ps excited-state lifetime, we have assumed the rate limiting decay step is  ${}^{3}MLCT \rightarrow$  ${}^{3}MC$  internal conversion by analogy to  $[Ru(ttpy)_{2}]^{2+}$ . The ttpy-localized  ${}^{3}MLCT$  is expected to be significantly stabilized compared to the  ${}^{3}MC$ , resulting in a considerable energetic barrier for  ${}^{3}MLCT \rightarrow {}^{3}MC$ inter-conversion. That the lifetime of  $[Ru(tpy)(ttpy)]^{2+}$  is somewhat shorter than that of  $[Ru(ttpy)_{2}]^{2+}$ , 422 ps vs. 680 ps, is thought be a result of the weaker sigma donation character of the tpy ancillary ligand in the former.[32] This would slightly destabilize the Ru(III) metal center (raising the energy of the  ${}^{3}MLCT$ ). In



Figure 2.13: Chirp corrected magic angle transient absorption spectrum of  $[Ru(tpy)(ttpy)]^{2+}$  (light blue) collected over the first 10 ps following photoexcitation. Data points were collected every 5 nm and are represented by the filled circles. Data contained between the two dashed lines has been omitted due to contamination by pump beam scatter. The arrows highlight the temporal evolution of the spectra.

turn, this would decrease the <sup>3</sup>MLCT  $\rightarrow$  <sup>3</sup>MC activation barrier and result in an increased rate of internal conversion. In assigning the 3.3 ps dynamic, we have ruled out <sup>3</sup>MLCT–<sup>3</sup>MC equilibration. Such dynamics would manifest as a loss of the <sup>3</sup>MLCT absorptions at 590 nm and not the observed increase (Figure 2.13). Instead, we find the spectral dependence of the 3.3 ps dynamic to be consistent with interligand electron transfer (ILET). As discussed prior, excitation at 525 nm is expected to form initial MLCT population that is heterogeneous in nature with approximately 25% being tpy-localized and the remaining 75% being ttpylocalized. Of these two species, our electrochemical measurements suggest the tpy-localized MLCT species

is higher in energy. Therefore, as the initial population evolves, tpy-localized species can be expected to interconvert to ttpy-localized species via ILET. Increasing ttpy-localized absorbance features should herald this process and in our studies, these are experimentally manifest in the growth of absorption centered near 590 nm (Figures 2.13 and 2.4). On the other hand, in spectral regions where the tpy-localized species is more absorptive than the ttpy-localized species, ILET would manifest as a decrease in excited-state absorption. This is what we observe to the blue of 445 nm where the tpy-localized <sup>3</sup>MLCT absorption is composed of both reduced tpy IL transitions and neutral ttpy ligand ILCT transitions while the ttpy-localized absorption is composed of only reduced ttpy IL transitions. Because it is not, a priori, obvious that the combined oscillator strength of the reduced tpy IL transition and the neutral ttpy ILCT transitions are greater than that of the reduced ttpy IL absorption, we used the isoabsorptive (at the pump central frequency) transient spectra of  $[Ru(tpy)_2]^{2+}$ ,  $[Ru(tpy)(ttpy)]^{2+}$  and  $[Ru(ttpy)_2]^{2+}$  collected 10 ps after excitation (Figure 2.11) to estimate the relative molar absorptivity of each of these transitions at 400 nm. A brief description of the methodology used to make these estimates is given below with a more detailed account provided in Appendix A. First, bleach contributions were assumed to be equal to the ground state molar absorptivity of the samples given in Figure 2.3. The reduced tpy and ttpy ligand molar absorption were then quantified using the transient spectra of  $[Ru(tpy)_2]^{2+}$  and  $[Ru(tpy)(ttpy)]^{2+}$ , respectively, given in Figure 2.12 (as well as 2.6 and 2.9). Finally, the neutral ttpy ligand ILCT molar absorption was estimated using the transient spectra of  $[Ru(ttpy)_2]^{2+}$  and the reduced ttpy absorption from above. Based on this analysis we conclude that the tpy-localized <sup>3</sup>MLCT, which again consists of reduced tpy ligand and neutral ttpy ligand absorption, is  $\sim 1.3$  times more absorptive than the ttpy-localized <sup>3</sup>MLCT at 400 nm. Therefore, the 3.3 ps decrease in absorption on the blue side corresponds to loss of the tpy-localized species (due to ILET) with growth of the feature centered near 590 nm reflecting formation of the ttpy-localized species. The ILET process in Ru(II) and Os(II) tris polypyridyl complexes has been the topic of much previous research. [70, 86–89] The current consensus, based on both experimental [51, 90] and computational [45, 46] results, suggests that ILET occurs on a sub-picosecond timescale in both  $[Ru(bpy)_3]^{2+}$  and  $[Os(bpy)_3]^{2+}$ . Moreover, the computational results paint a rich picture where the electron can be seen to flow, with processes of delocalizing over more than one ligand and re-localizing on a single ligand occurring on an ultrafast timescale. This suggests some degree of electronic communication between the ligands, particularly if the excited electron delocalizes over more than one ligand during the ILET mechanism. In contrast to tris-polypyridyl complexes, the  $\pi$ -systems of the ligands in [Ru(tpy)(ttpy)]<sup>2+</sup> are nominally orthogonal (analogous to geometrically constrained donorbridge-acceptor system[26, 82, 91, 92]) and this may be expected to influence ILET leading to the longer 3.3 ps timescale. Electronic coupling may be facilitated by molecular distortions in the coordination sphere leading to direct interaction of ligand  $\pi$ -systems or unoccupied metal orbitals serving within a superexchange pathway. It is noted that our 3.3 ps ILET time scale is similar to one inferred (10 ps) for a comparable Os(II) bis-terpyridine moiety within a metal-complex/porphyrin dyad. This similarity of Ru(II) and Os(II) ILET mirrors observations in the tris complexes [Ru(bpy)<sub>3</sub>]<sup>2+</sup> and [Os(bpy)<sub>3</sub>]<sup>2+</sup>.

### 2.5 Conclusion

Working towards our long term goal of interrogating and controlling molecular dynamics using shaped laser fields, we have developed a foundational understanding of photophysics in three bis-terpyridine Ru(II) complexes:  $[Ru(tpy)_2]^{2+}$ ,  $[Ru(ttpy)_2]^{2+}$ , and  $[Ru(tpy)(ttpy)]^{2+}$  in room temperature acetonitrile using linear absorption, electrochemical, spectroelectrochemical, and ultrafast pump-probe techniques. In the nominal parent complex of this series  $[Ru(tpy)_2]^{2+}$  the overall excited-state lifetime was found to be 124 ps with equilibration of population between the <sup>3</sup>MLCT and <sup>3</sup>MC states observed shortly after <sup>1</sup>MLCT  $\leftarrow$  <sup>1</sup>GS photoexcitation. The spectroscopic hallmark of this equilibration process is loss of the reduced ligand absorption band in the near UV – a marker of the <sup>3</sup>MLCT – without concomitant recovery of the groundstate bleach. Decreased intensity of the LMCT absorption also accompanied the <sup>3</sup>MLCT-<sup>3</sup>MC equilibration and gives some indirect experimental evidence for elongated Ru-ligand bond lengths in the <sup>3</sup>MC state, which is predicted in computational results.[17] A majority of the excited state population was found to reside in the  $^{3}$ MLCT with an approximate equilibrium constant of 0.17. The rate limiting decay step in the ground-state recovery is assigned to  ${}^{3}MC \rightarrow {}^{1}GS$  intersystem crossing and based on the observed 124 ps lifetime and the estimated equilibrium constant we predict the timescale for this intersystem crossing to be approximately 18 ps. In  $[Ru(ttpy)_2]^{2+}$  no  ${}^{3}MLCT-{}^{3}MC$  equilibration dynamics were observed with their absence attributed to stabilization of the  ${}^{3}MLCT$  in  $[Ru(ttpy)_{2}]^{2+}$  resulting in an effective localizing all the excited-state population

in the <sup>3</sup>MLCT. Accordingly, <sup>3</sup>MLCT  $\rightarrow$  <sup>3</sup>MC internal conversion becomes the rate limiting step in groundstate recovery and a much longer 680 ps excited-state lifetime is observed. A poorly determined  $\sim 30$  ps dynamics was also found to be present in the kinetics collected at 620 nm and is thought to reflect vibrational cooling within the photo-reduced ttpy ligand. The <sup>3</sup>MLCT excited-state of  $[Ru(tpy)(ttpy)]^{2+}$ , as compared to the two homoleptic complexes, has distinct dynamics at times shortly after photoexcitation. These have been assigned to interligand electron transfer (ILET) of the type  $[\operatorname{Ru}^{\operatorname{III}}(\operatorname{typ}^{-})(\operatorname{ttpy})]^{2+} \rightarrow [\operatorname{Ru}^{\operatorname{III}}(\operatorname{tpy})(\operatorname{ttpy}^{-})]^{2+}$ which occurs on a 3.3 ps timescale. Because of the nominal orthogonality of the two ligand  $\pi$ -systems, electronic coupling would require molecular distortions in the coordination sphere that affect direct ligandligand interactions or superexchange via unoccupied metal orbitals. An alternate mechanism involving transient population of the <sup>3</sup>MC state,  $([Ru^{III}(tpy^{-})(ttpy)]^{2+} \rightarrow {}^{3}MC (d\pi^{5}\sigma^{*}) \rightarrow [Ru^{III}(tpy)(ttpy^{-})]^{2+},$ may also be possible. However, in  $[Ru(tpy)_2]^{2+}$  the timescale for  ${}^{3}MLCT \rightarrow {}^{3}MC$  internal conversion is significantly slower ( $\sim 15$  ps) suggesting this pathway in the heteroleptic species is likely not important. The rate limiting step for ground-state recovery in  $[Ru(tpy)(ttpy)]^{2+}$  was assigned to <sup>3</sup>MLCT (ttpy-localized)  $\rightarrow$  ${}^{3}MC$  internal conversion. The excited-state lifetime was found to be 422 ps and the reduction in lifetime relative to the bis-homoleptic  $[Ru(ttpy)_2]^{2+}$  (which also contains a low energy ttpy ligand) is attributed to decreased stabilization of the Ru(III) center by the tpy ancillary ligand.

In the lens of the proposed AFC control experiments, the observed ILET dynamics are of particular import. They demonstrate that the initially excited MLCT excited state should not be conceptualized as a "single" state but as two distinct ligand-localized MLCT excited states. These states can then interconvert on a picosecond timescale with population flowing towards the thermodynamically more stable configuration. Importantly, this interconversion occurs on a timescale for which vibrational coherences may persist persist.[93–98] One could imagine a scenario where, in the dual acceptor  $[Ru(tpy-An)(tpy-\phi-MV)]^{4+}$ , if vibrational wavepackets created could enhance/suppress ILET then the relative yield of EnT and ET product could be controlled if the EnT and ET timescales were fast enough to pull population out of the MLCT before full thermalization.\* Of course, such control is predicated on the impulsive excitation of vibrational wavepackets and the current data set shows no evidence that such wavepackets can be created. Resonance

<sup>\*</sup> i.e. before the long-time statistical limit for population in each MLCT configuration is reached.

Raman spectra of  $[Ru(tpy)_2]^{2+}$  in room temperature solvent[42] suggest pertinent vibrational modes, such as a Ru-N stretching vibration at 334 cm<sup>-1</sup>, are within the bandwidth of our laser to impulsively excite. Vibrational coherences in bromo-containing bis-terpyridine Ru(II)[98] and Fe(II) bis-terpyridine complexes<sup>†</sup> have been observed in our lab, therefore, it is not inconceivable that vibrational coherence could be observed in the ET and EnT dyads and/or the dual acceptor system. Finally, the excitation laser pulse used in the AFC pulse shaping experiments is shorter, ~ 36 fs (see Chapter 6), than the laser pulse used here.

One may also question why AFC pulse shaping experiments were not undertaken to try and modulate the rate of ILET in  $[Ru(tpy)(ttpy)]^{2+}$ . The problem with such an experiment is the lack of a robust feedback signal. If one could affect faster ILET via interaction with a shaped excitation pulse then the rise feature in the kinetics data should become sharper; however, given the nature of pulse shaping one loses control over "t = 0". The simple addition of linear phase can shift the pulse  $\pm$  picoseconds relative to the probe. Moreover, if the optimal pulse were temporally broad, made up of a train of sub pulses for example, the ILET dynamic would become convolved with the pulse envelope making extraction of the true ILET timescale very difficult. In essence the transient signal at early times can no longer be assumed to accurately reflect the molecular dynamics.<sup>‡</sup> Because of these uncertainties AFC experiments were not conducted on any of the complexes detailed in this chapter.

 $<sup>^\</sup>dagger$  Initial results from work done by Sam Shepard

<sup>&</sup>lt;sup> $\ddagger$ </sup> This is shown in more detail in Chapter 6.

# Chapter 2 Bibliography

- (1) C. Brif, R. Chakrabarti, and H. Rabitz, New Journal of Physics, 2010, 12, 075008.
- (2) M. Dantus and V. V. Lozovoy, *Chemical Reviews*, 2004, **104**, 1813–1859.
- (3) S. A. Rice and M. Zhao, Optical Control of Molecular Dynamics, Wiley, New York, 2000.
- (4) T. Brixner, N. H. Damrauer, and G. Gerber, Advances in Atomic, Molecular, and Optical Physics, 2001, 46, 1–54.
- (5) M. L. Stone and G. A. Crosby, Chemical Physics Letters, 1981, 79, 169–173.
- (6) J. R. Kirchhoff, D. R. McMillin, P. A. Marnot, and J. P. Sauvage, Journal of the American Chemical Society, 1985, 107, 1138–1141.
- J. Winkler, T. L. Netzel, and N. Sutin, Journal Of The American Chemical Society, 1987, 109, 2381–2392.
- (8) R. Berger and D. Mcmillin, Inorganic Chemistry, 1988, 27, 4245–4249.
- (9) C. R. Hecker, A. K. I. Gushurst, and D. R. McMillin, Inorganic Chemistry, 1991, 30, 538–541.
- (10) J. P. Collin, S. Guillerez, J. P. Sauvage, F. Barigelletti, L. Decola, L. Flamigni, and V. Balzani, *Inorganic Chemistry*, 1991, **30**, 4230–4238.
- (11) E. Amouyal, M. Mouallem-Bahout, and G. Calzaferri, *Journal of Physical Chemistry*, 1991, 95, 7641–7649.
- (12) J. P. Sauvage, J. P. Collin, J. C. Chambron, S. Guillerez, C. Coudret, V. Balzani, F. Barigelletti, L. Decola, and L. Flamigni, *Chemical Reviews*, 1994, 94, 993–1019.
- (13) K. Hutchison, J. C. Morris, T. A. Nile, J. L. Walsh, D. W. Thompson, J. D. Petersen, and J. R. Schoonover, *Inorganic Chemistry*, 1999, **38**, 2516–2523.
- (14) O. Johansson, M. Borgström, R. Lomoth, M. Palmblad, J. Bergquist, L. Hammarström, L. C. Sun, and B. Åkermark, *Inorganic Chemistry*, 2003, 42, 2908–2918.
- (15) U. Siemeling et al., Chemistry A European Journal, 2003, 9, 2819–2833.
- (16) E. A. Medlycott and G. S. Hanan, Coordination Chemistry Reviews, 2006, 250, 1763–1782.
- (17) T. Österman, M. Abrahamsson, H. C. Becker, L. Hammarström, and P. Persson, Journal of Physical Chemistry A, 2012, 116, 1041–1050.
- (18) K. Lashgari, M. Kritikos, R. Norrestam, and T. Norrby, Acta Crystallographica Section C: Crystal Structure Communications, 1999, 55, 64–67.
- (19) K. Kalyanasundaram, S. M. Zakeeruddin, and M. K. Nazeeruddin, Coordination Chemistry Reviews, 1994, 132, 259–264.
- (20) A. Islam, N. Ikeda, A. Yoshimura, and T. Ohno, *Inorganic Chemistry*, 1998, **37**, 3093–3098.
- (21) F. Neve, A. Crispini, S. Campagna, and S. Serroni, *Inorganic Chemistry*, 1999, **38**, 2250–2258.
- (22) B. P. Sullivan, J. M. Calvert, and T. J. Meyer, *Inorganic Chemistry*, 1980, 19, 1404–1407.
- (23) H. Hofmeier, E. Herdtweck, and U. S. Schubert, Zeitschrift Fur Anorganische Und Allgemeine Chemie, 2004, 630, 683–688.
- (24) K. J. Takeuchi, M. S. Thompson, D. W. Pipes, and T. J. Meyer, *Inorganic Chemistry*, 1984, 23, 1845–1851.
- (25) V. V. Pavlishchuk and A. W. Addison, Inorganica Chimica Acta, 2000, 298, 97–102.
- (26) H. A. Meylemans, J. T. Hewitt, M. Abdelhaq, P. J. Vallett, and N. H. Damrauer, Journal of the American Chemical Society, 2010, 132, 11464–11466.
- (27) A. Shirakawa and T. Kobayashi, Applied Physics Letters, 1998, 72, 147.
- (28) T. Wilhelm, J. Piel, and E. Riedle, Optics Letters, 1997, 22, 1494–1496.
- (29) U. Megerle, I. Pugliesi, C. Schriever, C. F. Sailer, and E. Riedle, Applied Physics B, 2009, 96, 215–231.
- (30) R. J. Watts, Journal of Chemical Education, 1983, 60, 834–842.
- (31) S. Campagna, F. Puntoriero, F. Nastasi, G. Bergamini, and V. Balzani, Photochemistry and Photophysics of Coordination Compounds I, 2007, 280, 117–214.
- (32) M. Maestri, N. Armaroli, V. Balzani, E. C. Constable, and A. M. W. C. Thompson, *Inorganic Chem-istry*, 1995, 34, 2759–2767.

- (33) C. C. Phifer and D. R. McMillin, *Inorganic Chemistry*, 1986, **25**, 1329–1333.
- (34) N. H. Damrauer, G. Cerullo, A. Yeh, T. R. Boussie, C. V. Shank, and J. K. McCusker, *Science*, 1997, 275, 54–57.
- (35) M. Presselt, B. Dietzek, M. Schmitt, S. Rau, A. Winter, M. Jager, U. S. Schubert, and J. Popp, Journal of Physical Chemistry A, 2010, 114, 13163–13174.
- (36) M. K. DeArmond and C. M. Carlin, Coordination Chemistry Reviews, 1981, 36, 325–355.
- (37) D. Braun, P. Huber, J. Wudy, J. Schmidt, and H. Yersin, Journal of Physical Chemistry, 1994, 98, 8044–8049.
- (38) H. Riesen and E. Krausz, Journal of Chemical Physics, 1993, 99, 7614–7618.
- (39) H. Riesen, L. Wallace, and E. Krausz, Journal of Physical Chemistry, 1996, 100, 17138–17144.
- (40) H. Riesen and E. Krausz, Chemical Physics Letters, 1996, 260, 130–135.
- (41) C. Turro, Y. C. Chung, N. Leventis, M. E. Kuchenmeister, P. J. Wagner, and G. E. Leroi, *Inorganic Chemistry*, 1996, **35**, 5104–5106.
- (42) P. W. Hansen and P. W. Jensen, Spectrochimica Acta Part a-Molecular and Biomolecular Spectroscopy, 1994, 50, 169–183.
- (43) R. F. Dallinger and W. H. Woodruff, Journal of the American Chemical Society, 1979, 101, 4391–4393.
- (44) P. G. Bradley, N. Kress, B. A. Hornberger, R. F. Dallinger, and W. H. Woodruff, Journal of the American Chemical Society, 1981, 103, 7441–7446.
- (45) M. E. Moret, I. Tavernelli, M. Chergui, and U. Rothlisberger, *Chemistry A European Journal*, 2010, 16, 5889–5894.
- (46) D. A. Hoff, R. Silva, and L. G. C. Rego, Journal Of Physical Chemistry C, 2011, 115, 15617–15626.
- (47) D. H. Oh and S. G. Boxer, Journal of the American Chemical Society, 1989, 111, 1130–1131.
- (48) L. Karki and J. T. Hupp, Inorganic Chemistry, 1997, 36, 3318–3321.
- (49) M. A. Webb, F. J. Knorr, and J. L. McHale, Journal of Raman Spectroscopy, 2001, 32, 481–485.

- (50) E. M. Kober, B. P. Sullivan, and T. J. Meyer, *Inorganic Chemistry*, 1984, 23, 2098–2104.
- (51) S. Wallin, J. Davidsson, J. Modin, and L. Hammarström, *Journal of Physical Chemistry A*, 2005, 109, 4697–4704.
- (52) A. Yeh, C. V. Shank, and J. K. McCusker, Science, 2000, 289, 935–938.
- (53) J. K. McCusker, Accounts of Chemical Research, 2003, 36, 876–887.
- (54) A. Juris, V. Balzani, F. Barigelletti, S. Campagna, P. Belser, and A. von Zelewsky, *Coordination Chemistry Reviews*, 1988, 84, 85–277.
- (55) J. C. Curtis, B. P. Sullivan, and T. J. Meyer, *Inorganic Chemistry*, 1983, 22, 224–236.
- (56) F. Tessore, D. Roberto, R. Ugo, M. Pizzotti, S. Quici, M. Cavazzini, S. Brun, and F. De Angelis, *Inorganic Chemistry*, 2005, 44, 8967–8978.
- (57) N. H. Damrauer and J. K. McCusker, Journal of Physical Chemistry A, 1999, 103, 8440–8446.
- (58) M. K. Nazeeruddin, S. M. Zakeeruddin, and K. Kalyanasundaram, Journal of Physical Chemistry, 1993, 97, 9607.
- (59) J. F. Michalec, S. A. Bejune, and D. R. McMillin, Inorganic Chemistry, 2000, 39, 2708-.
- (60) K. Nakamura, Bulletin of the Chemical Society of Japan, 1972, 45, 1943.
- (61) P. S. Braterman, J. I. Song, and R. D. Peacock, *Inorganic Chemistry*, 1992, **31**, 555–559.
- (62) S. Záliš, C. Consani, A. El Nahhas, A. Cannizzo, M. Chergui, F. Hartl, and A. Vlček, *Inorganica Chimica Acta*, 2011, **374**, 578–585.
- (63) P. A. Anderson, F. Richard Keene, T. J. Meyer, J. A. Moss, G. F. Strouse, and J. A. Treadway, Journal of the Chemical Society-Dalton Transactions, 2002, 3820–3831.
- (64) A. C. Bhasikuttan, M. Suzuki, S. Nakashima, and T. Okada, *Journal of the American Chemical Society*, 2002, **124**, 8398–8405.
- (65) A. Cannizzo, F. van Mourik, W. Gawelda, G. Zgrablic, C. Bressler, and M. Chergui, Angewandte Chemie-International Edition, 2006, 45, 3174–3176.

- (66) S. Yoon, P. Kukura, C. M. Stuart, and R. A. Mathies, *Molecular Physics*, 2006, **104**, 1275–1282.
- (67) A. Cannizzo, C. J. Milne, C. Consani, W. Gawelda, C. Bressler, F. van Mourik, and M. Chergui, *Coordination Chemistry Reviews*, 2010, 254, 2677–2686.
- (68) A. C. Albrecht, Journal of Molecular Spectroscopy, 1961, 6, 84.
- (69) H. S. Tan, I. R. Piletic, and M. D. Fayer, Journal Of The Optical Society Of America B-Optical Physics, 2005, 22, 2009–2017.
- (70) G. B. Shaw, D. J. Styers-Barnett, E. Z. Gannon, J. C. Granger, and J. M. Papanikolas, Journal of Physical Chemistry A, 2004, 108, 4998–5006.
- (71) W. Henry et al., Journal of Physical Chemistry A, 2008, 112, 4537–4544.
- (72) P. S. Braterman, A. Harriman, G. A. Heath, and L. J. Yellowlees, Journal of the Chemical Society-Dalton Transactions, 1983, 1801–1803.
- (73) A. Yoshimura, M. Z. Hoffman, and H. Sun, Journal of Photochemistry and Photobiology A: Chemistry, 1993, 70, 29–33.
- (74) A. Amini, A. Harriman, and A. Mayeux, Physical Chemistry Chemical Physics, 2004, 1157–1164.
- E. Jakubikova, W. Z. Chen, D. M. Dattelbaum, F. N. Rein, R. C. Rocha, R. L. Martin, and E. R. Batista, *Inorganic Chemistry*, 2009, 48, 10720–10725.
- (76) A. O. Borg, S. S. M. C. Godinho, M. J. Lundqvist, S. Lunell, and P. Persson, Journal of Physical Chemistry A, 2008, 112, 4470–4476.
- (77) M. K. DeArmond, Accounts of Chemical Research, 1974, 7, 309–315.
- (78) M. Rae and M. N. Berberan-Santos, Journal of Chemical Education, 2004, 81, 436–440.
- (79) O. A. Borg, S. Godinho, M. J. Lundqvist, S. Lunell, and P. Persson, Journal of Physical Chemistry A, 2008, 112, 4470–4476.
- (80) H. A. Meylemans, C. F. Lei, and N. H. Damrauer, Inorganic Chemistry, 2008, 47, 4060–4076.
- L. Hammarström, F. Barigelletti, L. Flamigni, M. T. Indelli, N. Armaroli, G. Calogero, M. Guardigli,
  A. Sour, J. P. Collin, and J. P. Sauvage, *Journal of Physical Chemistry A*, 1997, 101, 9061–9069.

- (82) P. P. Laine, F. Bedioui, F. Loiseau, C. Chiorboli, and S. Campagna, Journal of the American Chemical Society, 2006, 128, 7510–7521.
- (83) M. T. Indelli, M. Orlandi, C. Chiorboli, M. Ravaglia, F. Scandola, F. Lafolet, S. Welter, and L. De Cola, Journal of Physical Chemistry A, 2012, 116, 119–131.
- (84) P. P. Laine, F. Bedioui, E. Amouyal, V. Albin, and F. Berruyer-Penaud, Chemistry A European Journal, 2002, 8, 3162–3176.
- (85) M. Beley, J. P. Collin, J. P. Sauvage, H. Sugihara, F. Heisel, and A. Miehé, Journal of the Chemical Society-Dalton Transactions, 1991, 11, 3157–3159.
- (86) R. A. Malone and D. F. Kelley, Journal of Chemical Physics, 1991, 95, 8970.
- (87) J. L. Pogge and D. F. Kelley, Chemical Physics Letters, 1995, 238, 16.
- (88) J. P. Cushing, C. Butoi, and D. F. Kelley, Journal of Physical Chemistry A, 1997, 101, 7222–7230.
- (89) G. B. Shaw, C. L. Brown, and J. M. Papanikolas, Journal of Physical Chemistry A, 2002, 106, 1483– 1495.
- (90) S. A. Miller and A. M. Moran, Journal of Physical Chemistry A, 2010, 114, 2117–2126.
- (91) A. C. Benniston and A. Harriman, *Chemical Society Reviews*, 2006, **35**, 169–179.
- W. B. Davis, M. A. Ratner, and M. R. Wasielewski, Journal of the American Chemical Society, 2001, 123, 7877–7886.
- J. Kallioinen, G. Benko, P. Myllyperkio, L. Khriachtchev, B. Skårman, R. Wallenberg, M. Tuomikoski,
   J. Korppi-Tommola, V. Sundstrom, and A. P. Yartsev, *Journal of Physical Chemistry B*, 2004, 108, 6365–6373.
- (94) C. Consani, M. Prémont-Schwarz, A. ElNahhas, C. Bressler, F. van Mourik, A. Cannizzo, and M. Chergui, Angewandte Chemie International Edition, 2009, 48, 7184–7187.
- (95) J. N. Schrauben, K. L. Dillman, W. F. Beck, and J. K. McCusker, *Chemical Science*, 2010, 1, 405.
- (96) R. M. van der Veen, A. Cannizzo, F. van Mourik, A. Vlček, and M. Chergui, Journal of the American Chemical Society, 2011, 133, 305–315.

- (97) M. Iwamura, H. Watanabe, K. Ishii, S. Takeuchi, and T. Tahara, Journal of the American Chemical Society, 2011, 133, 7728–7736.
- (98) P. J. Vallett and N. H. Damrauer, "To be submitted for publication", 2012.

# Chapter 3

# Photophysical Characterization of $[Ru(tpy-An)(tpy)]^{2+}$ using Ultrafast and Nanosecond Pump-Probe Techniques: Observation of Ultrafast Triplet-Triplet Energy Transfer.

# 3.1 Overview

Having established a baseline understanding of the photophysics of Ru(II) bis-terpyridyl complexes in the previous chapter we now turn to a characterization of the photoinduced energy transfer (EnT) dynamics in  $[Ru(tpy-An)(tpy)]^{2+}$  (where tpy-An = 4'-(9-anthracenyl)-2,2':6',2''-terpyridine and tpy = 2,2':6',2''-terpyridine, see Figure 3.1). This dyad represents 1/2 of the target dual acceptor species



Figure 3.1:  $[Ru(tpy-An)(tpy)]^{2+}$ , the complex investigated in this chapter.

 $[Ru(tpy-An)(tpy-\phi-MV)]^{4+}$ . By studying its EnT dynamics we are establishing a framework for understanding the photoinduced dynamics of the dual-acceptor with the ultimate goal of establishing transient excited state features that can be used in the adaptive feedback controlled (AFC) pulse shaping experiments. EnT from Ru(II) polypyridyl complexes to covalently attached acene-like acceptors[1–9] have been of interest because of the ability to extend the lifetime of the energy stored in the MLCT excited state. For example, appending an anthracene to the 4'-position of a terpyridine ligands in  $[Ru(tpy)_2]^{2+}$ -i.e. the complex of interest in this chapter– results in robust excited state energy transfer from the <sup>3</sup>MLCT to the lowest energy T<sub>1</sub> state of the anthracene[3] via a Dexter-type energy transfer process.[10]\* The much longer excited state lifetime of the anthracene T<sub>1</sub> results in the excited state lifetime increasing from about 124 ps ( $[Ru(tpy)_2]^{2+}$ ) to  $\approx 1000$  ns.[8] The timescle of the <sup>3</sup>MLCT  $\rightarrow$  T<sub>1</sub> EnT process has, however, has not been experimentally resolved in this or closely related systems[2, 3, 6, 11, 12]. Considering that the <sup>3</sup>MLCT lifetime in  $[Ru(tpy)_2]^{2+}$  is only about 124 ps (See Chapter 2) the EnT must be taking place on a sub-ten picosecond timescale. In this chapter we detail the excited state dyanimes of  $[Ru(tpy-An)(tpy)]^{2+}$  following <sup>1</sup>MLCT photoexcitation as monitored using transient pump-probe techniques.

Following the same general structure of Chapter 2, the first part of this chapter is devoted to discussion of the linear absorption and electrochemical properties of  $[Ru(tpy-An)(tpy)]^{2+}$  with comparisons drawn to  $[Ru(tpy)_2]^{2+}$ so that perturbative effects of appending the anthracene at the 4' position of the terpyridine ligand can be understood. Results of the ultrafast pump-probe transient spectra and kinetics are then presented. Dynamics indicative of ultrafast  ${}^3MLCT \rightarrow T_1$  energy transfer are clearly observed. Finally, results of nanosecond pump-probe transient kinetics and spectra are presented and the long time behavior of the complex characterized.

# 3.2 Experimental

#### 3.2.1 General

It is well know that the  $T_1$  state anthracene can be quenched by  $O_2$  and, more importantly, in its ground state readily undergoes irreversible oxidation, therefore, all synthetic steps were conducted under an argon atmosphere. Synthesis of  $[Ru(tpy-An)(tpy)]^{2+}$  was accomplished in a manner similar to previously published procedures.[8] Tpy-An (4'-(9-anthracenyl)-2,2':6',2''-terpyridine) was purchased from HetCat (Hetcat.com) and re-crystalized from methanol prior to use. Terpyridine (tpy; 2,2':6',2''-terpyridine) was

<sup>\*</sup> i.e. triplet-triplet energy transfer

purchased from Aldrich and used as received. Cleaning of the complex was accomplished via silica gel column chromatography. This was not undertaken in an inert environment, however, the eluent of 8:1:1 acetonitrile, water and saturated potassium nitrate was argon sparged before use and ambient room lights were kept at a minimum. The identity and purity of  $[Ru(tpy-An)(tpy)]^{2+}$  was confirmed using <sup>1</sup>H-NMR and mass spectrometry. The <sup>1</sup>H-NMR spectra were collected on a Varian Inova 500 MHz spectrometer and are given in Appendix A. All duterated solvents were purchased from Cambridge Isotope Laboratories Inc. and used as received. Mass spectrometry and accurate mass analyses were performed by the Central Analytical Laboratory at the University of Colorado at Boulder.

All linear absorption, electrochemical and ultrafast pump-probe data<sup>†</sup> were, collected in sealed sample cells (Kontes Valves) and made use of solvent that had been thoroughly degassed with Argon. Overlays of Uv-Vis absorption taken before and after each experiment showed no evidence of anthracene oxidation or sample degradation. Oxidation of the anthracene is readily observable as decreased  ${}^{1}\text{An}^{*} \leftarrow {}^{1}\text{An}_{\text{GS}}$ absorption between 350 and 400 nm.

## 3.2.2 Nanosecond Transient Pump-Probe

Nanosecond transient kinetics and spectra were collected using a home built spectrometer that has been described in detail elsewhere.[13] Briefly, the pump pulse is derived from the second harmonic of a Continuum Minilight II Q-switched Nd:YAG laser (532 nm, ~ 20 ns FWHM, 2 Hz, ~1.5  $\mu$ J/pulse). The probe continuum is derived from a Newport/Oriel current intensified 75 W Xe arc lamp (ozone free, part number 6263). Prior to the sample the light is passed through a 3 inch quartz tube filled with water to remove infrared radiation. The pump and probe beams are then directed towards a 1 cm x 1 cm quartz cuvette sample cell, entering through orthogonal faces (90° to one another), and are spatially overlapped in the sample volume. The probe is focused using a 100 mm lens yielding a spot size of ≈1 mm which is approximately constant throughout the sample volume. The pump beam is focused using a 50 mm cylindrical lens. After exiting the sample the probe beam is collimated and then focused into a monochromator with entrance and exit slits set to 1 mm which yields an experimentally measured spectral resolution of ± 2

 $<sup>^\</sup>dagger$  Instrumentation detailed in Chapter 2

mm. Probe intensity as a function of time is measured using a negatively-biased Hammamatsu R-928 PMT operating at -1000 Vdc. The PMT signal was monitored using a LeCroy 9384L Oscilloscope terminated with a 50  $\Omega$  resistor. The transient absorption kinetics presented herein represents an average of 30 time traces of the probe intensity with pump on. Data processing and global fitting was accomplished using the commercially available Igor Pro 6.20B02 (WaveMetrics).

#### 3.2.3 Linear Absorption and Electrochemical Properties

The visible region absorption spectrum of  $[Ru(tpy-An)(tpy)]^{2+}$  in room temperature acetonitrile (Figure 3.2) is dominated by an intense <sup>1</sup>MLCT  $\leftarrow$  <sup>1</sup>GS absorption feature centered at 482 nm ( $\epsilon = 11,000$  $cm^{-1} M^{-1}$ ).[3] This feature is a slightly more intense and red-shifted compared to that observed in  $[Ru(tpy)_2]^{2+1}$ (Figure 3.2;  $\lambda_{max} = 476 \text{ nm}, \epsilon = 10,400 \text{ cm}^{-1} \text{ M}^{-1}$ ). This is not expected to be a result of overlapping <sup>1</sup>MLCT  $\leftarrow$  <sup>1</sup>GS and S<sub>1</sub>  $\leftarrow$  S<sub>0</sub> absorptions of the anthracene as the latter is observable in the near UV, between about 350 and 400 nm, as the highly structured absorption feature.[3, 14] In free tpy-An this features does to not extend much beyond 400 nm however, coordination with the di-cationic  $Zn^{2+}$  metal center results in a weak, low energy absorptive tail extending just past 440 nm (but not to 475 nm).[3] Instead, we suspect red-shifting of <sup>1</sup>MLCT is due to stabilization of the  $\pi^*$  on the tpy-An ligand involved in the <sup>1</sup>MLCT  $\leftarrow$  <sup>1</sup>GS absorption. Experimentally this is born out in a 70 mV decrease in the first reduction potential of  $[Ru(tpy-An)(tpy)]^{2+}$  relative to  $[Ru(tpy)_2]^{2+}$  (See Table 3.1). This decrease in reduction potential should not be construed as addition of an electron to the anthracene moiety as this occurs at a significantly more negative potential of -2.44 vs. 0.01 M Ag/AgNO<sub>3</sub>.[15] Instead, the decreased reduction potential is attributed to delocalization of the electron added to the tpy onto the anthracene, analogous to that observed in ttpy containing complexes. [16, 17] This idea is supported by crystal structure measurements of tpy-An containing Ru(II) complexes which show a slightly deflected dihedral between the tpy and An portion of the ligand (76.8° to 82.3°) despite the presence of strong crystal packing forces. [6, 9] Moreover, computational work by Meylemans and Damrauer [18, 19] exploring steric interactions in related Ru(II) systems suggest that the potential energy surface governing rotation about the tpy to anthracene bond would be relatively soft allowing for modest co-planarity in room temperature solution. The slight increase in the



Figure 3.2: Linear absorption spectrum of  $[Ru(tpy-An)(tpy)]^{2+}$  in degassed  $CH_3CN$  (red). The absorption spectrum of  $[Ru(tpy)_2]^{2+}$  (grey, dashed) is given for reference.

molar absorptivity of  $[Ru(tpy-An)(tpy)]^{2+}$  relative to  $[Ru(tpy)_2]^{2+}$  is also consistent with delocalization between the tpy and An portion of the tpy-An ligand. Such delocalization would lead to an increased <sup>1</sup>MLCT  $\leftarrow$  <sup>1</sup>GS transition dipole length.[16, 20, 21] In regards to the MLCT excited state, the tpy-An

Table 3.1: Electrochemical data for  $[Ru(tpy-An)(tpy)]^{2+}$  and related complexes collected in room temperature  $CH_3CN$ 

Complex	$E_{ox}(V)^{a}$	$E_{\rm red}(V)^{\rm a}$
$\left[\mathrm{Ru}(\mathrm{tpy}\mathrm{-An})(\mathrm{tpy})\right]^{2+}$	$0.99 (0.104); 1.29^{b}$	-1.54 (0.082); -1.25 <sup>b</sup>
$\left[\mathrm{Ru(tpy)}_2\right]^{2+\mathrm{c}}$	$0.95 (0.098); 1.25^{b}$	$-1.61$ (0.095); $-1.31^{\rm b}$
Anthracene <sup>d</sup>	$1.07$ ; $1.37^{\rm b}$	$-2.27$ ; $-1.97^{\rm b}$

<sup>a</sup>All electrochemical measurements were recorded vs. a freshly prepared 0.01 M Ag/AgNO<sub>3</sub> reference electrode in ACN. The anodic and cathodic wave separation is given in parentheses. A scan rate of 200 mV/s was used with 0.1 M TBAP as the supporting electrolyte.

<sup>b</sup>Values reported vs. SCE using the conversion factors of Pavlishchuck and Addison.[22] <sup>c</sup>Taken from Chapter 2.

<sup>d</sup>Taken from the cited reference.[23]

localized  $([Ru^{III}(tpy-An^{-})(tpy)]^{2+})$  configuration is expected to be lower in energy than the tpy-localized  $([Ru^{III}(tpy-An)(tpy^{-})]^{2+})$  species. The slight increase in molar absorptivity of  $[Ru(tpy-An)(tpy)]^{2+}$  at

525 nm (the pump pulse central frequency) relative to  $[Ru(tpy)_2]^{2+}$  to suggests there will be slightly more tpy-An localized MLCT excited-states in the initial <sup>1</sup>MLCT ensemble. Conversion of the higher energy  $[Ru^{III}(tpy-An)(tpy^-)]^{2+}$  to  $[Ru^{III}(tpy-An)(tpy^-)]^{2+}$  is expected to occur via interligand electron transfer (ILET) as discussed in Chapter 2.

# 3.3 Ultrafast Pump-Probe Results

As was the case in Chapter 2, we have assumed ultrafast intersystem crossing of the initially excited <sup>1</sup>MLCT to the <sup>3</sup>MLCT[24–28]. Therefore, absorptive features observed in the transient kinetics and spectral data described here are attributed to either the <sup>3</sup>MLCT or anthracene T<sub>1</sub>. The <sup>1</sup>MLCT  $\leftarrow$  <sup>1</sup>GS photoexcitation process is also understood to involve promotion of an electron to a single ligand as opposed to an excited state delocalized over both ligands.[29–34] We note here that red detuning of the excitation pulses to ~ 525 nm was undertaken for two reasons. First, the anthracene S<sub>1</sub>  $\leftarrow$  S<sub>0</sub> absorption in [Ru(tpy–An)(tpy)]<sup>2+</sup> likely extends to ~ 440 nm[3], therefore, excitation pulses with central frequencies corresponding to the blue edge of the MLCT feature are likely to result in creation of both the <sup>1</sup>MLCT and anthracene S<sub>1</sub> excited states. This is supported by preliminary data collected using a 400 nm excitation pulse (not shown) which shows more complicated EnT dyanimes than those reported here. Secondly, red-detuning the pump pulse minimizes the amount of excess energy deposited in chromophore upon <sup>1</sup>MLCT excitation. This helps to minimize the amplitude of vibrational cooling dynamics in the data.[35] For reference, vibrational cooling of the MLCT in Ru(II) and Os(II) polypyridyl complexes have been reported to occur on a 2 to 30 ps timescale.[35–39]

To characterize the evolution of the MLCT excited state of  $[Ru(tpy-An)(tpy)]^{2+}$  we first collected chirp corrected magic angle spectra at a variety of time points after photoexcitation (Figure 3.3). Beginning with the spectrum collected at 0.5 ps, the broad feature from 370 to 440 nm is similar to the reduced tpyligand absorption ( $\pi^* \leftarrow \pi^{*,-}$ ) and is thought to indicate population of a  $[Ru(tpy)_2]^{2+}$ -like <sup>3</sup>MLCT.[39–42] It should be noted that the sharp absorption feature centered between 420 and 430 nm is not present in transient spectra of  $[Ru(tpy)_2]^{2+}$ . Instead, this feature is characteristic of the anthracene T<sub>1</sub> excited-state and can attributed to T<sub>3</sub>  $\leftarrow$  T<sub>1</sub>absorption.[14, 43–45] Therefore, the absorption between 370 and 440 nm 0.5 ps after excitation is attributed to both <sup>3</sup>MLCT and anthracene T<sub>1</sub> transitions. Accordingly, the broad



Figure 3.3: Chirp corrected magic angle transient spectra of  $[Ru(tpy-An)(tpy)]^{2+}]$  in room temperature acetonitrile collected at a variety of time points after excitation. Spectral points were collected every 5 nm and are represented by the filled circles. Arrows have been added to highlight the temporal evolution of the features. The portion of each spectrum between the dashed lines has been omitted due to contamination by pump scatter.

and featureless absorption from 550 nm to 680 nm is thought to contain both <sup>3</sup>MLCT and T<sub>1</sub> absorption features with ligand-to-metal charge transfer transitions[39, 46] (LMCT) contributing from the former and T<sub>2</sub>  $\leftarrow$  T<sub>1</sub> absorption from the latter.[47] The bleach feature from about 440 to 550 nm is attributed to loss of the <sup>1</sup>MLCT  $\leftarrow$  <sup>1</sup>GS absorption. That absorptive features of the anthracene T<sub>1</sub> are present only 500 fs after excitation suggests <sup>3</sup>MLCT  $\rightarrow$  T<sub>1</sub> EnT is occurring on a sub-picosecond timescale.

The time evolution of the spectra from 0.5 to 100 ps clearly shows growth of the anthracene  $T_3 \leftarrow T_1$  absorption at ~ 425 nm coupled with recovery of the <sup>1</sup>MLCT  $\leftarrow$  <sup>1</sup>GS absorption bleach. Because the anthracene  $T_1$  has minimal absorptive intensity from 450 to 540 nm[44] the bleach recovery is expected to reflect predominantly reformation of the Ru(II) oxidation state. This is expected as the <sup>3</sup>MLCT  $\rightarrow T_1$  EnT can be conceptualized as a double electron transfer involving movement of the photoexcited electron from the tpy  $\pi^{*,-}$  to the anthracene  $\pi^*$  coupled with transfer of an electron from the anthracene  $\pi$  orbital to the hole in the ruthenium(III) d $\pi$  orbitals. Accordingly, we interpret these dyanimes as a clear indication of the excited state EnT process. That the spectra undergo minimal evolution from 10 to 100 ps after excitation

suggests the initial MLCT population has undergone almost complete EnT to the lowest energy anthracene triplet. For comparison transient spectra were collected 100 ns after excitation, when all EnT and cooling processes should be complete, and are shown in Figure 3.4. As is clear, the spectral features 10 ps after excitation are essentially identical to those observed at 100 ns verifying that population of the long lived anthracene T<sub>1</sub> excited state occurs on an ultrafast timescale.



Figure 3.4: Normalized transient spectra of  $[Ru(tpy-An)(tpy)]^{2+}$  collected at 10 ps and 100 ns after excitation.

Interestingly, the <sup>1</sup>MLCT  $\leftarrow$  <sup>1</sup>GS absorption bleach is not fully recovered even 100 ns after excitation. This could be construed as evidence of the excited state population equilibrating between the T<sub>1</sub> and <sup>3</sup>MLCT. The T<sub>1</sub>, however, is much lower in energy (~ 1.85 eV[43, 48] vs. ~ 2.10 eV for the <sup>3</sup>MLCT)[49] resulting in an equilibrium constant ( $K_{eq} = \frac{[MLCT]}{[T_1]}$ ) between the two excited states of approximately  $9 \cdot 10^{-6}$ . We expect then, essentially all of the excited-state population to be residing in the T<sub>1</sub>. Instead, the persistent bleach is attributed to perturbation of the <sup>1</sup>MLCT  $\leftarrow$  <sup>1</sup>GS excitation due to the proximal nature of the anthracence T<sub>1</sub> excited state. The tpy-An ligand is expected to develop some  $\pi$ -donor character as a result of the electron residing in anthracene  $\pi^*$  orbital. This would cause the <sup>1</sup>MLCT  $\leftarrow$  <sup>1</sup>GS absorption red-shifting and broadening,[50] which is constant with the spectra collected at long times

To quantify in detail the timescale of the  ${}^{3}MLCT \rightarrow T_{1}$  EnT process, triplicate sets of single wavelength

kinetics were collected probing the excited state absorptions at 420 nm and 620 nm and the ground state bleach at 490 nm. Representative data are shown in Figure 3.5. Global fitting of the data to a model

Probe Wavelength/nm	Tau Values <sup>a</sup> /ps ( $\pm 2\sigma$ )	Averaged pre-exponential values <sup>a</sup> $(\pm 2\sigma)$
420	$\begin{array}{l} \tau_1 = 0.5 \; (0.10);  \tau_2 = 2.2 \; (0.9);  \tau_3 \\ = 6 \; (1) \end{array}$	
490	$\begin{array}{l} \tau_1 = 0.5  (0.10);  \tau_2 = 2.2  (0.9);  \tau_3 \\ = 6  (1) \end{array}$	$egin{array}{llllllllllllllllllllllllllllllllllll$
620	$\begin{array}{l} \tau_1 = 0.5 \; (0.10);  \tau_2 = 2.2 \; (0.9);  \tau_3 \\ = 6 \; (1) \end{array}$	$\begin{array}{l} {\rm A_1} = 0.01 \; (0.02);  {\rm A_2} = \text{-}0.04 \\ (0.03); \; {\rm A_3} = \text{-}0.3 \; (0.2) \end{array}$

 $Table \ 3.2: \ Global \ fitting \ results \ for \ \left[ Ru(tpy-An)(tpy) \right]^{2+} \ kinetics \ data \ collected \ in \ room \ temperature \ CH_3CN \ results \ CH_3CN \ results \$ 

<sup>a</sup>Average values resulting from global fitting three independent data sets. The values given in parenthesis represent  $\pm$  two times the standard deviation.

consisting of three exponentials yielded time constants of  $0.5 \pm 0.1$ ,  $2.2 \pm 0.9$ , and  $6 \pm 1$  ps with the magnitude of each found to be strongly wavelength dependent (Table 3.2). Details of the global fitting methodologies and data collection procedure are given in Appendix A. We note that a variety of bi-exponential fitting models were tested, however, none yielded satisfactory fits. The 0.5 ps component was found to contribute most strongly to the data collected at 420 and 490 nm where it comprises approximately 77% and 74% of the total signal change, respectively. The 2.2 ps component accounts for a further 21% and 16% of the signal change at these wavelengths while the 6 ps component was found to amount for 10% or less of the dynamics. On the other hand, the data collected at 620 nm has a relatively small contribution from the 0.5 and 2.2 ps component with the 6 ps dynamic accounting for close to 90% of the signal increase.

In assigning physical processes to each kinetic components we considered first the data collected 420 and 490 nm. Because these colors probe formation of the anthracene  $T_1$  and recovery of the Ru(II) ground state, respectively, their dynamics should closely mirror one another. As stated earlier, formation of the anthracene  $T_1$  results in recovery of the Ru(II) metal center. That the kinetics observed at these probe wavelengths have strong bi-exponential suggests two  ${}^3MLCT \rightarrow T_1$  EnT pathways exist. Recalling that  ${}^1MLCT \leftarrow {}^1GS$  photoexcitation creates both tpy-An localized ( $[Ru^{III}(tpy-An^-)(tpy)]^{2+}$ ) and tpy-



Figure 3.5: Magic angle transient kinetics of  $[Ru(tpy-An)(tpy)]^{2+}$  in room temperature acetonitrile collected at  $\lambda_{probe} = 420$  nm (top), 490 nm (middle), and 620 nm (bottom). The red open circles represent the raw data with global fits to a tri-exponential model shown in black. Taus of 0.5 ± 0.1 ps, 2.2 ± 0.9 ps and 6 ± 1 ps were found to be present at each wavelength with the 0.5 and 2.2 ps component contributing most strongly at 420 and 490 nm and the 6 ps component contributing most strongly at 620 nm (see Table 3.2).

localized  $[Ru^{III}(tpy-An)(tpy)^{-}]^{2+}$  MLCT excited-states the bi-exponential nature of the EnT process is interpreted as reflecting this initial heterogeneity. Because the rate of triplet-triplet energy transfer depends on orbital overlap and decreases exponentially as the donor-acceptor distance increases[10, 51, 52] the faster 0.5 ps component is attributed to EnT from tpy-An localized <sup>3</sup>MLCT species. The relatively slower 2.2 ps component is attributed to interligand electron transfer (ILET) from the distal tpy-localized MLCT to the tpy-An (  $([Ru^{III}(tpy-An)(tpy)^{-}]^{2+} \xrightarrow{ILET} [Ru^{III}(tpy-An^{-})(tpy)]^{2+}$ ), which is followed by sub-picosecond EnT to form the anthracene T<sub>1</sub>. That the timescale for ILET observed here is faster than that observed in  $[Ru(tpy)(ttpy)]^{2+}$  (3.3 ps, see Chapter 2) is consistent with the slightly lower reduction potential of tpy-An as compared to ttpy. For reference, the reduction potential of ttpy in  $[Ru(tpy)(ttpy)]^{2+}$  is -1.29 V (vs. SCE) while that of tpy-An in  $[Ru(tpy)(tpy-An)]^{2+}$  is -1.25 V (vs. SCE). The driving force for ILET in  $[Ru(tpy)(tpy-An)]^{2+}$  is, therefore, larger than in  $[Ru(tpy)(ttpy)]^{2+}$  and should result in faster ILET baring Marcus inverted region behavior.[53, 54]

Turning now to the data collected at 620 nm, the 0.5 and 2.2 ps components contribute minimally to the observed dyanimes. This suggest LMCT absorption of the <sup>3</sup>MLCT and  $T_2 \leftarrow T_1$  absorption of the <sup>3</sup>An are nearly iso-absorptive and is supported by the negligible evolution of the transients spectra red of about 550 nm in the first few picoseconds after excitation (Figure 3.3). The 6 ps component, therefore, is not thought to reflect <sup>3</sup>MLCT  $\rightarrow$  T<sub>1</sub> EnT or ILET dynamics but, instead, evolution of the T<sub>1</sub> state of the anthracene. Specifically, we think it reflects vibrational cooling within T<sub>1</sub>. Despite exciting on the red edge of the MLCT absorption (525 nm or ~ 2.36 eV) approximately 0.51 eV of energy must be dissipated to thermalize the anthracene T<sub>1</sub>(~ 1.85 eV)[43, 48]. This timescale correlates well with the 4 to 5 picosecond IVR timescale reported by Laubereau and co-workers for the S<sub>1</sub> excited state of anthracene can be ruled out due to the latter being far to high in energy (T<sub>2</sub>~ 3.21 eV)[56] relative to the initially excited MLCT (~ 2.36 eV).

Combining these observations and interpretations, the evolution of the MLCT excited state in  $[Ru(tpy-An)(tpy)]^{2+}$  on an ultrafast timescale is summarized in Figure 3.6. The 0.5 ps <sup>3</sup>EnT timescale we observe is much faster than that reported for a related Ru(II) polypyridyl where the anthracene is

attached via an ethylene tether.[7] Moreover, <sup>3</sup>EnT must be occurring promptly after <sup>1</sup>MLCT  $\rightarrow$  <sup>3</sup>MLCT intersystem crossing and prior to full vibrational cooling.



Figure 3.6: Energy level diagram and photoinduced dynamics of  $[Ru(tpy-An)(tpy)]^{2+}$  based on the ultrafast pump-probe spectra and kinetics.

#### 3.3.1 Nanosecond Pump-Probe Results

The long time behavior of  $[Ru(tpy-An)(tpy)]^{2+}$  was characterized using nanosecond transient techniques. These experiments were conducted using excitation pulses with a central frequency of 532 nm corresponding to the red edge of the <sup>1</sup>MLCT  $\leftarrow$  <sup>1</sup>GS absorption feature. This prevents simultaneous excitation of the <sup>1</sup>MLCT and S<sub>1</sub> state of the anthracene. The strong agreement between the spectral features observed at 10 ps and 100 ns (Figure 3.4) establishes that the electronic excited-state probed on the nanosecond timescale is the same as that observed in the ultrafast experiments. The excited state lifetime was monitored by collecting single wavelength kinetics at a wide range of probe wavelengths. Representative data with  $\lambda_{probe}$ = 420, 490, 580, 610, and 650 nm are shown in Figure 3.7. Global fitting of these data to a mono-exponential



Figure 3.7: Nanosecond transient kinetics of  $[Ru(tpy-An)(tpy)]^{2+}$  collected in room temperature acetonitrile at a variety of probe wavelengths. The raw data is represented by open circles. Global fits to the data using a single exponential model are represented by the solid black lines.

model returned a lifetime of  $1000 \pm 20$  ns, which is in good agreement with the previously reported 973 ns lifetime of  $[Ru(tpy-An)(tpy)]^{2+}$  following MLCT photoexcitation.[8] This is, however, significantly shorter than the millisecond T<sub>1</sub> lifetime reported for free anthracene in solution.[45, 57] We suspect the shortened T<sub>1</sub> lifetime in  $[Ru(tpy-An)(tpy)]^{2+}$  is likely due to the presence of a proximal second-row transition metal which helps to relax the intersystem crossing restriction on the anthracene. Work by Campagna, Loiseau and co-workers on related complexes has shown that the anthracene T<sub>1</sub> and <sup>3</sup>MLCT can interconvert, and may represent an additional decay pathway. It should be note, however, that the <sup>3</sup>MLCT in those systems was energetically much closer to the T<sub>1</sub> and, as a result, such a decay pathway likely makes only a minor contribution in  $[Ru(tpy-An)(tpy)]^{2+}$ .

# 3.4 Conclusion

We have characterized the photophysical behavior of  $[Ru(tpy-An)(tpy)]^{2+}$  in room temperature acetonitrile using both femtosecond and nanosecond transient spectra and kinetics. Triplet-triplet energy transfer (EnT) from the <sup>3</sup>MLCT to the T<sub>1</sub> state of the anthracene was observed to occur with time constants of 0.5 and 2.2 ps. The 0.5 ps dynamic is assigned to EnT timescale from the tpy-An localized <sup>3</sup>MLCT. The relatively longer 2.2 ps component is attributed to ILET from the relatively higher energy tpy-localized MLCT to the lower energy tpy-An localized MLCT, which is then assumed to undergo prompt EnT to form the T<sub>1</sub>. An additional 6 ps dynamic was also observed and has been attributed to vibrational cooling of the T<sub>1</sub> state of the anthracene. The overall lifetime of the T<sub>1</sub> excited state in  $[Ru(tpy-An)(tpy)]^{2+}$  was found to be 1000 ns and is in good agreement with previous measurements.[8]

AFC  $\operatorname{control}$ In the context of the pulse shaping experiments proposed for  $[Ru(tpy-An)(tpy-\phi-MV)]^{4+}$ , the ultrafast <sup>3</sup>EnT timescales observed are intriguing. If, for example, pulse shaping could be used to preferentially populate the EnT reactive MLCT then a large yield of anthracene  $T_1$  could be expected; the much faster timescale of EnT compared to ILET could be expected to result in unit quenching of the MLCT population initially created on the tpy-An ligand. Again, however, like the complexes characterized in Chapter 2, no vibrational coherences are observed in the transient data presented here. Such coherences may, however, still be observed in the AFC pulse shaping experiments given the shorter temporal duration of the excitation pulse.

# Chapter 3 Bibliography

- C. Weinheimer, Y. Choi, T. Caldwell, P. Gresham, and J. Olmsted, Journal Of Photochemistry And Photobiology A-Chemistry, 1994, 78, 119–126.
- (2) G. Wilson, W. Sasse, and A. Mau, Chemical Physics Letters, 1996, 250, 583–588.
- G. Albano, V. Balzani, E. C. Constable, M. Maestri, and D. R. Smith, *Inorganica Chimica Acta*, 1998, 277, 225–231.
- B. Maubert, N. McClenaghan, M. Indelli, and S. Campagna, The Journal of Physical Chemistry A, 2003, 107, 447–455.
- (5) R. Passalacqua, F. Loiseau, S. Campagna, Y. Q. Fang, and G. S. Hanan, Angewandte Chemie-International Edition, 2003, 42, 1608–1611.
- (6) J. Wang, G. Hanan, F. Loiseau, and S. Campagna, Chemical Communications, 2004, 2068–2069.
- (7) J. R. Schoonover, D. M. Dattelbaum, A. Malko, V. I. Klimov, T. J. Meyer, D. J. Styers-Barnett, E. Z. Gannon, J. C. Granger, W. S. Aldridge, and J. M. Papanikolas, *Journal of Physical Chemistry A*, 2005, **109**, 2472–2475.
- (8) H. Y. Ding, X. S. Wang, L. Q. Song, J. R. Chen, J. H. Yu, Chao-Li, and B. W. Zhang, Journal of Photochemistry and Photobiology A: Chemistry, 2006, 177, 286–294.
- J. H. Wang, E. A. Medlycott, G. S. Hanan, F. Loiseau, and S. Campagna, *Inorganica Chimica Acta*, 2007, 360, 876–884.
- (10) D. L. Dexter, Journal of Chemical Physics, 1953, 21, 836–850.
- (11) R. Passalacqua, F. Loiseau, S. Campagna, Y. Fang, and G. Hanan, Angewandte Chemie International Edition, 2003, 42, 1608–1611.
- (12) Y. Fang, N. Taylor, G. Hanan, F. Loiseau, R. Passalacqua, S. Campagna, H. Nierengarten, and A. Van Dorsselaer, *Journal Of The American Chemical Society*, 2002, **124**, 7912–7913.
- (13) A. M. McDaniel, H. W. Tseng, N. H. Damrauer, and M. P. Shores, *Inorganic Chemistry*, 2010, 49, 7981–7991.

- (14) Y. H. Meyer, R. Astier, and J. Leclercq, The Journal of Chemical Physics, 1972, 56, 801.
- (15) T. T. Goodnow and A. E. Kaifer, Journal Of Physical Chemistry, 1990, 94, 7682–7683.
- (16) M. Presselt, B. Dietzek, M. Schmitt, S. Rau, A. Winter, M. Jager, U. S. Schubert, and J. Popp, Journal of Physical Chemistry A, 2010, 114, 13163–13174.
- (17) E. Amouyal, M. Mouallem-Bahout, and G. Calzaferri, *Journal of Physical Chemistry*, 1991, 95, 7641–7649.
- (18) H. A. Meylemans, Ph.D. Thesis, 2010.
- (19) H. A. Meylemans and N. H. Damrauer, Inorganic Chemistry, 2009, 48, 11161–11175.
- (20) C. C. Phifer and D. R. McMillin, *Inorganic Chemistry*, 1986, **25**, 1329–1333.
- (21) N. Damrauer, T. Boussie, M. Devenney, and J. K. McCusker, Journal Of The American Chemical Society, 1997, 119, 8253–8268.
- (22) V. V. Pavlishchuk and A. W. Addison, Inorganica Chimica Acta, 2000, 298, 97–102.
- (23) V. D. Parker, Journal Of The American Chemical Society, 1976, 98, 98–103.
- (24) N. H. Damrauer, G. Cerullo, A. Yeh, T. R. Boussie, C. V. Shank, and J. K. McCusker, *Science*, 1997, 275, 54–57.
- (25) A. C. Bhasikuttan, M. Suzuki, S. Nakashima, and T. Okada, *Journal of the American Chemical Society*, 2002, **124**, 8398–8405.
- (26) A. Cannizzo, F. van Mourik, W. Gawelda, G. Zgrablic, C. Bressler, and M. Chergui, Angewandte Chemie-International Edition, 2006, 45, 3174–3176.
- (27) S. Yoon, P. Kukura, C. M. Stuart, and R. A. Mathies, *Molecular Physics*, 2006, **104**, 1275–1282.
- (28) L. X. Xiao, Y. Q. Xu, M. Yan, D. Galipeau, X. J. Peng, and X. Z. Yan, *Journal of Physical Chemistry* A, 2010, **114**, 9090–9097.
- (29) D. H. Oh and S. G. Boxer, Journal of the American Chemical Society, 1989, 111, 1130–1131.
- (30) H. Riesen, L. Wallace, and E. Krausz, Journal of Physical Chemistry, 1996, 100, 17138–17144.

- (31) H. Riesen and E. Krausz, *Chemical Physics Letters*, 1996, 260, 130–135.
- (32) L. Karki and J. T. Hupp, Inorganic Chemistry, 1997, 36, 3318–3321.
- (33) M. A. Webb, F. J. Knorr, and J. L. McHale, Journal of Raman Spectroscopy, 2001, 32, 481-485.
- (34) E. M. Kober, B. P. Sullivan, and T. J. Meyer, *Inorganic Chemistry*, 1984, 23, 2098–2104.
- (35) G. B. Shaw, D. J. Styers-Barnett, E. Z. Gannon, J. C. Granger, and J. M. Papanikolas, Journal of Physical Chemistry A, 2004, 108, 4998–5006.
- (36) S. Wallin, J. Davidsson, J. Modin, and L. Hammarström, Journal of Physical Chemistry A, 2005, 109, 4697–4704.
- (37) W. Henry et al., Journal of Physical Chemistry A, 2008, 112, 4537–4544.
- (38) N. H. Damrauer and J. K. McCusker, Journal of Physical Chemistry A, 1999, 103, 8440–8446.
- (39) J. T. Hewitt, P. J. Vallett, and N. H. Damrauer, The Journal of Physical Chemistry A, 2012, 116, 11536–11547.
- (40) J. Winkler, T. L. Netzel, and N. Sutin, Journal Of The American Chemical Society, 1987, 109, 2381–2392.
- (41) R. Berger and D. Mcmillin, *Inorganic Chemistry*, 1988, 27, 4245–4249.
- (42) P. S. Braterman, J. I. Song, and R. D. Peacock, *Inorganic Chemistry*, 1992, **31**, 555–559.
- (43) G. Porter and M. W. Windsor, Proceedings of the Royal Society of London Series A-Mathematical and Physical Sciences, 1958, 245, 238–258.
- (44) T. G. Pavlopoulos, Spectrochimica Acta Part A-Molecular and Biomolecular Spectroscopy, 1991, 47, 517–518.
- (45) G. Jackson, R. Livingston, and A. C. Pugh, Transactions of the Faraday Society, 1960, 56, 1635–1639.
- (46) S. Záliš, C. Consani, A. El Nahhas, A. Cannizzo, M. Chergui, F. Hartl, and A. Vlček, *Inorganica Chimica Acta*, 2011, **374**, 578–585.
- (47) R. Katoh, Y. Tamaki, and A. Furube, Journal of Photochemistry and Photobiology A: Chemistry, 2006, 183, 267–272.

- (48) M. R. Padhye, S. P. McGlynn, and M. Kasha, The Journal of Chemical Physics, 1956, 24, 588.
- (49) A. Amini, A. Harriman, and A. Mayeux, *Physical Chemistry Chemical Physics*, 2004, 1157–1164.
- (50) M. Maestri, N. Armaroli, V. Balzani, E. C. Constable, and A. M. W. C. Thompson, *Inorganic Chem-istry*, 1995, 34, 2759–2767.
- (51) R. D. Harcourt, G. D. Scholes, and K. P. Ghiggino, Journal of Chemical Physics, 1994, 101, 10521– 10525.
- (52) D. L. Andrews, C. Curutchet, and G. D. Scholes, Laser and Photonics Reviews, 2011, 5, 114–123.
- (53) R. A. Marcus, Annual Review of Physical Chemistry, 1964, 15, 155–196.
- (54) P. F. Barbara, T. J. Meyer, and M. A. Ratner, *Journal of Physical Chemistry*, 1996, **100**, 13148–13168.
- (55) F. Emmerling, M. Lettenberger, and A. Laubereau, Journal of Physical Chemistry, 1996, 100, 19251– 19256.
- (56) Z. Wang, S. J. Weininger, and W. G. Mcgimpsey, Journal of Physical Chemistry, 1993, 97, 374–378.
- (57) G. Jackson and R. Livingston, Journal of Chemical Physics, 1961, 35, 2182–2186.

# Chapter 4

Photophysical Characterization of  $[Ru(tpy)(tpy-\phi-MV]^{4+}$  and  $[Ru(ttpy)(tpy-\phi-MV]^{4+}$ : Ultrafast Forward and Back Electron Transfer Resulting in Formation of a Vibrationally Hot Ground State.

# 4.1 Overview

This chapter details the photophysics of the electron transfer (ET) reactive portion of the target dualacceptor species  $[Ru(tpy-An)(tpy-\phi-MV)]^{4+}$ . In a broader context, ET dyads making use of a Ru(II) polypyridyl chromophores have been widely reported[1–13] with much research focused on the role that molecular conformation plays in the rates of photoinduced charge separation and recombination.[3, 14–19] A detailed understanding of such processes is important by way of designing systems that achieve efficient conversion of solar photons to energy, which is arguably the only avenue for satisfying the growing global energy demand without drastically increasing atmospheric CO<sub>2</sub> levels.[20, 21] Much of the aforementioned research employed tris-bidentate Ru(II) chromophores based on the parent complex  $[Ru(bpy)_3]^{2+}$  because of long <sup>3</sup>MLCT lifetimes and relatively good photo-stability.[22–24] As detailed in Chapter 1, we have eschewed the use of a tris-bidentate central chromophore in our dual-acceptor species because of the possibility of multiple stereoisomers. Bis-terpyridyl Ru(II) based ET dyads have received some attention in the literature.[1, 4, 8, 25, 26] Almost without exception, these complexes exhibit slow rates of photoinduced electron transfer from the MLCT excited state leading to negligible yields of ET product species. Because we desire fast ET dynamics<sup>\*</sup> in the dual-acceptor species we set about developing a novel ET reactive complex based on a  $[Ru(tpy)_2]^{2+}$  central chromophore. Recent work in our lab exploring the role of molecular motion in excited

<sup>\*</sup> Ideally ET will occur before information encoded in the MLCT by a shaped pulse is lost.

state electron transfer reactions[27] lead us to believe that direct attachment of the methyl viologen-like moiety  $(\phi - MV^{2+})$  (where  $(\phi - MV^{2+}) = N$ -methyl-N'-phenyl-4,4'-bipyridinium) to the terpyridine ligand would result in ultrafast electron transfer from the MLCT excited state to the  $(\phi - MV^{2+})$  acceptor–i.e.  $[Ru^{III}(tpy)(tpy^- - \phi - MV^{2+})]^{4+} \rightarrow [Ru^{III}(tpy)(tpy - \phi - MV^{-/+})]^{4+}$ . Synthesis of this acceptor and its incorporation at the 4'-position of the tpy ligand, yielding  $tpy - \phi - MV^{2+}$  (4'-(1-(1'-Methyl-4,4'-bipyridinium-1-yl)-phenyl)-2,2':6',2''-terpyridine, see Figure 4.1), was recently accomplished in our lab and found to be high yielding and synthetically facile.[27] We note that the  $tpy - \phi - MV^{2+}$  ligand we synthesized is similar to



Figure 4.1: The novel electroactive ligand tpy $-\phi - MV^{2+}$  synthesized in our lab. The blue, dashed ellipse denotes the  $(\phi - MV^{2+})$  electron acceptor portion of the ligand.

the methyl viologen containing tpy ligand utilized by Balzani, Barigeletti, Sauvage and co-workers,[1] which shows negligible yields of photoinduced ET implying slow rates of excited state ET. In those systems studied by Balzani *et al.* a methylene spacer separates the tpy ligand from the  $MV^{2+}$  electron acceptor whereas in  $tpy-\phi-MV^{2+}$  the electron acceptor is directly linked to the tpy ligand. This direct connection is expected to significantly accelerate the timescale of forward ET; in related tris-bidentate species, elimination of the methylene spacer between the coordinating ligand and the ET acceptor resulted in the forward ET timescale decreasing from about 40 ps[16, 28] to less than a picosecond.[27]

Two different Ru(II) ET dyads containing the tpy $-\phi-MV^{2+}$  ligand were synthesized, one with a tpy ancillary ligand,  $[Ru(tpy)(tpy-\phi-MV)]^{4+}$ , and the other with a ttpy ancillary ligand,  $[Ru(ttpy)(tpy-\phi-MV)]^{4+}$  (see Figure 4.2). By contrasting the ET dynamics observed in these two complexes we hope to understand the effect that an aryl-substituent at the 4' position of the ancillary ligand



Figure 4.2: The two complexes investigated in this chapter.

has on the photoinduced ET process. Such effects are likely to play a role in the dual-acceptor species  $[Ru(tpy-An)(tpy-\phi-MV)]^{4+}$  in which, from the perspective of the  $tpy-\phi-MV^{2+}$  ligand, the ancillary tpy ligand contains a large aryl substituent (anthracene) at the position para to the central pyridine ring.

# 4.2 Experimental

#### 4.2.1 General

Terpyridine (2,2':6',2''-terpyridine) was purchased from Aldrich and used as received. 4'-(4methylphenyl)-2,2':6',2''-terpyridine (ttpy) was synthesized via Kröhnke condensation of pyridines.[29] The electroactive ligand tpy- $\phi$ -MV<sup>2+</sup> (4-(1-(1'-Methyl-4,4'-bipyridinium-1-yl)-phenyl)-2,2':6',2''terpyridine) was synthesized by Dr. Mirvat Abdelhaq with details given in Chapter 2 of her PhD. thesis.[27] The target complexes  $[Ru(tpy)(tpy-\phi-MV)]^{4+}$  and  $[Ru(ttpy)(tpy-\phi-MV)]^{4+}$  were synthesized using a procedure similar to those previously published[30–32] with  $[Ru(tpy)Cl_3]$  or  $[Ru(ttpy)Cl_3]$  used as the precursor complex and triethylamine as the reductant. Ag(CF<sub>3</sub>SO<sub>3</sub>) was also employed as a chloride scavenger. All samples were purified via silica gel column chromatography using 8:1:1 acetonitrile, water, and saturated potassium nitrate in water as the eluent. The identity and purity of each complex was confirmed by <sup>1</sup>H-NMR and mass spectrometry. The <sup>1</sup>H-NMR spectra are given in Appendix C. <sup>1</sup>H-NMR spectra were recorded using a Varian Inova 500 MHz spectrometer. All deuterated solvents were purchased from Cambridge Isotopes Laboratories Inc. and used as received. Mass spectrometry measurements and accurate mass analyses were performed by the Central Analytical Laboratory at the University of Colorado at Boulder, Department of Chemistry and Biochemistry. Steady state absorption measurements were made using of a Hewlett-Packard HP8452A diode array UV-Vis spectrometer. Acetonitrile was purchased from Burdick and Jackson (UV-Grade) and used as received.

## 4.2.2 Electrochemistry and Spectroelectrochemistry

Cyclic voltammetry and spectroelectrochemistry measurements used the same instrumentation and experimental methodologies detailed in Chapter 2.

## 4.2.3 Ultrafast Transient Pump-Probe Kinetics and Spectra

Ultrafast pump-probe measurements used the same instrumentation and experimental methodologies detailed in Chapter 2 and Appendix A.

# 4.3 Results and Discussion

### 4.3.1 Ground State Absorption Properties

The visible region ground state absorption spectra of  $[Ru(tpy)(tpy-\phi-MV)]^{4+}$  and  $[Ru(ttpy)(tpy-\phi-MV)]^{4+}$  are dominated by intense <sup>1</sup>MLCT  $\leftarrow$  <sup>1</sup>GS transitions (Figure 4.3) with peak absorption at 486 nm (16,400 M<sup>-1</sup> cm<sup>-1</sup>) at 493 nm (30,000 M<sup>-1</sup> cm<sup>-1</sup>), respectively. As expected, substitution of the terpyridine ligand at the 4' position leads to both a red-shifted absorption maximum and



Figure 4.3: Steady state absorption spectra of  $[\operatorname{Ru}(\operatorname{tpy})(\operatorname{tpy}-\phi-\operatorname{MV})]^{4+}$  (sea foam) and  $[\operatorname{Ru}(\operatorname{tpy})(\operatorname{tpy}-\phi-\operatorname{MV})]^{4+}$  (ash blue). The MLCT absorption maxima are 486 nm (16,400 M<sup>-1</sup> cm<sup>-1</sup>) and 493 nm (30,000 M<sup>-1</sup> cm<sup>-1</sup>), respectively. The absorption spectrum of  $[\operatorname{Ru}(\operatorname{tpy})(\operatorname{ttpy})]^{2+}$  (sea foam, dashed) and  $[\operatorname{Ru}(\operatorname{ttpy})_2]^{2+}$  (ash blue, dashed) are included for reference.

an increases in the molar absorption coefficient of the transition.[33–35] The maximum molar absorption of the  $(tpy-\phi-MV^{2+})$ -containing complexes are slightly higher than those of the analogous non-electroactive complexes,  $[Ru(tpy)(ttpy)]^{2+}$  (15,500 M<sup>-1</sup> cm<sup>-1</sup>, 482 nm) and  $[Ru(ttpy)_2]^{2+}$  (28,900 M<sup>-1</sup> cm<sup>-1</sup>, 490 nm), which suggests further elongation of the transition dipole. This is supported by time dependent density functional and attachment-detachment calculations<sup>†</sup> [36, 37] on related tris-bidentate Ru(II) complexes containing a  $(\phi-MV^{2+})$  moiety[27] where it was observed that the MLCT-excited electron is promoted deeper into the  $(\phi-MV^{2+})$  containing ligands than in analogous non- $(\phi-MV^{2+})$  containing ligands. We, however, do not think that direct optical charge transfer from Ru(II) center to the  $(\phi-MV^{2+})$  acceptor is occurring in  $[Ru(tpy)(tpy-\phi-MV)]^{4+}$  or  $[Ru(ttpy)(tpy-\phi-MV)]^{4+}$ . Such optical ET would manifest as a significant perturbation to the MLCT absorption feature that distinct from that observed in the non- $(\phi-MV^{2+})$  containing species.[27, 38]

 $<sup>^\</sup>dagger$  a computational technique useful for visualizing the change in charge distribution commensurate with an electronic absorption transition

#### 4.3.2 Electrochemistry

The electrochemical properties of  $[\text{Ru}(\text{tpy})(\text{tpy}-\phi-\text{MV})]^{4+}$  and  $[\text{Ru}(\text{ttpy})(\text{tpy}-\phi-\text{MV})]^{4+}$  were measured using cyclic voltammetry and are reported in Table 4.1.  $E_{\text{ox}}$  corresponds to an average of the anodic and cathodic  $^{1/2}$ -wave potentials for removal of an electron from a nominally Ru(II) based orbital (i.e. the Ru(II)/Ru(III) couple), while the reduction potentials correspond to an average of the anodic and cathodic  $^{1/2}$ -wave potentials for addition of an electron to the  $(\phi-\text{MV}^{2+})$  acceptor ( $E_{\text{red}(1)}$  and  $E_{\text{red}(2)}$ ) and the tpy-like portion of each ligand ( $E_{\text{red}(3)}$  and  $E_{\text{red}(4)}$ ). Using the formulation of Weller[40] the driving for ET from the MLCT excited state to the  $(\phi-\text{MV}^{2+})$  acceptor, as well as the driving force for back electron transfer (BET) from the reduced ( $\phi-\text{MV}^{2+}$ ) acceptor to the Ru(III) metal center can be estimated from the first oxidation and reduction potentials as shown in Equations 4.1-4.3

$$\Delta G^o_{IP}(eV) = E_{ox} - E_{red} - \frac{e^2}{4\pi\varepsilon_o\varepsilon_s R_{DA}} \cdot 6.242 \cdot 10^{18} \frac{eV}{J}$$

$$\tag{4.1}$$

$$\Delta G^o_{ET}(eV) = -\Delta G^o_{MLCT} + \Delta G^o_{IP} \tag{4.2}$$

$$\Delta G^o_{BET}(eV) = -\Delta G^o_{IP} \tag{4.3}$$

In these expressions,  $\Delta G_{IP}^{o}$  corresponds to the free energy needed to create the charge separated species in solution with *e* being the fundamental charge,  $\varepsilon_{o}$  the permittivity of free space,  $\varepsilon_{s}$  the static dielectric constant of the solvent (36.2 for acetonitrile) and  $R_{DA}$  a measurement of the center-to-center donor-acceptor separation. The final term in this expression,  $\frac{e^2}{4\pi\varepsilon_{o}\varepsilon_{s}R_{DA}} \cdot 6.242 \cdot 10^{18} \frac{eV}{J}$ , accounts for the work necessary to separate the positive and negative charge in a dielectric continuum and is typically small.  $\Delta G_{MLCT}^{o}$ is a measure of the energy stored in the MLCT excited state and was set to 1.98 eV based on emission of  $[\text{Ru}(\text{ttpy})_2]^{2+}$  at the 77 K.<sup>‡</sup> [8] The value of  $R_{DA}$  was set to 14.1 Å based on geometry-optimized computations of  $(\phi-\text{MV}^{2+})$  containing Ru(II) tris-bidentate complexes.[27] The values of  $\Delta G_{IP}^{o}$ ,  $\Delta G_{ET}^{o}$  and  $\Delta G_{BET}^{o}$ calculated are reported in Table 4.2 and clearly show that ET in both complexes should be a strongly exergonic process ( $\Delta G_{ET}^{o} \approx -0.4$  eV). Compared to previously reported bis-terpyridine based ET dyads[1,

<sup>&</sup>lt;sup>‡</sup> These complexes have negligible emissive quantum yield at room temperature

Complex	$E_{ox}(V)^{a}$	$\mathrm{E}_{\mathrm{red}(1)}(\mathrm{V})^{\mathrm{a}}$	$\mathrm{E}_{\mathrm{red}(2)}(\mathrm{V})^{\mathbf{a}}$	$\mathrm{E}_{\mathrm{red}(3)}(\mathrm{V})^{\mathrm{a}}$	$\mathrm{E}_{\mathrm{red}(4)}(\mathrm{V})^{\mathrm{a}}$
$[{\rm Ru(tpy)(tpy-\phi-MV)}]^{4+}$	$0.98 \ (0.066), 1.28^{\rm b}$	-0.60 (0.062), -0.30 <sup>b</sup>	-0.93 (0.060), -0.64 <sup>b</sup>	-1.58 (0.058), -1.29 <sup>b</sup>	-1.81 (0.080), -1.52 <sup>b</sup>
$[{\rm Ru(ttpy)(tpy-\phi-MV)}]^{4+}$	$0.97 \ (0.066), \ 1.27^{\rm b}$	-0.59 (0.059), -0.30 <sup>b</sup>	-0.92 (0.065), -0.63 <sup>b</sup>	-1.56 (0.061), -1.27 <sup>b</sup>	-1.78 (0.062), -1.43 <sup>b</sup>
$(\mathrm{tpy}-\phi\mathrm{-MV}^{2+})^{\mathrm{c}}$	I	-0.60, -0.30 <sup>b</sup>	-0.96 , -0.67 <sup>b</sup>	I	I
$\left[\mathrm{Ru(ttpy)}_2 ight]^{2+\mathrm{d}}$	$0.90 \ (0.069), \ 1.20^{\rm b}$	I	I	-1.59 (0.066), -1.29 <sup>b</sup>	-1.83 $(0.074)$ , -1.53 <sup>b</sup>
<sup>a</sup> All electrochemical measure wave separation is given in p <sup>b</sup> Values reported vs. SCE usi	ements were recorded vs. barentheses. A scan rate of ing the conversion factor	a freshly prepared $0.01$ of $200 \text{ mV/s}$ was used wi s of Pavlishchuck and Ac	M Ag/AgNO <sub>3</sub> in CH <sub>3</sub> C th 0.1M TBAP the supp ddison.[39]	N reference electrode. J oorting electrolyte.	The anodic and cathodi

) collected in room temperature $\rm CH_3CN$	
<sup>+</sup> , and $(tpy-\phi-MV^{2+})$	
${ m Ru(ttpy)(tpy-\phi-MV)]^{4+}}$	
$u(tpy)(tpy-\phi-MV)]^{4+}$ , []	
llectrochemical data for [R	
Table 4.1: F	

<sup>•</sup> Taken from the PhD. thesis of Dr. Mirvat Abdelhaq. <sup>•</sup> Taken from Chapter 2.

Complex	$R_{DA}$ (Å)	$\Delta G_{IP}^o$ (eV)	$\Delta G^o_{ET}$ (eV)	$\Delta G^o_{BET}$ (eV)
$\left[\mathrm{Ru}(\mathrm{tpy})(\mathrm{tpy}{-}\phi{-}\mathrm{MV})\right]^{4+}$	14.1	1.58	-0.40	-1.58
$\left[\mathrm{Ru}(\mathrm{ttpy})(\mathrm{tpy}{-}\phi{-}\mathrm{MV})\right]^{4+}$	14.1	1.56	-0.42	-1.58

Table 4.2: Calculated Driving Forces for Photoinduced Forward and Back Electron Transfer in  $[Ru(tpy)(tpy-\phi-MV)]^{4+}$  and  $[Ru(ttpy)(tpy-\phi-MV)]^{4+}$ 

8, 15, 41] the  $\Delta G_{ET}^o$  we calculate is about 0.1 eV more favorable. We expect ET to occur in the Marcus normal region[42–44] based on the reorganization energy ( $\lambda_{\rm ET}$ ) for ET from the MLCT to an MV<sup>2+</sup> acceptor reported in related Ru(II) polypyridyl dyads, reported to be approximately 1.2 eV,[28, 45] which is much larger than 0.4 eV value we have estimated for  $|\Delta G_{ET}^o|$ .

Our calculations also suggest that the BET process will be highly exergonic with a driving force of approximately -1.58 eV. The much larger negative  $\Delta G_{ET}^o$  could result in the rate of BET being faster than that of ET; however, based on the previously referenced studies of MV<sup>2+</sup> containing Ru(II) dyads, BET in these types of complexes is expected to occur in the Marcus inverted region ( $\lambda_{BET} \leq |\Delta G_{BET}^o|$ ). The reorganization energy for BET ( $\lambda_{BET}$ ) in similar systems was measured to be approximately 1.0 eV[16, 28] and is much smaller than the 1.58 eV  $|\Delta G_{BET}^o|$  we estimate. Therefore, we expect that BET in [Ru(tpy)(tpy- $\phi$ -MV)]<sup>4+</sup> and [Ru(ttpy)(tpy- $\phi$ -MV)]<sup>4+</sup> will occur in the Marcus inverted region and, accordingly, the timescale for BET may be *slower* than that for ET despite the almost 4 fold increase in driving force.

## 4.3.3 Spectroelectrochemisty

Similar to Chapter 2, spectroelectrochemical measurements were undertaken to develop "optical tags" of species likely to be observed in the transient spectra and kinetics.[46] However, unlike Chapter 2, convolution of the one electron oxidized and reduced species spectra *is not* representative of the MLCT excited state. Instead it is demonstrative of the ET absorption features of the two complexes studied in this chapter species  $([Ru^{III}(tpy)(tpy-\phi-MV^{-/+})]^{4+}$  and  $[Ru^{III}(ttpy)(tpy-\phi-MV^{-/+})]^{4+}$ . As shown in Table 4.1, the first reduction potential measured in both  $[Ru(tpy)(tpy-\phi-MV)]^{4+}$  and  $[Ru(ttpy)(tpy-\phi-MV)]^{4+}$  occurs at a much less reducing potential than is observed in  $[Ru(ttpy)_2]^{2+}$ . In the electroactive species this

corresponds to addition of an electron to the  $(\phi - MV^{2+})$  acceptor and not the tpy-like portion of the ligand.

The change in the absorption spectra upon one-electron oxidation of  $[Ru(tpy)(tpy-\phi-MV)]^{4+}$  and  $[Ru(ttpy)(tpy-\phi-MV)]^{4+}$  was investigated using bulk electrolysis at a platinum mesh working electrode. The experimental set-up used is identical to that described in Chapter 2. The mesh was held at 1.10 V vs. 0.01 M Ag/AgNO<sub>3</sub> in acetonitrile (1.40 V vs. SCE) causing oxidation of the Ru(II) metal center to Ru(III). The most prominent spectral change that is observed with increased bulk electrolysis time observed in both complexes is loss of the visible region  ${}^{1}MLCT \leftarrow {}^{1}GS$  electronic transition (highlighted by a downward arrow in Figure 4.4). Loss of this feature is expected as <sup>1</sup>MLCT excitation from the Ru(III) center is significantly more energy than from the Ru(II). In  $[Ru(ttpy)(tpy-\phi-MV)]^{4+}$ , the new absorption feature that develops between 350 and 420 nm is attributed to intraligand charge transfer (ILCT) absorption of the ttpv ligand. [47, 48] Again, as was discussed in detail in Chapter 2, these transitions are thought to involve transfer of electron density from the  $\pi$ -system of the tolyl fragment of the ttpy ligand to tpy-localized  $\pi^*$  orbitals proximal to the metal center. That this feature is weaker in  $[Ru(tpy)(tpy-\phi-MV)]^{5+}$  suggests such transitions are still possible for the  $(tpy-\phi-MV^{2+})$  ligand but are reduced in intensity. This could be a result of the proximal dicationic 4.4'-bipyridinium withdrawing electron density from the phenyl ring thereby decreasing the electron donating nature of phenyl  $\pi$  orbitals involved in the ILCT transitions. A weak, featureless absorption from approximately 600 to 800 nm also develops in  $[Ru(ttpy)(tpy-\phi-MV)]^{5+}$ . This is ascribed to ligand-to-metal charge transfer (LMCT) absorption. [47, 49–52] These transitions involve promotion of an electron from  $\pi$  orbitals of the ligand(s) to the hole in the Ru(III)  $d\pi$  metal orbitals (t<sub>2g</sub> assuming octahedral symmetry). Somewhat surprisingly  $[Ru(tpy)(tpy-\phi-MV)]^{5+}$  shows negligible absorption in this spectral region. This suggests weakening of the LMCT transition below the noise level of the measurement. As LMCT transitions where observed in  $[Ru(tpy)_2]^{3+}$  their decreased intensity in  $[Ru(tpy)(tpy-\phi-MV)]^{5+}$ must be a result of the  $(tpy-\phi-MV^{2+})$  ligand. The mechanism underlying this effect, however, is currently not understood.

The one-electron reduced species of both complexes were generated using the same experimental setup with the platinum mesh working electrode held at a reducing potential, -0.80 V vs.  $0 \cdot 01 \text{ MAg/AgNO}_3$ in acetonitrile (-0.51 V vs. SCE). We reiterate that this initiates reduction of the ( $\phi$ -MV<sup>2+</sup>) acceptor



Figure 4.4: Oxidative spectroelectrochemistry of  $[Ru(tpy)(tpy-\phi-MV)]^{4+}$  (top) and  $[Ru(ttpy)(tpy-\phi-MV)]^{4+}$  (bottom) collected at room temperate with the potential held at 1.10 V vs. 0.01 Ag/AgNO<sub>3</sub> (1.4 V vs. SCE) with 0.1M TBAP in acetonitrile used as the supporting electrolyte. The jagged lines are a result of imperfect blanking of the spectrometer with light transmitted through the Pt wire mesh.

portion of the ligand and not the tpy-like portion (vide supra). For both complexes, absorption scans collected as a function of bulk electrolysis time show growth of new absorption features throughout the visible and UV region (Figure 4.5). Based on comparison with the absorption spectrum of one electron reduced  $MV^{2+}$  the feature centered near 410 nm as well as the structured absorptions from about 580 to 820 nm are assigned to  $\pi^* \leftarrow \pi^*$  (IL) transitions of the reduced  $(\phi - MV^{2+})$ .[53] The redder of the two features, between 580 and 820nm, is assigned to  $D_1 \leftarrow D_0$  absorption while the feature centered near 410 is



Figure 4.5: Reductive spectroelectrochemistry of  $[Ru(tpy)(tpy-\phi-MV)]^{4+}$  (top) and  $[Ru(tpy)(tpy-\phi-MV)]^{4+}$  (bottom) collected at -0.80 V vs. 0.01 Ag/AgNO<sub>3</sub> (-0.51 V vs. SCE) with 0.1 M TBAP as the supporting electrolyte. The jagged lines, most prominent in data collected for  $[Ru(tpy)(tpy-\phi-MV)]^{4+}$ , are a result of imperfect blanking of the spectrometer with light transmitted through the Pt wire mesh. The dotted lines have been added to allow for facile comparison of the new absorptive features in both complexes.

attributed to the  $D_2 \leftarrow D_0$  electron transition.<sup>§</sup> The spectral features we observe do differ in a meaningful way from those of one-electron reduced MV<sup>2+</sup>. The  $D_2 \leftarrow D_0$  absorption in MV<sup>+</sup>(centered at 410 nm) is sharp and contains a clear vibronic progression. The  $D_1 \leftarrow D_0$  absorption band also has a significantly different spectral profile than that observed here.[27, 54, 55] These variations have been investigated by our

 $<sup>\</sup>S$  The one electron reduced complex has an overall spin of 1/2 hence the doublet (D) designation

group[27] with the conclusion being that they are a manifestation of the added electron delocalization onto the phenyl portion of the  $(\phi-MV^{2+})$  acceptor. This delocalization also gives rise to the lower reduction potential of  $(\phi-MV^{2+})$  with respect to  $MV^{2+}$ . In the context of the ET from the MLCT excited state of  $[Ru(tpy)(tpy-\phi-MV)]^{4+}$  and  $[Ru(ttpy)(tpy-\phi-MV)]^{4+}$ , this means there is likely to be significant electron density overlap between the initially created MLCT (namely,  $[Ru^{III}(L)((tpy-\phi)^{-}-MV)]^{4+})$  and the ET product species  $[Ru^{III}(L)(tpy-(\phi-MV)^{-})]^{4+}$ . We expect this will contribute to promptness in ET following photoexcitation.

Combing the results of the oxidative and reductive spectroelectrochemistry we predict that formation of the ET product will be heralded by growth of an absorption peak centered near 410 nm, corresponding to  $D_2 \leftarrow D_0$  transition of the reduced acceptor, as well the development of a broad absorption feature from 550 to 820 nm  $(D_1 \leftarrow D_0)$ . Of course the growth of these features must be contrasted with the transient spectra of  $[Ru(tpy)_2]^{2+}$  and  $[Ru(ttpy)_2]^{2+}$  which also exhibits features at these wavelengths. Because the reduced ligand absorption in the MLCT excited state peaks close to 400 nm, formation of the ET species is likely to manifest as a red-shifting of the near-UV absorption feature and *may not* give rise to an entirely new transient feature. The  $D_2 \leftarrow D_0$  absorption of the ET product also overlaps with the intense IL transition of the reduced aryl-substituted terpyridine complexes observed in Chapter 2 (See the transient spectra of  $[Ru(tpy)(ttpy)]^{2+}$  and  $[Ru(tpy)(ttpy)]^{2+}$ ). ET dynamics may, therefore, be tempered in this region and only result in a more modest increase or decrease in absorptive intensity.

#### 4.3.4 Ultrafast Pump-Probe Spectroscopy

With an understanding of the spectral features likely to signify formation of the ET product we now turn to a discussion of the time-resolved UV-Vis pump-probe spectra and kinetics. As a reminder to the reader, intersystem crossing of the initially excited <sup>1</sup>MLCT to the <sup>3</sup>MLCT is assumed to occur on a sub-100 fs timescale,[56–59] therefore, any absorptive features observed are assumed to be <sup>3</sup>MLCT or <sup>3</sup>ET in character. Also, as detailed in the experimental section of Chapter 2 and Appendix A the relative electric field polarization between the pump and probe beam was set to the magic angle (54.7°) to ensure only population dynamics are being monitored.[60, 61] Finally, all of the transient measurements presented herein
made use of excitation pulses centered on the red edge of the <sup>1</sup>MLCT absorption feature (approximately 520 nm). Red-detuning of the pump central frequency decreases the amount of excess energy deposited in the chromophore during photoexcitation thereby minimizing the amplitude of any vibrational cooling dynamics in the transient data.[62]

## 4.3.5 $[{ m Ru}({ m tpy})({ m tpy}-\phi-{ m MV})]^{4+}$

Chirp corrected magic angle transient spectra of  $[Ru(tpy)(tpy-\phi-MV)]^{4+}$  collected at 1, 5, and 10 ps after <sup>1</sup>MLCT  $\leftarrow$  <sup>1</sup>GS excitation are shown in Figure 4.7. At 1 ps the spectrum is quite similar to that of  $[Ru(tpy)(ttpy)]^{2+}$  and  $[Ru(ttpy)_2]^{2+}$  with a broad absorption centered near 390 nm, a bleach centered close to the <sup>1</sup>MLCT absorption maximum, and an unstructured moderately intense absorption extending from about 530 to 650 nm. The two absorption features are attributed to IL transitions of the reduced  $(tpy-\phi-MV^{2+})$  ligand, analogous with the assignments made for the ttpy containing complexes in Chapter 2. This suggests that 1 ps after excitation a large portion of the <sup>3</sup>MLCT species are  $(tpy-\phi-MV^{2+})$ localized; i.e. the excited electron is localized on the phenyl terpyridine portion of  $(tpy-\phi-MV^{2+})$  ligand. MLCT excited states with the charge transferred electron localized on the tpy ligand are expected to have minimal absorptive intensity configuration from 530 to 650 nm as is manifest in the transient spectra of  $[Ru(tpy)_2]^{2+}$  presented in Chapter 2. The small shoulder at  $\approx 415$  nm is interpreted as population in the  $^{3}$ ET state. By 5 ps after excitation, the transient absorption between 350 and 500 nm undergoes a significant increase in intensity heralding generation of the ET species. Most notably, the shoulder at 415 nm 1 ps after excitation grows into a distinct and intense peak, as expected based on the reductive spectroelectrochemisty. The red side absorption future undergoes relatively little change implying that IL absorption by the reduced ligand within the <sup>3</sup>MLCT and the  $D_1 \leftarrow D_0$  transition of the reduced  $(\phi - MV^{2+})$  in the <sup>3</sup>ET have similar oscillator strength. At 10 ps after excitation the intensity of the spectral features is significantly reduced relative to those at 1 ps, however, their shape is essentially unchanged. This suggest that ET is fast, on the order of a picosecond, with BET (<sup>3</sup>ET  $\rightarrow$  <sup>1</sup>GS) likely occurring on a sub-ten picosecond timescale.

Based on the dyanimus observed in the transient spectra single wavelength kinetics collected 415, 480 and 620 nm. Representative data are shown in Figure 4.7. The overall excited-state lifetime of



Figure 4.6: Chirp corrected magic angle transient spectra of  $[Ru(tpy)(tpy-\phi-MV)]^{4+}$  collected in acetonitrile at a variety of time points after excitation. Data points were collected every 5 nm and are represented by the filled circles. The data between the vertical dashed lines has been omitted due to contamination by pump beam scatter.

 $[\operatorname{Ru}(\operatorname{tpy})(\operatorname{tpy}-\phi-\operatorname{MV})]^{4+}$  is observed to be quite short with total recovery of the ground state bleach occurring in less than 40 ps. The data collected at 415 and 620 nm display bi-exponential dynamics consisting of an early time growth and longer decay component while the bleach recovery data collected at 480 nm show a relatively complex exponential decay. Fitting of the data was initially undertaken assuming an  $A \rightarrow B \rightarrow C$  kinetics model with A designated as the <sup>3</sup>MLCT, B the <sup>3</sup>ET and C the ground state (see Appendix C for details and derivation). This model fit the data at 415 and 620 nm quite well, as judged by residuals. However this model was unable to satisfactorily fit the bleach dynamics at 480 nm. A mixed fitting routine was, therefore, adopted with the data at 415 and 620 nm fit using the  $A \rightarrow B \rightarrow C$  kinetics model while the data collected at 480 nm was fit using a tri-exponential model. In this approach, the  $\tau_1$  and  $\tau_2$  values were locked across all three probe wavelengths while the  $\tau_3$  value, present only in the data at 480 nm, was allowed to freely vary. The results of global fitting three independent sets<sup>¶</sup> of data with this fitting routine is detailed in Table .

When trying to assign  $\tau_1$  and  $\tau_2$  to either ET or BET we note that a priori assignment of the fast  $\P$  each "set" of data consists of kinetics collected at 415, 480 and 620 nm



Figure 4.7: Magic angle single wavelength transient kinetics of  $[Ru(tpy)(tpy-\phi-MV)]^{4+}$  collected in room temperature acetonitrile at  $\lambda_{probe} = 415 \text{ nm}$  (top), 480 nm (middle) and 620 nm (bottom) following excitation at 520 nm. The red solid lines represent the model used to global fit the data. The data collected at 415 and 620 nm were fit using an A $\rightarrow$ B $\rightarrow$ C kinetics model and returned tau values of 2.0  $\pm$  0.1 ps and 5.4  $\pm$  0.2 ps. The data collected at 480 was fit with a tri-exponential model and was found to contain a weak third tau of 20  $\pm$  11 ps. See text for details.

Probe Wavelength/nm	Tau Values d/ps ( $\pm 2\sigma)$	Averaged pre-exponential values <sup>d</sup> $(\pm 2\sigma)$
$415^{a}$	$ au_1=2.0\;(0.1); au_2=5.4\;(0.2)$	$f A = 1.17 \; (0.02);  B = 3.3 \; (0.2);  C \ = 0.09 \; (0.04)$
$480^{\mathrm{b}}$	$egin{array}{ll}  au_1=2.0 \ (0.10); \  au_2=5.4 \ (0.2); \  au_3\ = 20 \ (11) \end{array}$	${f a_1=0.05}\;(0.07);{f a_2=-1.01}\;(0.07)\ ;{f a_3=-0.10}\;(0.07)$
$620^{\mathrm{a}}$	$\tau_1=2.0\;(0.1);\tau_2=5.4\;(0.2)$	${ m A}=0.87\;(0.03);{ m B}=1.78\;(0.07);\ { m C}=0.00$

Table 4.3: Global fitting results for  $[Ru(tpy)(tpy-\phi-MV)]^{4+}$  kinetics data collected in room temperature  $CH_3CN$ 

<sup>a</sup>Fit to an  $A \rightarrow B \rightarrow C$  kinetics model (details given in Appendix C). The pre-exponential terms A, B, and C for data collected 415 and 620 nm are proportional to the molar absorption of the <sup>3</sup>MLCT, ET, and ground state, respectively, at these wavelengths.

<sup>b</sup>Fit to a triexponential model with  $\tau_1$  and  $\tau_2$  linked across all three probe wavelengths.

<sup>c</sup>Constrained to zero because there is no ground state absorption at this wavelength.

<sup>d</sup>Average values resulting from global fitting three independent data sets. The values given in parenthesis represent  $\pm$  two times the standard deviation.

timescale,  $\tau_1$ , to ET and the slower timescale,  $\tau_2$ , to BET is incorrect. Using the  $A \rightarrow B \rightarrow C$  kinetics model, the data can be fit equally well assuming  $\tau_1 = BET$  and  $\tau_2 = ET$ . To definitively assign the  $\tau_1$  and  $\tau_2$  components one needs a direct measure of the rate of loss of the <sup>3</sup>MLCT excited state. However, absorption features of the <sup>3</sup>MLCT and <sup>3</sup>ET overlap at all the probe colors accessible with our current ultrafast spectrometer. Therefore, transient measurements probing exclusively loss of <sup>3</sup>MLCT are not possible. Time correlated photon counting could, in principle, be used to measure emission from the <sup>3</sup>MLCT thereby allowing for an independent measure of the <sup>3</sup>MLCT lifetime. The temporal response of this instrument in our lab is about 60 ps and, thus, far too slow to be of use. Instead, to assign  $\tau_1$  and  $\tau_2$ , we have relied on an analysis of the <sup>3</sup>MLCT and <sup>3</sup>ET excited state absorption intensities. For the interested reader, details of this analysis are given in Appendix C. Using this analysis and the magnitude of the absorption feature growth at 415 nm allow us to confidently assign the faster of the two measured timescales,  $\tau_1 = 2.0$  ps, to ET and the slower 5.4 ps component,  $\tau_2$ , to BET. To our knowledge, these are the fastest ET and BET timescales reported for dyads built upon a  $[Ru(tpy)_2]^{2+}$  chromophore platform.

With attribution of the 2.0 ps dyanimes to ET, the quantum yield for populating the <sup>3</sup>ET state ( $\Phi_{ET}$ )

from the <sup>3</sup>MLCT can be approximated using Equation 4.4 where  $k_{ET}$  is the rate of ET and  $\sum k_{decay}$  is the sum off all the other decay pathways.

$$\Phi_{ET} = \frac{k_{ET}}{k_{ET} + \sum k_{decay}} \tag{4.4}$$

Setting  $\sum k_{decay}$  equal to the lifetimes of the complexes studied in Chapter 2, which ranged from 1/124 ps for  $[\operatorname{Ru}(\operatorname{tpy})_2]^{2+}$  to 1/680 ps for and  $[\operatorname{Ru}(\operatorname{ttpy})_2]^{2+}$ , respectively,  $\Phi_{ET}$  for  $[\operatorname{Ru}(\operatorname{tpy})(\operatorname{tpy}-\phi-\operatorname{MV})]^{4+}$  lies between 0.984 and 0.997. Therefore, essentially all of the photoexcited population in  $[\operatorname{Ru}(\operatorname{tpy})(\operatorname{tpy}-\phi-\operatorname{MV})]^{4+}$  decays via ET.

For completeness, we note the 2.0 ps dynamic, could in principle, contain interligand electron transfer (ILET) dynamics. The heteroleptic nature of the ligand environment results in photoexcitation of both tpylocalized and  $(tpy-\phi-MV^{2+}-localized \ ^1MLCT \ species. As result, tpy-localized \rightarrow (tpy-\phi-MV^{2+})-localized \ ^2MLCT \ species. As result, tpy-localized \rightarrow (tpy-\phi-MV^{2+})-localized \ ^2MLCT \ species. As result, tpy-localized \rightarrow (tpy-\phi-MV^{2+})-localized \ ^2MLCT \ species. As result, tpy-localized \rightarrow (tpy-\phi-MV^{2+})-localized \ ^2MLCT \ species. As result, tpy-localized \rightarrow (tpy-\phi-MV^{2+})-localized \ ^2MLCT \ species. As result, tpy-localized \rightarrow (tpy-\phi-MV^{2+})-localized \ ^2MLCT \ species. As result, tpy-localized \ species. As result, tpy-localized \ ^2MLCT \ species. As result, tpy-localized \$ ILET can be expected. Based on the ILET timescales observed in Chapters 2 and 3, such dyanimes can be expected to manifest at times shortly after photoexcitation. To estimate the ratio of these two MLCT species in the initial photoexcited ensemble, and therefore the magnitude ILET dyanimes, we have relied on comparison of the ground state molar absorption coefficients like that detailed in previous chapters. The molar absorption coefficient for formation of the tpy-localized <sup>1</sup>MLCT at 520 nm, the excitation pulse central frequency, is assumed to be 1/2 the molar absorption of  $[Ru(tpy)_2]^{2+}$  namely, 1,450 M<sup>-1</sup> cm<sup>-1</sup>.<sup>||</sup> The molar absorption coefficient for formation of the  $(tpy-\phi-MV^{2+})$ -localized <sup>1</sup>MLCT at 520 nm is estimated to be about  $6,050 \text{ M}^{-1} \text{ cm}^{-1}$ , based on subtraction of the tpy-localized molar absorption from the 7,500 M<sup>-1</sup> cm<sup>-1</sup> molar absorption of  $[Ru(tpy)(tpy-\phi-MV)]^{4+}$  at 520 nm. Using these calculations we estimate there will be an approximate 4 fold excess of  $(tpy-\phi-MV^{2+})$ -localized MLCT species in the initial photoexcited ensemble. It is not inconceivable, therefore, that ILET dynamics could contribution to the early time dynamics. That being said, comparison of the  $\tau_1$  observed in  $[Ru(ttpy)(tpy-\phi-MV)]^{4+}$  (vide infra) with that observed in  $[Ru(tpy)(tpy-\phi-MV)]^{4+}$  suggests ILET dynamics are not do not contribute significantly to the early time dyanimcs. The 2 ps dynamic, therefore, is thought to reflective primarily the ET timescale.

The 5.5 ps timescale for BET we measure is much faster than those reported previously for bisterpyridine Ru(II) ET-dyads. Similarly fast BET timescale have, however, been reported for Ru(II) tris-

<sup>&</sup>lt;sup>||</sup> The molar absorption of  $[\text{Ru}(\text{tpy})_2]^{2+}$  at 520 nm is  $\approx 2500 \text{ M}^{-1} \text{ cm}^{-1}$ . See Chapter 2 for details.

bidentate complexes containing a  $(\phi-MV^{2+})$  acceptor moiety.[27] That the <sup>3</sup>ET states lifetime is so short could be indicative that BET is not occurring very deep in the Marcus inverted region and/or that their is strong electronic communication between the <sup>3</sup>ET and <sup>1</sup>GS. Ideally, such questions would be answered by conducting temperature-dependent studies to determine the values of the reorganization energy  $(\lambda)$  and H<sub>ab</sub> values for both the forward and back electron transfer process. Such studies are, however, beyond the scope of this work. Nonetheless, we speculate that large values of the electronic coupling, H<sub>ab</sub>between the <sup>3</sup>ET and <sup>1</sup>GS is likely the main driver of the fast BET process. Finally, we comment that classical Marcus theory may not be the most correct framework for interpreting the ET and BET dynamics of these complexes. Both ET and BET are likely occurring from non-thermalized excited states that have large electronic coupling with their respective product states. This is very different from the weak coupling statistical approach used in classical Marcus theory. A more appropriate staring point would be the formalisms of Brunschwig and Sutin[63] and Rips and Jortner[43, 64] which, respectively, extend the classical Marcus expression to the high-coupling limit and try to account for dynamical solvation effects occurring on the ET timescale.

Consider finally the weak  $20 \pm 11$  ps component, this dynamic is present only in the bleach recovery data collected at 480 nm and not in the excited state absorptions probed at 415 and 620 nm. This spectral dependence coupled with its long timescale relative to BET suggests evolution of the ground state *after* re-population via BET. Therefore, we tentatively assigned the 20 ps component to vibration cooling of the *ground state*. This assignment is supported by reports of vibrational cooling of the electronic ground state of  $MV^+$  in solution[53] and phenyl substituted terpyridines[65] occurring on a similar timescale. That similar cooling-like dynamics *were not* observed in the transient bleach kinetics of  $[Ru(tpy)_2]^{2+}$ ,  $[Ru(tpy)(ttpy)]^{2+}$ ,  $[Ru(ttpy)_2]^{2+}$ , and  $[Ru(ttpy)_2]^{2+}$  suggests BET occurs via a unique pathway.

## 4.3.6 $[Ru(ttpy)(tpy-\phi-MV)]^{4+}$

Transient spectra of  $[Ru(ttpy)(tpy-\phi-MV)]^{4+}$  collected at 0.4, 2.5, and 10 ps after excitation and are shown in Figure 4.8. The time evolution of the observed spectral features is qualitatively similar to that seen in  $[Ru(tpy)(tpy-\phi-MV)]^{4+}$  with the most prominent change being growth of an absorption peak near 415 nm. Growth of this feature in  $[Ru(ttpy)(tpy-\phi-MV)]^{4+}$ , which is interpreted as formation of the <sup>3</sup>ET state, is less pronounced than that observed in  $[Ru(tpy)(tpy-\phi-MV)]^{4+}$ . This is likely a result of contributions from ILCT absorption of the ancillary ttpy ligand. These transitions require only that a neutral ttpy ligand be proximal to a Ru(III). As a result they are present in both the MLCT and <sup>3</sup>ET excited states contributing to a less dramatic growth of the reduced ( $\phi-MV^{2+}$ ) peak at 410 nm. The dynamics



Figure 4.8: Chirp corrected magic angle transient spectra of  $[Ru(ttpy)(tpy-\phi-MV)]^{4+}$  in room temperature acetonitrile at a variety of time points after excitation. Data points were collected with 5 nm spacing and are represented by the filled circles. Data between the vertical dashed lines has been omitted due to contamination by pump beam scatter.

between 530 and 650 nm from 0.4 and 2.5 ps are also quite weak suggesting absorption of the <sup>3</sup>MLCT of  $[Ru(ttpy)(tpy-\phi-MV)]^{4+}$  and <sup>3</sup>ET are nearly iso-absorptive at these colors.

Detailed temporal dynamics of the ET and BET processes were followed by collecting triplicate sets of single wavelength kinetics at 415, 480, and 620 nm. Representative data are shown in Figure 4.9. Similar to what was observed in  $[Ru(tpy)(tpy-\phi-MV)]^{4+}$ , the kinetics collected at 415 and 620 nm were found to fit to a bi-exponential A $\rightarrow$ B $\rightarrow$ C kinetics model while the bleach data collected at 480 nm required a tri-exponential model. The same fitting methodology used in  $[Ru(tpy)(tpy-\phi-MV)]^{4+}$ , consisting  $\tau_1$  and  $\tau_2$ locked across all the data with  $\tau_3$  allowed to vary freely, was also used for  $[Ru(ttpy)(tpy-\phi-MV)]^{4+}$ . The results are given in Table 4.4.

By analogy to  $[Ru(tpy)(tpy-\phi-MV)]^{4+}$  the 1.55 ps component is assigned to ET and the 5.2 ps



Figure 4.9: Magic angle transient kinetics for  $[Ru(ttpy)(tpy-\phi-MV)]^{4+}$  in room temperature acetonitrile collected at  $\lambda_{probe} = 415$  nm (top), 480 nm (middle) and 620 nm (bottom) following excitation at 520 nm. The red solid lines represent global fits to the data. The data collected at 415 and 620 nm was fit using an  $A \rightarrow B \rightarrow C$  kinetics model and returned tau values of  $1.55 \pm 0.06$  ps and  $5.2 \pm 0.1$  ps. The data collected at 480 was fit with a tri-exponential model and found to contain a weak third tau of  $26 \pm 7$  ps.

component to BET. The ill-defined  $26 \pm 7$  ps component present in the bleach recovery data is ascribed to vibrational cooling of the ground state following BET. That the ET timescale observed in

Table 4.4: Global fitting results for  $\left[\mathrm{Ru}(\mathrm{ttpy})(\mathrm{tpy}-\phi-\mathrm{MV})\right]^{4+}$  kinetics data collected in room temperature  $\mathrm{CH}_3\mathrm{CN}$ 

Probe Wavelength/nm	Tau Values^/ps ( $\pm 2\sigma$ )	Averaged pre-exponential values <sup>c</sup> $(\pm 2\sigma)$
415 <sup>a</sup>	$\tau_1 = 1.55 \; (0.06);  \tau_2 = 5.2 \; (0.1)$	$egin{array}{llllllllllllllllllllllllllllllllllll$
$480^{\mathrm{b}}$	$ au_1 = 1.55 \; (0.06);   au_2 = 5.2 \; (0.1);   au_3 = 26 \; (7)$	$egin{aligned} { m a}_1 &= 0.18 \; (0.02);  { m a}_2 &= -1.1 \; (0.02) \ ;  { m a}_3 &= -0.06 \; (0.028) \end{aligned}$
$620^{\mathrm{a}}$	$\tau_1 = 1.55 \; (0.06);  \tau_2 = 5.2 \; (0.1)$	${ m A}=0.42\;(0.03);{ m B}=1.63\;(0.01);\ { m C}=0.00$

<sup>a</sup>Fit to an A  $\rightarrow$  B  $\rightarrow$  C kinetics model. See Appendix C for details. The pre-exponential terms A, B, and C for data collected 415 and 620 nm are proportional to the molar absorption of the <sup>3</sup>MLCT, ET, and ground state, respectively, at these wavelengths.

<sup>b</sup>Fit to a triexponential model with  $\tau_1$  and  $\tau_2$  linked across all three probe wavelengths .

<sup>c</sup>Average values resulting from global fitting three independent data sets. The values given in parenthesis represent  $\pm$  two times the standard deviation.

 $[\operatorname{Ru}(\operatorname{ttpy})(\operatorname{tpy}-\phi-\operatorname{MV})]^{4+}$  is faster relative to  $[\operatorname{Ru}(\operatorname{tpy})(\operatorname{tpy}-\phi-\operatorname{MV})]^{4+}$  suggests that ILET dynamics contribute minimally to the early time component observed in both complexes. If ILET were to play a significant role one would expect an elongated ET timescale in  $[\operatorname{Ru}(\operatorname{ttpy})(\operatorname{tpy}-\phi-\operatorname{MV})]^{4+}$  due to smaller driving force for ILET.\*\* On the other hand, the driving for ET,  $\Delta G_{ET}^o$ , is slightly larger in  $[\operatorname{Ru}(\operatorname{ttpy})(\operatorname{tpy}-\phi-\operatorname{MV})]^{4+}$ , -0.42 eV vs -0.40 eV for  $[\operatorname{Ru}(\operatorname{tpy})(\operatorname{tpy}-\phi-\operatorname{MV})]^{4+}$ , and may explain the slight difference in ET timescales. Again, because of the fast ET timescale, essentially all of the photoexcited MLCT population is assumed to decay via ET (vide supra).

The 5.2 ps timescale for BET observed in  $[Ru(ttpy)(tpy-\phi-MV)]^{4+}$  is essentially identical to that observed in  $[Ru(tpy)(tpy-\phi-MV)]^{4+}$  and agrees with driving forces for BET calculated in both complexes (Table 4.2).These results suggest the ancillary ligand has little effect on the ET and BET dynamics which mean that similar ET and BET timescales should be observed in the dual acceptor species despite the

<sup>\*\*</sup> Reduction of the ttpy ligand occurs at a less negative potential than that of tpy (-1.51 and 1.61 V vs 0.01 M Ag/AgNO<sub>3</sub> in ACN, respectively).

presence of a tpy-AN ancillary ligand. The weak third component present at 480 nm,  $26 \pm 7$  ps, again, suggests strong coupling of the <sup>3</sup>ET and the <sup>1</sup>GS along and possible involves excited vibrational levels of the (tpy- $\phi$ -MV<sup>2+</sup>) ligand.

### 4.4 Concluding Remarks

Working towards the overall goal of understanding the target energy and electron transfer reactive dual acceptor  $[Ru(tpy-An)(tpy-\phi-MV)]^{4+}$ , we have built and characterized two new electron transfer dyads,  $[Ru(tpy)(tpy-\phi-MV)]^{4+}$  and  $[Ru(ttpy)(tpy-\phi-MV)]^{4+}$ . These have been studied using linear absorption, electrochemical, spectroelectrochemical, and ultrafast pump-probe techniques. Our results clearly demonstrate that the initially photoexcited MLCT is quenched with essentially unit quantum yield via ET. The observed yield and ET timescale is superior to all perviously reported bis-terpyridine based ET-dyads. The BET process was also observed to be quite fast, approximately 5 ps, and results in prompt reformation of the ground state. The BET process is also thought to result in formation of a vibrationally hot ground state based on the presence of a weak 20 ps dynamics in the bleach recovery monitored at 480 nm. Such fast BET process a challenge if one wants to utilize the stored redox energy, however, in the context of the proposed AFC pulse shaping experiments this can actually be advantage. The fast ET and BET timescales relative to the long T<sub>1</sub> lifetime of anthracene will allow us to measure the branching ratio between the ET and EnT decay pathways via the transient signal measured at times long after excitation. This point will be discussed further in Chapters 5.

## Chapter 4 Bibliography

- J. P. Collin, S. Guillerez, J. P. Sauvage, F. Barigelletti, L. Decola, L. Flamigni, and V. Balzani, *Inorganic Chemistry*, 1991, **30**, 4230–4238.
- L. F. Cooley, S. L. Larson, C. M. Elliott, and D. F. Kelley, Journal of Physical Chemistry, 1991, 95, 10694–10700.
- (3) E. Yonemoto, G. Saupe, R. Schmehl, S. Hubig, R. Riley, B. Iverson, and T. E. Mallouk, *Journal Of The American Chemical Society*, 1994, **116**, 4786–4795.
- (4) J. P. Sauvage, J. P. Collin, J. C. Chambron, S. Guillerez, C. Coudret, V. Balzani, F. Barigelletti, L. Decola, and L. Flamigni, *Chemical Reviews*, 1994, 94, 993–1019.
- (5) F. Barigelletti and L. Flamigni, *Chemical Society Reviews*, 2000, **29**, 1–12.
- (6) H. Durr and S. Bossmann, Accounts of Chemical Research, 2001, 34, 905–917.
- R. Lomoth, T. Häupl, O. Johansson, and L. Hammarström, *Chemistry-A European Journal*, 2002, 8, 102–110.
- (8) O. Johansson, M. Borgström, R. Lomoth, M. Palmblad, J. Bergquist, L. Hammarström, L. C. Sun, and B. Åkermark, *Inorganic Chemistry*, 2003, 42, 2908–2918.
- (9) Y. Xu et al., Chemistry-A European Journal, 2005, 11, 7305–7314.
- (10) M. Falkenström, O. Johansson, and L. Hammarström, *Inorganica Chimica Acta*, 2007, **360**, 741–750.
- (11) S. Karlsson, J. Modin, H.-C. Becker, L. Hammarström, and H. Grennberg, *Inorganic Chemistry*, 2008, 47, 7286–7294.
- (12) M. R. Hartings, I. V. Kurnikov, A. R. Dunn, J. R. Winkler, H. B. Gray, and M. A. Ratner, *Coordination Chemistry Reviews*, 2010, **254**, 248–253.
- (13) J. Hankache and O. S. Wenger, *Physical Chemistry Chemical Physics*, 2012.
- (14) A. C. Benniston and A. Harriman, *Chemical Society Reviews*, 2006, **35**, 169–179.
- (15) P. P. Laine, S. Campagna, and F. Loiseau, Coordination Chemistry Reviews, 2008, 2552–2571.

- (16) H. A. Meylemans, C. F. Lei, and N. H. Damrauer, *Inorganic Chemistry*, 2008, 47, 4060–4076.
- (17) A. Benniston, A. Harriman, P. Li, P. Patel, and C. Sams, *Chemistry A European Journal*, 2008, 14, 1710–1717.
- (18) H. A. Meylemans and N. H. Damrauer, Inorganic Chemistry, 2009, 48, 11161–11175.
- (19) H. A. Meylemans, J. T. Hewitt, M. Abdelhaq, P. J. Vallett, and N. H. Damrauer, Journal of the American Chemical Society, 2010, 132, 11464–11466.
- (20) N. S. Lewis and D. G. Nocera, Proceedings of the National Academy of Sciences of the United States of America, 2006, 103, 15729–15735.
- (21) M. I. Hoffert et al., Science, 2002, 298, 981–987.
- (22) K. Kalyanasundaram, Coordination Chemistry Reviews, 1982, 46, 159–244.
- (23) A. Juris, V. Balzani, F. Barigelletti, S. Campagna, P. Belser, and A. von Zelewsky, *Coordination Chemistry Reviews*, 1988, 84, 85–277.
- (24) S. Campagna, F. Puntoriero, F. Nastasi, G. Bergamini, and V. Balzani, Photochemistry and Photophysics of Coordination Compounds I, 2007, 280, 117–214.
- (25) J. P. Collin, S. Guillerez, and J. P. Sauvage, Journal of the Chemical Society-Chemical Communications, 1989, 776–778.
- (26) K. Hutchison, J. C. Morris, T. A. Nile, J. L. Walsh, D. W. Thompson, J. D. Petersen, and J. R. Schoonover, *Inorganic Chemistry*, 1999, **38**, 2516–2523.
- (27) M. Abdelhaq, Physical Chemistry, University of Colorado at Boulder, 2012.
- (28) H. A. Meylemans, Ph.D. Thesis, 2010.
- (29) F. Neve, A. Crispini, S. Campagna, and S. Serroni, *Inorganic Chemistry*, 1999, 38, 2250–2258.
- (30) B. P. Sullivan, J. M. Calvert, and T. J. Meyer, *Inorganic Chemistry*, 1980, **19**, 1404–1407.
- (31) K. J. Takeuchi, M. S. Thompson, D. W. Pipes, and T. J. Meyer, *Inorganic Chemistry*, 1984, 23, 1845–1851.

- (32) H. Hofmeier, E. Herdtweck, and U. S. Schubert, Zeitschrift Fur Anorganische Und Allgemeine Chemie,
  2004, 630, 683–688.
- (33) C. C. Phifer and D. R. McMillin, *Inorganic Chemistry*, 1986, 25, 1329–1333.
- (34) C. R. Hecker, A. K. I. Gushurst, and D. R. McMillin, *Inorganic Chemistry*, 1991, 30, 538–541.
- (35) M. Maestri, N. Armaroli, V. Balzani, E. C. Constable, and A. M. W. C. Thompson, *Inorganic Chem-istry*, 1995, 34, 2759–2767.
- M. Head-Gordon, A. M. Grana, D. Maurice, and C. A. White, Journal of Physical Chemistry, 1995, 1995, 14261–14270.
- (37) A. Vlček and S. Záliš, Coordination Chemistry Reviews, 2007, 251, 258-287.
- (38) J. D. Henrich, H. Y. Zhang, P. K. Dutta, and B. Kohler, Journal of Physical Chemistry B, 2010, 114, 14679–14688.
- (39) V. V. Pavlishchuk and A. W. Addison, Inorganica Chimica Acta, 2000, 298, 97–102.
- (40) A. Weller, Zeitschrift für Physikalische Chemie, 1982, 133, 93–98.
- (41) M. Abrahamsson et al., Inorganic Chemistry, 2005, 44, 3215–3225.
- (42) R. A. Marcus, Annual Review of Physical Chemistry, 1964, 15, 155–196.
- (43) I. Rips and J. Jortner, Journal of Chemical Physics, 1987, 87, 6513–6519.
- (44) P. F. Barbara, G. C. Walker, and T. P. Smith, Science, 1992, 256, 975.
- (45) E. H. Yonemoto, R. L. Riley, Y. I. Kim, S. J. Atherton, R. H. Schmehl, and T. E. Mallouk, Journal of the American Chemical Society, 1992, 114, 8081–8087.
- (46) J. K. McCusker, Accounts of Chemical Research, 2003, 36, 876–887.
- (47) F. Tessore, D. Roberto, R. Ugo, M. Pizzotti, S. Quici, M. Cavazzini, S. Brun, and F. De Angelis, *Inorganic Chemistry*, 2005, 44, 8967–8978.
- (48) J. F. Michalec, S. Bejune, D. Cuttell, G. Summerton, J. Gertenbach, J. Field, R. Haines, and D. Mcmillin, *Inorganic Chemistry*, 2001, 40, 2193–2200.

- (49) J. C. Curtis, B. P. Sullivan, and T. J. Meyer, *Inorganic Chemistry*, 1983, 22, 224–236.
- (50) M. K. Nazeeruddin, S. M. Zakeeruddin, and K. Kalyanasundaram, Journal of Physical Chemistry, 1993, 97, 9607.
- (51) K. Kalyanasundaram, S. M. Zakeeruddin, and M. K. Nazeeruddin, Coordination Chemistry Reviews, 1994, 132, 259–264.
- (52) N. H. Damrauer and J. K. McCusker, Journal of Physical Chemistry A, 1999, 103, 8440–8446.
- (53) T. Häupl, R. Lomoth, and L. Hammarström, Journal of Physical Chemistry A, 2003, 107, 435–438.
- (54) T. Watanabe and K. Honda, Journal Of Physical Chemistry, 1982, 86, 2617–2619.
- (55) P. M. S. Monk, The viologens : physicochemical properties, synthesis, and applications of the salts of 4,4'-bipyridine, Wiley, Chichester ; New York, 1998.
- (56) N. H. Damrauer, G. Cerullo, A. Yeh, T. R. Boussie, C. V. Shank, and J. K. McCusker, *Science*, 1997, 275, 54–57.
- (57) A. C. Bhasikuttan, M. Suzuki, S. Nakashima, and T. Okada, *Journal of the American Chemical Society*, 2002, **124**, 8398–8405.
- (58) A. Cannizzo, F. van Mourik, W. Gawelda, G. Zgrablic, C. Bressler, and M. Chergui, Angewandte Chemie-International Edition, 2006, 45, 3174–3176.
- (59) S. Yoon, P. Kukura, C. M. Stuart, and R. A. Mathies, *Molecular Physics*, 2006, **104**, 1275–1282.
- (60) A. C. Albrecht, Journal of Molecular Spectroscopy, 1961, 6, 84.
- (61) H. S. Tan, I. R. Piletic, and M. D. Fayer, Journal Of The Optical Society Of America B-Optical Physics, 2005, 22, 2009–2017.
- (62) G. B. Shaw, D. J. Styers-Barnett, E. Z. Gannon, J. C. Granger, and J. M. Papanikolas, Journal of Physical Chemistry A, 2004, 108, 4998–5006.
- (63) B. S. Brunschwig and N. Sutin, Coordination Chemistry Reviews, 1999, 187, 233–254.
- (64) I. Rips and J. Jortner, Journal of Chemical Physics, 1987, 87, 2090–2104.

(65) R. Siebert, A. Winter, M. Schmitt, J. Popp, U. S. Schubert, and B. Dietzek, Macromolecular Rapid Communications, 2012, 33, 481–497.

# Chapter 5

# Photophysics of $[Ru(tpy-An)(tpy-\phi-MV]^{4+}$ : Observation of Both Photoinduced Energy and Electron Transfer Following <sup>1</sup>MLCT Photoexcitation.

#### 5.1 Introduction

The overarching goal of this thesis is use of adaptive feedback control (AFC) pulse shaping methodologies to control and probe electron transfer (ET) and energy transfer (EnT) reactivity in an novel ruthenium(II) polypyridyl complex  $[Ru(tpy-An)(tpy-\phi-MV)]^{4+}$ . Having built a solid understanding of the photophysics of the constituent parts of  $[Ru(tpy-An)(tpy-\phi-MV)]^{4+}$ ; namely, the central Ru(II) bis-terpyridine like chromophore (Chapter 2), the energy transfer (EnT) portion of the complex  $[Ru(tpy-An)(tpy)]^{2+}$  (Chapter 3), and the electron transfer (ET) dyads  $[Ru(tpy)(tpy-\phi-MV)]^{4+}$  and  $[Ru(ttpy)(tpy-\phi-MV)]^{4+}$  (Chapter 4) we now turn to characterization of the photoinduced dynamics of  $[Ru(tpy-An)(tpy-\phi-MV)]^{4+}$  following unshaped laser pulse excitation.

## 5.2 Experimental

#### 5.2.1 General

The target complexes  $[Ru(tpy-An)(tpy-\phi-MV)]^{4+}$  was synthesized using a procedure similar to those published elsewhere[1–3] with  $[Ru(tpy-An)Cl_3]$  used as the precursor complex. The electroactive ligand  $(tpy-\phi-MV^{2+})$  (4-(1-(1'-Methyl-4,4'-bipyridinium-1-yl)-phenyl)-2,2':6',2''-terpyridine) was synthesized by Dr. Mirvat Abdelhaq with details given in Chapter 2 of her PhD thesis.[4] Tpy-An (4'-



Figure 5.1:  $[Ru(tpy-An)(tpy-\phi-MV)]^{4+}$ , the complex investigated in this chapter.

(9-anthracenyl)-2,2':6',2''-terpyridine) was purchased from HetCat (Hetcat.com) and re-crystalized from methanol prior to use. Addition of the electroactive ligand prior to reduction of the Ru(III) metal center to Ru(II) with triethylamine resulted in much lower yield of the target complex. Because the tpy-An ligand is susceptibility to irreversible oxidation, the complexation reactions were conducted under an inert argon atmosphere. All samples were purified via silica gel column chromatography with room lights kept to a minimum. Argon sparged 8:1:1 acetonitrile, water, and saturated potassium nitrate in water was used as the eluent. The identity and purity of each complex was confirmed by <sup>1</sup>H-NMR and mass spectrometry (See Appendix D). <sup>1</sup>H-NMR spectra were recorded using a Varian Inova 500 MHz spectrometer and all deuterated solvents were purchased from Cambridge Isotopes Laboratories Inc. Mass spectrometry measurements and accurate mass analysis were performed by the Central Analytical Laboratory at the University of Colorado at Boulder, Department of Chemistry and Biochemistry. Linear absorption measurements were made using a Hewlett-Packard HP8452A diode array UV-Vis spectrometer. All photophysical measurements were made using acetonitrile from Burdick and Jackson (UV-Grade) that had been thoroughly bubbled with argon. Linear absorption and ultrafast pump-probe data were collected in sealed cells back filled with argon.

#### 5.2.2 Ultrafast Pump-Probe Measurements

Data were collected used the same instrumentation and experimental methodologies detailed in Chapter 2 and Appendix A.

#### 5.2.3 Nanosecond Pump-Probe Measurements

Data were collected used the same instrumentation and experimental methodologies detailed in Chapter 3.

## 5.3 Results and Discussion

#### 5.3.1 Ground State Absorption Properties

Like the complexes characterized heretofore, the visible region steady state absorption spectrum of  $[\operatorname{Ru}(\operatorname{tpy}-\operatorname{An})(\operatorname{tpy}-\phi-\operatorname{MV})]^{4+}$  is dominated by an intense <sup>1</sup>MLCT  $\leftarrow$  <sup>1</sup>GS feature with a maximum absorption at 490 nm (see Figure 5.2). As is shown, the absorption spectrum of  $[\operatorname{Ru}(\operatorname{tpy}-\operatorname{An})(\operatorname{tpy}-\phi-\operatorname{MV})]^{4+}$  closely resembles that of  $[\operatorname{Ru}(\operatorname{tpy})(\operatorname{tpy}-\phi-\operatorname{MV})]^{4+}$  especially on the red of the MLCT feature, which is photoexcitation in the ultrafast experiments discussed later will take place. Based on an analysis of the absorption spectrum of  $[\operatorname{Ru}(\operatorname{tpy}-\operatorname{An})(\operatorname{tpy})]^{2+}$  we estimate the molar absorption coefficient for excitation to the tpy-An ligand at 520 nm to be approximately 1825 M<sup>-1</sup> cm<sup>-1</sup>.\* Using a similar analysis, the molar absorption coefficient for excitation to the  $(\operatorname{tpy}-\phi-\operatorname{MV})$  ligand is expected to be about 4658 M<sup>-1</sup> cm<sup>-1</sup>. Based on this ratio we expect about 60% of the MLCT excited states created in the ultrafast experiments detailed later to be  $(\operatorname{tpy}-\phi-\operatorname{MV}^{2+})$ -localized with the remaining 40% being  $(\operatorname{tpy}-\operatorname{An})$ -localized. Given that the  $(\operatorname{tpy}-\phi-\operatorname{MV}^{2+})$ -localized MLCT species is expected to be lower in energy than the tpy-An localized MLCT, one may expected interligand electron transfer (ILET) dynamics to convert the tpy-An localized MLCT species into  $(\operatorname{tpy}-\phi-\operatorname{MV}^{2+})$ -localized MLCT species. Such mixing, however, is expected to be minimal given ILET is relatively slow (2-3 ps) compared to EnT (0.5 ps).

<sup>\*</sup> This number was arrived at by dividing the absorption of  $[Ru(tpy)_2]^{2+}$  at 520 nm, 2962 M<sup>-1</sup> cm<sup>-1</sup>, by two and then subtracting it from the molar absorption of  $[Ru(tpy)(tpy-An)]^{2+}$  at 520 nm (3306 M<sup>-1</sup> cm<sup>-1</sup>).



Figure 5.2: Steady state absorption spectrum of  $[Ru(tpy-An)(tpy-\phi-MV)]^{4+}$  (green) collected in room temperature acetonitrile. The MLCT absorption maxima occurs at 490 nm (16,000 M<sup>-1</sup> cm<sup>-1</sup>). The absorption spectrum of  $[Ru(tpy-An)(tpy)]^{2+}$  (red, dashed) and  $[Ru(tpy)(tpy-\phi-MV)]^{4+}$  (blue, dashed) are included for reference. The experimental absorption spectrum of  $[Ru(tpy-An)(tpy-\phi-MV)]^{4+}$  generated by a simple averaging of the  $[Ru(tpy-An)]^{2+}$  and  $[Ru(tpy-An)(tpy-\phi-MV)]^{4+}$  molar absorption intensities is also shown (grey, dashed).

#### 5.3.2 Ultrafast Pump-Probe Spectroscopy

Electrochemical and spectroelectrochemical characterization of  $[Ru(tpy-An)(tpy-\phi-MV)]^{4+}$  has not been undertaken. The results detailed in Chapters 2, 3, 4, and 5 will, therefore, be used to interpret the features observed in transient spectra and kinetics. Again, we assume the absorptive features observed are <sup>3</sup>MLCT, <sup>3</sup>ET, or <sup>3</sup>EnT in character due to ultrafast intersystem crossing of the initially excited <sup>1</sup>MLCT to the <sup>3</sup>MLCT.[5–8] For both the transient spectra and single wavelength kinetics, the relative electric field polarization between the pump and probe beam was set to the magic angle (54.7°) to ensure only excitedstate population dynamics were monitored.[9, 10]<sup>†</sup> All of the transient measurements presented herein used excitation pulses centered at approximately 525 nm, corresponding to the red edge of the <sup>1</sup>MLCT absorption band. We remind the reader red-detuning of the pump central frequency minimizes the possibility of direct excitation of the anthracene moiety as well as the amount of excess energy deposited into the chromophore

 $<sup>^\</sup>dagger$  See Chapter 2 and Appendix A for details.

during photoexcitation. The latter minimizes the amplitude of vibrational cooling dynamics in the data.[11]

As was the case in the previous chapters, we begin with characterization of the chirp-corrected magic angle transient spectra collected at a variety of time delays after  ${}^{1}MLCT \leftarrow {}^{1}GS$  excitation. Representative spectra collected at 0.5, 1.0, 2.0, 25, and 100 ps are shown in Figure 5.3. The top panel highlights early time dynamics, 0.5 to 2.0 ps, while the bottom panel shows spectra from 2.0 to 100 ps. Beginning with the spectra collected at 0.5 ps, features characteristic of population in the  ${}^{3}MLCT$  and  $T_{1}$  state of the anthracene are clearly present. The broad absorption from 350 to 450 nm and 550 to 680 nm as well as the bleach centered near 485 nm can be attributed to a mixture of  ${}^{3}MLCT[12]^{\ddagger}$  and  ${}^{3}EnT$  population (See Chapter 3). The peaked feature near 425 nm is characteristic of the lowest energy anthracene triplet and is assigned to  $T_3$  $\leftarrow$  T<sub>1</sub> absorption.[13–16] The broad spectral width of near-UV absorption feature is thought to a result of the reduced ligand absorption of the  ${}^{3}MLCT$  (See Chapters 2 and 4). The feature from 550 to 680 nm is assigned to a mixture of anthracene  $T_2 \leftarrow T_1$  absorption and reduced ligand and LMCT transitions of the  $^{3}$ MLCT (See Chapters 2 and 4). Evolution of the spectra from 0.5 ps to 2.0 ps after excitation shows growth of a shoulder near 425 nm. This is thought to indicate population of both the anthracene  $T_1$  (via EnT) and <sup>3</sup>ET states (via ET). We note that the overlapping nature of the anthracene  $T_1$  and <sup>3</sup>ET absorptive features between 350 and 460 nm will likely complicate disentanglement of the EnT and ET dynamics. Over this same time period (0.5 to 2.0 ps), the bleach undergoes moderate recovery while the broad absorption from 550 to 680 nm changes very little. Recovery of the bleach on this timescale is expected to be a result of primarily EnT quenching, however, ET and BET dynamics may also be contributing.

From 2 to 25 ps after excitation, all the transient features undergo a significant decrease in intensity. This suggests back electron transfer (BET) is still operative and repopulating the ground state on a timescale similar that observed in Chapter 5. From 25 to 100 ps the features in the transient spectra undergo essentially no change suggesting EnT to the anthracene T<sub>1</sub> is still occurring and the anthracene T<sub>1</sub> population is relatively static on these timescales. The transient spectra of  $[Ru(tpy-An)(tpy)]^{2+}$  and  $[Ru(tpy-An)(tpy-\phi-MV)]^{4+}$  collected at 100 ps are overlaid in Figure 5.4. Agreement of the 420 nm absorption feature, which is attributed to T<sub>3</sub>  $\leftarrow$  T<sub>1</sub> absorption of the anthracene, is taken as evidence

 $<sup>^\</sup>ddagger$  See Chapter 2 for more references and details of the assignments.



Figure 5.3: Chirp corrected magic angle transient spectrum of  $[Ru(tpy-An)(tpy-\phi-MV)]^{4+}$  collected in room temperature acetonitrile at a variety of time points after excitation. Data points were collected every 5 nm and are represented by the filled circles. The data between the vertical dashed lines has been omitted due to contamination by scatter from the pump beam centered near 525 nm.

that the long lived species is, indeed, the anthracene T<sub>1</sub>. That the absorption from 550 to 680 nm in  $[Ru(tpy-An)(tpy-\phi-MV)]^{4+}$  is much stronger than that of  $[Ru(tpy-An)(tpy)]^{2+}$  is not currently understood.

Details of the temporal evolution of the MLCT excited state in  $[Ru(tpy-An)(tpy-\phi-MV)]^{4+}$  were studied by collecting triplicate sets of single wavelength kinetics at 415, 480, and 620 nm. Representative data are shown in Figure 5.5. The dynamics observed in the single wavelength kinetics are readily under-



Figure 5.4: Normalized and overlaid magic angle transient spectra of  $[Ru(tpy-An)(tpy)]^{2+}$  and  $[Ru(tpy-An)(tpy-\phi-MV)]^{4+}$  collected 100 ps after excitation.

standable as a superposition of those observed in the energy transfer  $([Ru(tpy-An)(tpy)]^{2+})$  and ET transfer  $([Ru(tpy)(tpy-\phi-MV)]^{4+})$  dyads. The data collected at 420 and 620 nm display bi-exponential dynamics consisting of an early time growth and a longer decay with an absorptive offset at times greater than about 30 ps. The bleach recovery monitored at 480 nm shows more complex recovery dynamics with fast early time component(s) followed by a slower recovery and a longtime bleach offset.

When fitting the kinetics, the data collected at 420 and 620 nm fit to a bi-exponential model, therefore, the A  $\rightarrow$  B  $\rightarrow$  C kinetics model detailed in Chapter 4 was used. The bleach recovery at 480 nm, however, could not be fit to a bi-exponential model. Instead, a tri-exponential model was needed. We also found that global fitting of all the wavelengths was not possible. Linking the  $\tau_1$  and  $\tau_2$  values across the 420 and 620 nm data returned reasonable fits, however, when the 480 nm data was included poor fits resulted. As a result the kinetics collected at 480 nm were fit in isolation. As was the case in the previous chapters, three independent sets of data were collected and fit. The results are given in Table 5.1.

Considering the data collected at 620 nm, it was not surprising to find that it fit well to the  $A \rightarrow B \rightarrow C$  kinetics model. The anthracene  $T_1$  has relatively minimal dynamics at this color (see Chapter 3). That



Figure 5.5: Magic angle single wavelength transient kinetics of  $[Ru(tpy-An)(tpy-\phi-MV)]^{4+}$  in room temperature acetonitrile collected at  $\lambda_{probe} = 420$  nm (top), 480 nm (middle) and 620 nm (bottom). The red solid lines represent global fits to the data. The data collected at 420 and 620 nm were found to contain two common tau values of  $1.1 \pm 0.1$  ps and  $5.5 \pm 0.2$  ps. The bleach data collected at 480 nm was fit using a tri-exponential model yielding taus of  $0.32 \pm 0.05$  ps and  $4.8 \pm 0.3$  ps  $27 \pm 8$  ps.

Probe Wavelength/nm	Tau Values <sup>b</sup> /ps ( $\pm 2\sigma$ )	Averaged pre-exponential values <sup>b</sup> $(\pm 2\sigma)$
420	$\tau_1 = 1.1 \; (0.1);  \tau_2 = 5.5 \; (0.2)$	${ m A}_1=$ -0.55 (0.01); ${ m A}_2=1.29$ (0.02)
480 <sup>a</sup>	$\begin{split} \tau_{1^{*}} &= 0.32 \; (0.05);  \tau_{2^{*}} = 4.8 \; (0.3); \\ \tau_{3^{*}} &= 27 \; (8) \end{split}$	$\begin{array}{l} A_{1^{*}}=\text{-}0.3~(0.1);A_{2^{*}}=\text{-}1.0~(0.6)\\ ;A_{3^{*}}=\text{-}0.09~(0.05) \end{array}$
620	$\tau_1 = 1.1 \; (0.1);  \tau_2 = 5.5 \; (0.2)$	${ m A}_1=$ -0.20 (0.01); ${ m A}_2=1.16$ (0.02)

Table 5.1: Global fitting results for  $[Ru(tpy-An)(tpy-\phi-MV)]^{4+}$  kinetics data collected in room temperature  $CH_3CN$ 

<sup>a</sup>Data collected at 480 was found not to fit with data collected at 420 and 620 nm, therefore, this data was fit individually.

<sup>b</sup>Average values resulting from global fitting three independent data sets.

The values given in parenthesis represent  $\pm$  two times the standard deviation.

the 420 nm data also fit to the  $A \rightarrow B \rightarrow C$  model was unexpected. A priori, we expected the early time dyanimes at this probe color to be a convolution of the sub-picosecond EnT dyanimes and the picosecond ET dyanimes. Curiously, the signal immediately after the "coherence spike" (~ 400 fs) is almost equal in intensity to that observed at 100 ps. Because the long lived absorption is attributed to the anthracene  $T_1$ , this could be interpreted as <sup>3</sup>MLCT  $\rightarrow T_1$  EnT occurring so fast it is near complete by the time the pump-probe overlap is over. This, however, not supported by the  $0.32 \pm 0.05$  ps component in the bleach recovery, which is approximately equal to the EnT timescale observed in  $[Ru(tpy-An)(tpy)]^{2+}$ . Instead, we suspect relatively intense absorption of the tpy-An localized MLCT is muting the EnT dynamics at this probe wavelength. Unlike  $[Ru(tpy-An)(tpy)]^{2+}$ , both reduced ligand and interligand charge transfer absorption (ILCT) are expected to contribute the tpy-An localized MLCT absorption of  $[Ru(tpy-An)(tpy-\phi-MV)]^{4+}$ . The oxidative spectroelectrochemistry of  $[Ru(tpy)(tpy-\phi-MV)]^{4+}$  and  $[Ru(ttpy)(tpy-\phi-MV)]^{4+}$ , given in Chapter 4, shows significant ILCT absorptive intensity develops near 400 nm when a tpy- $\phi$ -MV<sup>2+</sup> ligand is proximal to a Ru(III) center. It is useful to recall that the loss of such absorption in  $[Ru(tpy)(ttpy)(ttpy)]^{2+}$ , due to ILET, leads to a net *decrease* in absorptive intensity between 380 and 450 nm. Therefore, we suspect the increase absorption at 420 nm as a result of <sup>3</sup>MLCT  $\rightarrow$  T<sub>1</sub> EnT is being offset by the loss of ILCT and reduced ligand IL transition, thereby, leading to negligible EnT dyanimous at 420 nm. The  $1.1 \pm 0.1$  ps and  $5.5 \pm 0.2$  ps components observed at 420 and 620 nm are, therefore, attributed to the ET and BET timescale, respectively. These values are quite close to the timescales observed for the two ET dyads characterized in Chapter 4 and suggest the ET and BET process in  $[Ru(tpy-An)(tpy-\phi-MV)]^{4+}$  is relatively unperturbed from that of the ET dyads  $[Ru(tpy)(tpy-\phi-MV)]^{4+}$  and  $[Ru(ttpy)(tpy-\phi-MV)]^{4+}$ .

Moving to the kinetics collected at 480 nm, the need for a tri-exponential model was not entirely surprising considering such a model was needed to fit the bleach recovery dynamics of both the EnT and ET dyads. As discussed above, the fastest component,  $0.32 \pm 0.05$  ps, is close to the EnT timescale observed in  $[Ru(tpy-An)(tpy)]^{2+}$  and is, therefore, ascribed to the <sup>3</sup>MLCT  $\rightarrow$  T<sub>1</sub> EnT timescale in  $[Ru(tpy-An)(tpy-\phi-MV)]^{4+}$ . The intermediate component of  $4.8 \pm 0.3$  ps is thought to reflect primarily BET but likely also contains some cooling of the anthracene T<sub>1</sub> (see Chapter 3). We note here if this component is held at 5.5 ps (per the global fitting at 420 and 620 nm) poor fits result. The long 27 ± 8 ps component is attributed to vibrational cooling of the ground state following BET, analogous to the dyanimcs observed in Chapter 4.

We now move to an estimation of the ratio of MLCT excited states quenched via ET and EnT. Considering there is no indication of ILET dyanimes in the transient data, one would expect the ratio of EnT to ET quenching to be quite close to the initial MLCT ensemble configuration predicted from the steady state absorption (1:2 in favor of the tpy- $\phi$ -MV<sup>2+</sup>-localized MLCT). Because the molar absorption coefficients of the <sup>3</sup>MLCT, T<sub>1</sub>, and <sup>3</sup>ET are not currently know, and accurate determination of such excited state molar absorptions is difficult,[17] and alternatively indirect measure has been devised and relies on the magnitude of the longtime bleach intensity measured at 480 nm. For [Ru(tpy-An)(tpy)]<sup>2+</sup>, where unit quenching of the MLCT via EnT is assumed, the intensity of the bleach signal at 480 nm is about 27% of its initial maximum 100 ps after excitation. As discussed in Chapter 2, this offset is attributed to perturbation of the <sup>1</sup>MLCT  $\leftarrow$  <sup>1</sup>GS absorption as a result of the proximal anthracene T<sub>1</sub>, therefore, its long time magnitude can be used as crude indicator of the fraction of the photoexcited MLCT population quenched via EnT. In [Ru(tpy-An)(tpy- $\phi$ -MV)]<sup>4+</sup>, the bleach intensity measured at 100 ps is about 10 % of the maximum, implying only a fraction of the MLCT excited states are quenched via EnT. If all the MLCT population was quenched via EnT then the bleach intensity at 100 ps would be expected to be on the order of 27%. Therefore, we estimate about 37% of the photoexcited MLCT population is quenched via EnT reactivity.<sup>§</sup> This analysis is quite simple and does not account for the greater molar absorption of  $[Ru(tpy-An)(tpy-\phi-MV)]^{4+}$  (14,000 cm<sup>-1</sup> M<sup>-1</sup>) relative to  $[Ru(tpy-An)(tpy)]^{2+}$  (11,000 cm<sup>-1</sup> M<sup>-1</sup>) at 480 nm, nonetheless, the 37% estimate is very close to the ratio MLCT excited state configuration predicted from the linear absorption analysis (40% tpy-An localized and 60% tpy- $\phi$ -MV<sup>2+</sup>-localized). This implies ILET dynamics in  $[Ru(tpy-An)(tpy-\phi-MV)]^{4+}$  are negligible and interconversion (or scrambling) of the initially prepared MLCT population (tpy-An localized and tpy- $\phi$ -MV<sup>2+</sup>-localized) is not expected. Stated differently,  $[Ru(tpy-An)(tpy-\phi-MV)]^{4+}$  behaves as if it were two uncoupled chromophores in solution with one of the chromophores bing  $[Ru(tpy-An)(tpy)]^{2+}$ -like, undergoing quenching via EnT, while the other is  $[Ru(tpy)(tpy-\phi-MV)]^{4+}$ -like and undergoes exclusively ET quenching.

Based on the above results the time dependence of the initial photoexcited population can be approximated using Equations 5.1 and 5.2.

$${}^{3}MLCT_{tpy-An} \xrightarrow{k_{EnT}} {}^{3}An \tag{5.1}$$

$${}^{3}MLCT_{(tpy-\phi-MV^{2}+)} \stackrel{k_{ET}}{\to} {}^{3}ET \stackrel{k_{BET}}{\to} GS$$

$$(5.2)$$

Here  ${}^{3}MLCT_{tpy-An}$  is the tpy-An localized MLCT,  ${}^{3}MLCT_{(tpy-\phi-MV^{2+})}$  is the tpy- $\phi$ -MV<sup>2+</sup>-localized MLCT,  ${}^{3}ET$  is the electron transfer species ([Ru<sup>III</sup>(tpy-An)(tpy- $\phi$ -MV<sup>-/+</sup>)]<sup>4+</sup>),  ${}^{3}An$  is the lowest energy anthracene triplet T<sub>1</sub>, and GS is the ground state. Ground state recovery from the anthracene T<sub>1</sub> has been omitted as this process is slow on the timescales investigated with the ultrafast spectrometer. The rate constant  $k_{EnT}$  was set to 1/0.5 ps,  $k_{ET}$  to 1/1.5 ps, and  $k_{BET}$  to 1/5.2 ps. The population in the  ${}^{3}MLCT_{tpy-An}$ ,  ${}^{3}MLCT_{(tpy-\phi-MV^{2+})}$  and GS t=0 were set to 0.33, 0.67, and -1.0 respectively. The initial population of the  ${}^{3}ET$  and  ${}^{3}An$  states was set to zero. The resulting population dynamics are shown in Figure 5.6. As can be seen, at times greater than approximately 30 ps only the T<sub>1</sub> excited state remains. This agrees with the lack of spectral evolution observed between 25 and 100 ps after excitation (see Figure 5.3).

 $<sup>^{\$}</sup>$  The percentage of excited states undergoing EnT is approximated as 0.10/0.27 = 0.37. The denominator is the maximum long time bleach intensity assuming all the MLCT population is quenched via EnT taken from the  $[Ru(tpy-An)(tpy)]^{2+}$ 



Figure 5.6: Population simulations using Equations 5.1 and 5.2 along with the timescales and initial conditions detailed in the text.

the AFC experiments, the magnitude of the transient signal measured at long times (i.e. greater than 30 ps) can be used as a measure of the photoexcited MLCT population undergoing EnT. A shaped pulses ability to increase *or* decrease such a signal would be a strong indication that the relative yield of EnT verses ET is being modulated.

#### 5.3.3 Nanosecond Pump-Probe Characterization

For completeness, the overall excited state decay of  $[Ru(tpy-An)(tpy-\phi-MV)]^{4+}$  was also characterized using nanosecond resolution pump-probe experiments. Representative single wavelength kinetics collected at 420 nm are shown in Figure 5.7. Fitting of kinetics collected at 420 and 650 nm to a single exponential model returned a tau of  $10 \pm 3$  ns.<sup>¶</sup> This is three orders of magnitude shorter than the 1000 ns lifetime observed in  $[Ru(tpy-An)(tpy)]^{2+}$  and suggests a new decay pathway(s) is accessible to the anthracene T<sub>1</sub> excited state. Given that the energy of the anthracene T<sub>1</sub> is 1.85 eV while that of ET product is estimated to be 1.58 eV, based on the 0.40 eV ET driving force reported Chapter 4 and the <sup>3</sup>MLCT energy of 1.98 eV,[18] it seems likely that new decay pathway involves <sup>3</sup>EnT  $\rightarrow$  <sup>3</sup>ET type reactivity. This type of

<sup>¶</sup> The small portion of the initial MLCT excited states quenched via EnT made collection of reliable kinetics at wavelengths with relatively weak absorbance untenable.



Figure 5.7: Nanosecond transient pump probe kinetics of  $[Ru(tpy-An)(tpy-\phi-MV)]^{4+}$  collected in degassed room temperature acetonitrile at  $\lambda_{probe} = 420$  nm. The pump beam was centered at 532 nm and found to have a temporal FWHM of  $\approx 3$  ns (superimposed on the plot in grey). The solid red line represents a single exponential fit to the data.

reactivity is not unprecedented, and similar order of magnitude  ${}^{3}EnT \rightarrow {}^{3}ET$  timescales have been observed in related Ru(II) polypyridyl complexes containing a naphthalenediimide acceptor.[18]

## 5.4 Concluding Remarks

The target dual energy and electron transfer reactive species,  $[Ru(tpy-An)(tpy-\phi-MV)]^{4+}$ , has been characterized using steady state absorption and time resolved pump-probe techniques. Strong agreement between the steady state absorption spectra of  $[Ru(tpy-An)(tpy-\phi-MV)]^{4+}$  and an average of the two dyad species,  $[Ru(tpy-An)(tpy)]^{2+}$  and  $[Ru(tpy-An)(tpy-\phi-MV)]^{4+}$ , respectively, suggests <sup>1</sup>MLCT  $\leftarrow$ <sup>1</sup>GS excitation in the latter involves creation of tpy-An localized and tpy- $\phi$ -MV<sup>2+</sup>-localized MLCT configurations which are minimally perturbed from those observed in the individual dyads. Accordingly, using the molar absorptivities of the EnT and ET dyads at the pump central excitation frequency (520 nm), we predicted the initially formed <sup>1</sup>MLCT ensemble in  $[Ru(tpy-An)(tpy-\phi-MV)]^{4+}$  to be about <sup>1</sup>/3 tpy-An localized and <sup>2</sup>/3 tpy- $\phi$ -MV<sup>2+</sup>-localized species. The time-resolved ultrafast pump-probe spectra and kinetics of  $[\text{Ru}(\text{tpy}-\text{An})(\text{tpy}-\phi-\text{MV})]^{4+}$  were also found to behave like a superposition of the dynamics observed in the EnT and ET dyad species. This lends further support to the interpretation that tpy-An and  $\text{tpy}-\phi-\text{MV}^{2+}$  MLCT excited states interact minimally. Using the magnitude of the transient bleach at 480 nm we estimated about 37% of the photoexcited MLCT population undergoes EnT quenching with the other 63% decaying via ET. These values are quite similar to the initial MLCT make-up predicted by the linear absorption analysis leading us to conclude that ILET dynamics, which could mix the two different MLCT populations, are negligible.  $[\text{Ru}(\text{tpy}-\text{An})(\text{tpy}-\phi-\text{MV})]^{4+}$  can, therefore be thought of as two independent, uncoupled chromophores. This has important implication for controlling the yield of EnT and ET products using weak-field AFC pulse shaping methodologies and will be discussed in the next chapter.

## Chapter 5 Bibliography

- (1) B. P. Sullivan, J. M. Calvert, and T. J. Meyer, *Inorganic Chemistry*, 1980, **19**, 1404–1407.
- (2) K. J. Takeuchi, M. S. Thompson, D. W. Pipes, and T. J. Meyer, *Inorganic Chemistry*, 1984, 23, 1845–1851.
- H. Hofmeier, E. Herdtweck, and U. S. Schubert, Zeitschrift Fur Anorganische Und Allgemeine Chemie, 2004, 630, 683–688.
- (4) M. Abdelhaq, Physical Chemistry, University of Colorado at Boulder, 2012.
- N. H. Damrauer, G. Cerullo, A. Yeh, T. R. Boussie, C. V. Shank, and J. K. McCusker, *Science*, 1997, 275, 54–57.
- (6) A. C. Bhasikuttan, M. Suzuki, S. Nakashima, and T. Okada, *Journal of the American Chemical Society*, 2002, **124**, 8398–8405.
- (7) A. Cannizzo, F. van Mourik, W. Gawelda, G. Zgrablic, C. Bressler, and M. Chergui, Angewandte Chemie-International Edition, 2006, 45, 3174–3176.
- (8) S. Yoon, P. Kukura, C. M. Stuart, and R. A. Mathies, *Molecular Physics*, 2006, 104, 1275–1282.
- (9) A. C. Albrecht, Journal of Molecular Spectroscopy, 1961, 6, 84.
- (10) H. S. Tan, I. R. Piletic, and M. D. Fayer, Journal Of The Optical Society Of America B-Optical Physics, 2005, 22, 2009–2017.
- (11) G. B. Shaw, D. J. Styers-Barnett, E. Z. Gannon, J. C. Granger, and J. M. Papanikolas, Journal of Physical Chemistry A, 2004, 108, 4998–5006.
- J. T. Hewitt, P. J. Vallett, and N. H. Damrauer, The Journal of Physical Chemistry A, 2012, 116, 11536–11547.
- (13) G. Porter and M. W. Windsor, Proceedings of the Royal Society of London Series A-Mathematical and Physical Sciences, 1958, 245, 238–258.
- (14) Y. H. Meyer, R. Astier, and J. Leclercq, The Journal of Chemical Physics, 1972, 56, 801.

- (15) D. N. Dempster, T. Morrow, and M. F. Quinn, Journal of Photochemistry, 1974, 2, 329–341.
- T. G. Pavlopoulos, Spectrochimica Acta Part A-Molecular and Biomolecular Spectroscopy, 1991, 47, 517–518.
- (17) R. Bonneau, I. Carmichael, and G. L. Hug, Pure and Applied Chemistry, 1991, 63, 290–299.
- (18) O. Johansson, M. Borgström, R. Lomoth, M. Palmblad, J. Bergquist, L. Hammarström, L. C. Sun, and B. Åkermark, *Inorganic Chemistry*, 2003, 42, 2908–2918.

# Chapter 6

Adaptive Feedback Control Pulse Shaping Experiments to Modulate The Yield of Electron Transfer and Energy Transfer in  $[Ru(tpy-An)(tpy-\phi-MV)]^{4+}$ 

## 6.1 Introductory Comments

Having developed a firm understanding of the photoinduced dynamics of the MLCT excited state in  $[Ru(tpy-An)(tpy-\phi-MV)]^{4+}$  we detail here the adaptive feedback control (AFC) pulse shaping experiments undertaken. By way of background, the first AFC experiments employing Ru(II) polypyridyls were those of Damrauer, Brixner, and Gerber where it was found that phase shaped laser pulses could be used to discriminate between two-photon excitation of  $[Ru(dpb)_3]^{2+}$  and organic laser dye DCM (where dpb = 4,4' $diphenyl-2,2`-\ bipyridine\ and\ DCM=4-dicyanomethylene-2-methyl-6-p-dimethylaminostyryl-\ 4H-pyran). [1]$ Work by Montgomery and Damrauer also employed Ru(II) polypyridyls, namely  $[Ru(dpb)_3]^{2+}$ , to develop statistical tools that allow for extraction of control mechanisms from AFC results. [2-5] Yartzev and coworkers have also undertaken AFC experiments using Ru(II) polypyridyls.[6] In their study, AFC pulse shaping was used to investigate the electron injection process in Ru(II) dye sensitized TiO<sub>2</sub>. The optimal pulse shape consisted of a series of sub-pulses with inter-pulse spacings that correlated with vibrational modes of the Ru(II) dye leading the authors to concluded these modes are coupled to the photoinduced electron injection process. To the best of this authors knowledge, no other AFC pulse shaping experiments involving Ru(II) polypyridyl complexes have been published. These types of systems, therefore, would seem to be ripe grounds for exploring the utility of AFC pulse shaping methodologies to elucidate information about photoinduced reactivity.

### 6.2 Experimental

#### 6.2.1 Ultrafast Spectrometer

The spectrometer used for the AFC experiments detailed in this chapter is different from the one used for the characterizations detailed in Chapters 2 through 6. This laser system employed for the AFC experiments been described in detail elsewhere, [7, 8] therefore, only a brief overview is given here. A 1 kHz pulse train centered at  $\sim 800$  nm (50 fs FHWM) is derived from a Quantronix Odin Ti:Sapphire multi-pass amplifier seeded by a K&M Ti:Sapphire oscillator. Of the 1 mJ, output approximately 200 µJ is directed to a homebuilt non-collinear optical parametric amplifier (NOPA)[9, 10] which is used to generate laser pulses with a central frequency between 515 - 550 nm. The resultant visible pulse train is compressed with a pair of fused silica prisms to a temporal width of 40 to 45 fs FWHM (as measured at the sample). After the prism compressor the pulse train then passes thought an optical pulse shaper (see subsection 6.2.2) and directed towards the sample. This beam, which acts as the "pump", is focused into the sample with a 125 mm achromatic lens (Thor Labs, AC254-125-A) resulting in spot diameter of  $\sim 100 \ \mu m$  as measured by transmission through a pinhole. Variable intensity neutral density filters are used to attenuate the pump pulse energy to less than or equal to 100 nJ/pulse as measured at the sample (~  $3.3 \cdot 10^{10} \frac{W}{cm^2}$ ). AFC pulse shaping is used to further compress the pulse resulting in a near bandwidth limited pulses at the sample. Intensity auto-correlation at the sample position before and after adaptive compression are given in Figure 6.1. Such a compression typically takes on the order of 20 minutes. A small portion of the 800 nm fundamental output of the amplifier is routed through a translation stage (Newport;  $\sim 1.5$  ns of travel, 3.3 fs/step) and then focused into a sapphire window (Thor Labs, WG30530) to generate a white light continuum. Directly after the sapphire plate a beam splitter is used to divide the white light continuum into two beam. One of these white light beams functions as the probe and is spatially overlapped with pump in the sample (2 mm cuvette). The other white light beam functions as a reference (for differential detection) and travels through an un-pumped portion of the sample. Focusing of the pump and two white light beams is accomplished using the achromatic lens detailed above. The pump and probe intra-beam angle is  $\sim$  7°. The pump beam polarization was rotated to the so-called magic angle  $(54.7^{\circ})$  using a half wave plate just



Figure 6.1: Representative intensity auto-correlation of the excitation pulse pre (red) and post (blue) compression. The intensity of the compressed and uncompressed pulses have been normalized to aide comparison. This data was collected by Paul Vallett.

before entering the sample. Cleaning of the pump beam polarization was found to be unnecessary due to the polarization selective nature of the pulse shaper. After exiting the sample, the probe and reference beams are coupled into an Acton 2300i monochromator and spectrally dispersed. The probe and reference beams were monitored using a differential detector (Newport, 2307) coupled to the spectrometer output. The difference signal between these two beams is sent to a Stanford Research SR250 boxcar integrator and then to Stanford Research SR810 lock-in amplifier synchronized with an optical chopper that is used to modulate the pump beam repetition rate (500 Hz). The data collection software was written in house (National Instruments, Labview 2010). Plotting and fitting of the data was accomplished using Igor Pro (6.02B).

#### 6.2.2 Pulse Shaper Details

This section is intended to give a brief overview of the pulse shaper used in our lab. For readers interested in a more detailed description a number of informative reviews have been published by Weiner.[11, 12] Briefly, a commercially available dual mask liquid crystal based spatial light modulator (CRi; SLM-648)\* is placed at the Fourier Plane of a home-built all reflective zero dispersion 4-f compressor with a folded

<sup>\*</sup> Readers interested in a more detailed description of the pulse shaper are directed to the CRi SLM user manual.

geometry (see Figure 6.2). The use of all reflective optics in the 4-f compressor-i.e. curved mirrors instead



Figure 6.2: Diagram of the pulse shaper used for the experiments detailed in this chapter. G1 and G2 are gratings. CM1 and CM2 are cylindrical mirrors. The SLM is placed at the Fourier plane to allow for the highest spectral resolution. The left side of the compressor (CM1 and G1) Fourier transform the pulse from the time to the frequency domain while the right side performs the inverse.

of lenses-is important for minimizing dispersions effects.[13] For the experiments detailed in this chapter the total bandwidth of the optical pulses used was about 20 - 25 nm and was spectrally dispersed over approximately 120 - 140 pixels. This resulting in a resolution of about 0.1 nm/pixel. The index of refraction of each pixel is independently controllable by application of a drive voltage ranging between 0 - 10 volts with 12-bit resolution. This voltage is converted to an applied phase using a home-built calibration procedure. For typical experiments the applied phase is allowed to vary from zero to two  $\pi$ .

#### 6.3 Results and Discussion

Before embarking on goal AFC pulse shaping experiments an experimental observable must be chosen as feedback to direct the optimization algorithm (See Figure 6.3). Considering our interests lie in trying to modulate the yield of EnT vs. ET a transient signal reflective of population in the <sup>3</sup>ET or the  $T_1$ excited states would be appropriate. An adaptively discovered pulses ability to increase (or decrease) such a signal this would be strong evidence that shaped laser excitation can increase (or decrease) the <sup>3</sup>ET or  $T_1$ yield. The absorption features of the <sup>3</sup>ET and  $T_1$ , however, overlap at all the probe colors accessible with the current ultrafast spectrometer layout. Therefore, it would seem a transient signal dependent only on



Figure 6.3: Cartoon representation of the optimization experiments undertaken in this chapter (reproduced from Chapter 1).

population in the <sup>3</sup>ET or the  $T_1$  excited states is not accessible. Fortunately, the fast ET/BET timescales relative to the long lived anthracene  $T_1$  results in a situation were absorptive signals present a times greater than 30 ps after excitation are likely to be due only to the anthracene  $T_1$  (See Figure 6.4).<sup>†</sup> As a result, the



Figure 6.4: Simulated population dynamics of  $[Ru(tpy-An)(tpy-\phi-MV)]^{4+}$  following MLCT photoexcitation. This a reproduction of a figure presented in Chapter 5.

<sup>&</sup>lt;sup>†</sup> Details of the timescales and model are provided in Chapter 5.
transient absorption intensities measured at time delays of greater than 30 ps after excitation were chosen as the feedback. For the first AFC experiments, the transient signal at 607, 620, or 650 nm measured 50 ps after excitation were used as feedback.<sup> $\ddagger$ </sup>

Moving to the AFC experiments, due to recent successes in our lab[7] the first AFC experiments undertaken were limited to pulses generated using the sinusoidal phase function shown in Equation 6.1.<sup>§</sup> Here  $\alpha$  controls the number and intensity of the pulses in the pulse train,  $\tau$  controls the inter-pulse temporal spacing, and  $\phi$  controls the inter-pulse temporal phase.

$$P(w_n) = \alpha \cdot [\cos(w_n \cdot \tau + \phi)] \tag{6.1}$$

An example of the pulse train generated using this type of pulse shaper parameterization are shown in Figure 6.5. We point out that the temporal duration of the sub-pulses in the train are identical to that of the input pulse. Also, the pulse trains generated using Equation 6.1 require phase-only shaping-i.e. does not involve attenuation of any frequency components-therefore, the fluence and spectrum of the shaped vs. unshaped pulse are identical (verified by power and spectrum measurements at the sample). This method of pulse train generation differs from that employed by our group for collection of 2-D electronic spectra. [15] In these initial pulse train AFC experiments  $\alpha$ ,  $\tau$ , and  $\phi$  were allowed to vary.<sup>¶</sup> AFC experiments trying to increase or decrease the transient signal intensity at long were undertaken, however, no difference in the transient signal size was observed. An example of the dynamics observed when exciting with a train of pulses is shown in Figure 6.6. Clearly evident in the early-time dyanimous is the multi-pulse character of the pulse train excitation with the temporal envelope increasing as the number of pulses in the train increases (i.e. as  $\alpha$ increase). We stress that the difference in early time dyanimum observed when exciting with a pulse train should not be construed as evidence of modulation of the ET/EnT yield. Simulations of the signal resulting from multi-pulse excitation are given in Appendix D and, suffice it to say, the deceased peak absorption as well as convergence of the shaped and unshaped pulse transient signal after about 6 ps are all expected features. In light of these results additional pulse train based AFC experiments were undertaken using the

 $<sup>\</sup>ddagger$  Redder probe wavelengths where chosen as a result of the differential detector used in the ultrafast spectrometer being less sensitive to bluer wavelengths (i.e. the 420 nm absorption feature).

 $<sup>\</sup>S$  Details of this phase function are available elsewhere [8, 14].

<sup>&</sup>lt;sup>¶</sup> Because non-ideal shaping effects (amplitude shaping) can result if the values of  $\alpha$  or  $\tau$  become too large these variables were constrained to be less than 3.1 and 1 ps, respectively.



Figure 6.5: Intensity auto-correlation of a single input pulse (grey, dashed) and the train generated from using phase only shaping. To highlight that the temporal duration of each pulse in the train is not significantly longer than that of the near bandwidth-limited input pulse the auto-correlation of the input pulse has also been super imposed on the pulse train pulses centered at  $\pm$  240 fs (light grey, dashed). This data was collected by Paul Vallett.



Figure 6.6: Magic angle transient absorption kinetics of  $[Ru(tpy-An)(tpy-\phi-MV)]^{4+}$  collected in room temperature acetonitrile at 650 nm when exciting with a bandwidth limited pulse (black) and three different pulse trains (red, green, and blue) generated using the sinusoidal phase function given in Equation 6.1. For the pulse trains the inter-pulse spacing  $(\tau)$  was kept constant at 500 fs while the amplitude  $(\alpha)$ , which controls the number of sub-pulses in the train, was varied. Inset: an expanded view of the early time dynamics.

transient absorptive signal measured at 400, 410, 420, 430, and 480 nm *as well as* time delays ranging from 2 to 50 ps after excitation. In all of these additional experiments no difference in the long time absorptive signal was observed for shaped vs. unshaped laser excitation.

The negative results of the above pulse train optimization experiments lead us to conduct more general AFC pulse shaping experiments. Analogous with the above experiments, only phase shaping of the excitation laser pulse was undertaken. To reduced the optimization search space and, accordingly, the algorithm search time[16] a number of these additional AFC experiments were conducted with the SLM parameterized via phase functions such as n-order polynomials, binned pixels,<sup> $\parallel$ </sup> and Chebyshev polynomials. Full parameter space optimizations, where the voltage applied to each pixel of the SLM is allowed to freely vary, were also conducted. No evidence that phase-only shaped laser pulses influence the amount of EnT or EnT was observed.

#### 6.4 Concluding Remarks

Manipulation of the EnT and ET reactivity of  $[Ru(tpy-An)(tpy-\phi-MV)]^{4+}$  following <sup>1</sup>MLCT excitation via phase-only adaptive feedback control pulse shaping methodologies proved unsuccessful. The null results of the experiments detailed in this chapter, however, do not lead to a concise interpretation. Considering the photoinduced dyanimes of  $[Ru(tpy-An)(tpy-\phi-MV)]^{4+}$  following excitation with an unshaped laser pulse (Chapter 5), we suspected the "one-photon" type control observed elsewhere [17–22] would not be observed. Such control requires bifurcation of the initially excited population between two or more states. Given the lack of interligand electron transfer (ILET) dyanimes in  $[Ru(tpy-An)(tpy-\phi-MV)]^{4+}$  the two initially created MLCT population (tpy-An and  $tpy-\phi-MV^{2+}$ -localized configurations, respectively) have only one decay pathway. The tpy-An localized MLCT undergoes quenching via energy transfer and the  $tpy-\phi-MV^{2+}$ -localized MLCT undergoes photoinduced ET. Furthermore, the results detailed in Chapters 2 thought 6, as well as this Chapter, show no evidence that vibrational coherences can be created with the excitation pulses employed. Therefore, manipulation of the EnT and ET yield via creation of such coherences[6, 15] would also seem to be out of reach. It may be the case that nuclear motions important to

<sup>&</sup>lt;sup>||</sup> This entails grouping adjacent pixels into "bins" with the voltage applied to each bin a control variable. The reduces the number of free parameters needed to be optimized for a given experiment.

EnT and ET reactivity in  $[Ru(tpy-An)(tpy-\phi-MV)]^{4+}$  are to high frequency to be impulsively excited. Moreover, such motions may not be strongly coupled to the MLCT excitation process. In conclusion, the implementation of phase-only AFC pulse shaping detailed here was not able to control the EnT and ET reactivity of the MLCT excited state in  $[Ru(tpy-An)(tpy-\phi-MV)]^{4+}$ .

In thinking ahead, preliminary work investigating the pump color dependence of the EnT and ET yield in  $[Ru(tpy-An)(tpy-\phi-MV)]^{4+}$  do show some interesting results. Kinetics collected at 607 nm resulting from excitation with two different pulses (see Figure 6.7) are given in Figure 6.8. As is evident, the long



Figure 6.7: Spectra of the two different excitation pulses used for the pump color dependence study presented below.

time absorptive signal, thought to be indicative of the EnT yield, is larger for the 510 nm excitation pulse as compared to the 530 nm excitation pulse. What is surprising about this observation is based on the ground state absorption spectrum of the EnT and ET dyads  $([Ru(tpy-An)(tpy)]^{2+}$  and  $[Ru(tpy)(tpy-\phi-MV)]^{4+}$ , respectively) one would expect a *decrease* in the relative EnT yield when exciting at 510 nm as compared to 530 nm. The ratio of  $[Ru(tpy)(tpy-\phi-MV)]^{4+}$  ground state absorption to that of  $[Ru(tpy-An)(tpy)]^{2+}$  is 1.81 at 530 nm and 2.00 at 510 nm. AFC pulse shaping experiments employing both phase *and* amplitude shaping[17, 18] may prove useful in trying to untangling this anomalous pump color dependence.



Figure 6.8: Normalized magic angle transient kinetics of  $[Ru(tpy-An)(tpy-\phi-MV)]^{4+}$  collected at  $\lambda_{probe} = 607$  nm in room temperature acetonitrile with excitation pulses centered at 510 nm (blue) and 530 nm (red). As is clear, the intensity of the long time absorption relative to that of peak absorption is much larger for the 510 nm excitation pulse. This would suggest a relative increase in the yield of EnT product for the bluer excitation pulse.

## Chapter 6 Bibliography

- (1) T. Brixner, N. H. Damrauer, P. Niklaus, and G. Gerber, *Nature*, 2001, 414, 57–60.
- M. A. Montgomery, R. R. Meglen, and N. H. Damrauer, Journal of Physical Chemistry A, 2006, 110, 6391–6394.
- (3) M. A. Montgomery, R. R. Meglen, and N. H. Damrauer, Journal of Physical Chemistry A, 2007, 111, 5126–5129.
- (4) M. A. Montgomery and N. H. Damrauer, New Journal of Physics, 2009, 11, 105053.
- (5) M. A. Montgomery, E. M. Grumstrup, and N. H. Damrauer, Journal Of The Optical Society Of America B-Optical Physics, 2010, 27, 2518–2533.
- (6) B. Brüggemann, J. Organero, T. Pascher, T. Pullerits, and A. Yartsev, *Physical Review Letters*, 2006, 97, 208301.
- (7) E. M. Grumstrup, J. C. Johnson, and N. H. Damrauer, *Physical Review Letters*, 2010, 105, 257403.

- (8) E. Grumstrup, Ph.D. Thesis, University of Colorado at Boulder, 2011.
- (9) A. Shirakawa and T. Kobayashi, Applied Physics Letters, 1998, 72, 147.
- (10) T. Wilhelm, J. Piel, and E. Riedle, *Optics Letters*, 1997, 22, 1494–1496.
- (11) A. M. Weiner, Review of Scientific Instrumentation, 2000, 71, 1929–1960.
- (12) A. M. Weiner, Optical Communications, 2011, 284, 3669–3692.
- (13) D. H. Reitze, A. M. Weiner, and D. E. Leaird, Applied Physics Letters, 1992, 61, 1260.
- (14) J. L. Herek, W. Wohlleben, R. J. Cogdell, D. Zeidler, and M. Motzkus, Nature, 2002, 417, 533–535.
- (15) E. M. Grumstrup, S.-H. Shim, M. A. Montgomery, N. H. Damrauer, and M. T. Zanni, *Optics Express*, 2007, **15**, 16681–16689.
- (16) J. Savolainen, R. Fanciulli, N. Dijkhuizen, A. L. Moore, J. Hauer, T. Buckup, M. Motzkus, and J. L. Herek, Proceedings of the National Academy of Sciences of the United States of America, 2008, 105, 7641–7646.
- (17) V. I. Prokhorenko, A. M. Nagy, S. A. Waschuk, L. S. Brown, R. R. Birge, and R. J. D. Miller, *Science*, 2006, **313**, 1257–1261.
- (18) V. I. Prokhorenko, A. M. Nagy, L. S. Brown, and R. J. Dwayne Miller, *Chemical Physics*, 2007, 341, 296–309.
- (19) P. van der Walle, M. T. W. Milder, L. Kuipers, and J. L. Herek, Proceedings of the National Academy of Sciences of the United States of America, 2009, 106, 7714–7717.
- (20) M. Spanner, C. A. Arango, and P. Brumer, The Journal of Chemical Physics, 2010, 133, 151101.
- (21) G. Katz, M. A. Ratner, and R. Kosloff, New Journal of Physics, 2010, 12, 015003.
- (22) C. A. Arango and P. Brumer, The Journal of Chemical Physics, 2013, 138, 071104.

# Chapter 7

## Addendum: Photophysics Of The Aqua-Coordinated Ru(II) Species $[Ru(bpy)(tpy)(OH_2)]^{2+}$ in $H_2O$ and $D_2O$ .

In addition to the work detailed in Chapters 1-5, a good portion of my time in graduate school was spent characterizing the MLCT excited state of the aqua coordinated  $\operatorname{Ru}(\operatorname{II})$  species  $[\operatorname{Ru}(\operatorname{bpy})(\operatorname{tpy})(\operatorname{OH}_2)]^{2+}$  in room temperature H<sub>2</sub>O and D<sub>2</sub>O. Because this work is not directly related to AFC pulse shaping experiments it was not originally intended to be included in this thesis. The results of these experiments where, however, found to illustrate in a clear way how solute-solvent interactions can influence reactivity of the MLCT excited state in Ru(II) polypyridyls. As this is one of the fundamental questions posited in this thesis the results have been included here in the form of an addendum.

## 7.1 Introduction

Sustainable conversion of solar photons to chemical fuels demands molecules and materials able to negotiate light absorption, charge-separation, energy storage, as well as the multi-electron/proton redox chemistry associated with oxidation/reduction of  $H_2O$  to  $H_{2(g)}$  and  $O_{2(g)}$ . It is likely that multi-component assemblies will be required to accomplish such complex chemistry. At this stage it is critical that species with promising reactivity/functionality be characterized under ambient conditions to assess their potential role in energy conversion processes and to guide future structural and synthetic modifications. Mononuclear Ru(II) polypyridyl complexes with one or more aqua ligands have been scrutinized as electrochemical water oxidation catalysts with [Ru(bpy)(tpy)(OH<sub>2</sub>)]<sup>2+</sup> (where, tpy = 2,2',2''-terpyridine and bpy = 2,2'-bipyridine, see Figure 7.1) and derivatives thereof receiving much attention.[1–9] In the Ru(II) oxidations

state this complex is highly colored with the visible region absorption dominated by metal-to-ligand charge transfer (MLCT). One can imagine participation of this photoexcited state, by design or as spectators, in the process of light harvesting coupled to multi-electron proton/electron redox chemistry. We, therefore, have been interested in assessing whether these photophysics can be exploited or should be avoided due to deleterious photochemistry or the rapid loss of excited state energy. Surprisingly little is known about the MLCT photo-reactivity of Ru(II) metal-aquo species in solution and the data reported herein are the first measurements of the excited-state lifetime of  $[Ru(bpy)(tpy)(OH_2)]^{2+}$  in H<sub>2</sub>O (1) and its isotopolouge  $[Ru(bpy)(tpy)(OD_2)]^{2+}$  in D<sub>2</sub>O (2).

## 7.2 Experimental

#### 7.2.1 General

All photophysical measurements were made using HPLC grade  $H_2O$  (Fischer Scientific) or 99.9%  $D_2O$  (Cambridge Isotopes Laboratories Inc). Steady state electronic absorption spectra were recorded on a Hewlett-Packard HP8452A diode array UV-Vis spectrometer. All transient measurements were made at 294 K (the temperature of our laser lab). [Ru(bpy)(tpy)(OH\_2)](OTf)\_2, where OTf = trifluoromethanesulfonate, was a gift from TJ Meyer and used without further purification. Conversion of [Ru(bpy)(tpy)(OH\_2)]<sup>2+</sup> to [Ru(bpy)(tpy)(OD\_2)]<sup>2+</sup> was accomplished by bringing up solid [Ru(bpy)(tpy)(OD\_2)](OTf)\_2, in D\_2O. Complete substitution of the OH<sub>2</sub> ligand for OD<sub>2</sub> was verified by <sup>1</sup>H-NMR (See Appendix F). The <sup>1</sup>H-NMR were collected using a 500 MHz Varian spectrometer with duterated solvents purchased from Cambridge Isotope labs Inc. and used as received.

#### 7.2.2 Transient pump-probe spectra and kinetics

The ultrafast transient pump-probe spectra and kinetics were collected using the spectrometer detailed in Chapter 2. The sample absorbance at the pump laser central frequency was adjusted to approximately 0.6. A small magnetic stir bar was used to circulate the sample in the cell and comparison of steady-state absorption before and after exposure to the laser indicated no degradation. Analyte concentrations and pump powers were adjusted to maintain an excitation probability of less than 1 molecule in 100 per pump



Figure 7.1: Steady state absorption spectrum of  $[Ru(bpy)(tpy)(OH_2)]^{2+}$  (blue) and  $[Ru(bpy)(tpy)(OD_2)]^{2+}$  (green) collected in neat H<sub>2</sub>O and D<sub>2</sub>O, respectively.

pulse.

## 7.3 Results and Discussion

#### 7.3.1 Ground State Absorption Properties

As stated in the introduction, the visible absorption spectrum of (1) is dominated by an intense absorption feature ( $\lambda_{max} = 480 \text{ nm}$ ;  $\varepsilon_{480 \text{ nm}} = 9600 \text{ M}^{-1}\text{cm}^{-1}$ ), Figure 7.1, which is singlet metal-to-ligand charge transfer (<sup>1</sup>MLCT) in nature and will serve as the access point for our investigation of the charge transfer excited-state photophysics in this complex.[1, 10] We note that the visible absorption spectrum of (1) and (2) are essentially identical suggesting substitution of OH<sub>2</sub> for OD<sub>2</sub> in both the coordination and solvation sphere has negligible effect on the <sup>1</sup>MLCT  $\leftarrow$  <sup>1</sup>GS photoexcitation process (Figure 7.1). The heteroleptic ligand environment of (1) (and (2)) allows for excitation of two distinct <sup>1</sup>MLCT states. The photoexcited electron could be promoted to either the tpy or the bpy ligand.<sup>\*</sup> Raman studies in related Ru(II) polypyridyl complexes[16] have found photoexcitation on the low energy side of the <sup>1</sup>MLCT feature

<sup>\*</sup> As has been detailed in previous chapters, the results of Stark spectroscopy,[11] resonance Raman,[12] solvent dependent experiments[13] and time resolved experiments[14, 15] indicate the <sup>1</sup>MLCT  $\leftarrow$  <sup>1</sup>GS photoexcitation process involves ligand-localized states meaning the excited electron is localized on a single ligand and not delocalized over many/all of the ligands.



Figure 7.2: Chirp corrected magic angle transient absorptions spectrum of  $[Ru(bpy)(tpy)(OH_2)]^{2+}$  collected in room temperature H<sub>2</sub>O. Data points were collected every 5 nm and are represented by the filled circles. The portion of the spectrum contained between the dashed line has been omitted due to contamination by pump scatter. Arrows (black) have been included to highlight the absorptive feature change between the two time points. The <sup>1</sup>MLCT  $\leftarrow$  <sup>1</sup>GS absorption spectrum has been super-imposed for reference (light blue, right axis).

preferential promotes electrons to the ligand with the lowest energy  $\pi^*$  system. Based on electrochemical<sup>†</sup> and computational results,[10] photoexcitation of  $[Ru(bpy)(tpy)(OH_2)]^{2+}$  (or  $[Ru(bpy)(tpy)(OD_2)]^{2+}$ ) on the red edge of the <sup>1</sup>MLCT feature should, therefore, result in preferential excitation of the tpy-localized MLCT configuration. As a result, the transient pump-probe kinetics detailed later in this chapter employ reddetuned excitation pulses as a means of minimizing possible inter-ligand electron transfer (ILET) dyanimcs in the data.

#### 7.3.2 Ultrafast Pump-Probe Spectroscopy

Our characterization of the MLCT excited state of (1) and (2) has relied exclusively on ultrafast time resolved pump-probe spectra and kinetics. Emission spectra of  $[Ru(bpy)(tpy)(OH_2)]^{2+}$  in a variety of room temperature solvents has been reported by Jakubikova and co-workers[10], however, we were unable to collect high fidelity emission data with the emission spectrometer in our lab. Beginning with (1), we

<sup>&</sup>lt;sup>†</sup> The reduction potential of tpy in  $[Ru(tpy)_2]^{2+}$  is -1.31 V vs. SCE (see Chapter 2) while bpy reduction in  $[Ru(bpy)_3]^{2+}$  is -1.38 V vs. SCE.[17]

first assign the features present in the chirp corrected magic angle transient spectra collected at 2 and 100 ps after excitation (Figure 7.2). The absorbance feature peaked near 390 nm is assigned to reduced ligand absorbance, and is indicative of the MLCT excited state. [18-20] The spectral width of this feature and its peak absorption wavelength correlate quite well with that of  $[Ru(tpy)_2]^{2+}$  (see Chapter 2), suggesting that 2 ps after photoexcitation the tpy-localized MLCT configuration  $([Ru^{III}(bpy)(tpy^{-})(OH_2)]^{2+})$  is dominant. The bpy-localized MLCT excited state is expected to have an absorption profile similar to that of the MLCT excited state of  $[Ru(bpy)_3]^{2+}$ , which is spectrally more narrow and peaks closer to 370 nm. [15, 19, 21] For reference the transient spectrum of  $[Ru(bpy)_3]^{2+}$  collected 10 ps after <sup>1</sup>MLCT photoexcitation is provided in Appendix F. That the tpy-localized species is dominant agrees with electrochemical<sup> $\ddagger$ </sup> and theoretical work<sup>[10]</sup> suggesting the tpy-localized configuration is the lowest energy MLCT species. The minimal evolution of the reduced ligand feature from 2 to 100 ps also suggest any ILET dyanimes are complete by 2 ps after excitation. Moving beyond the reduced ligand feature, the bleach centered near 480 nm is attributed to loss of  $^{1}MLCT \leftarrow$ <sup>1</sup>GS absorption; promotion of an electron from a Ru(III) to one of the ligands is significantly more energetic. The weak, featureless absorption from 565 to 650 nm is assigned to ligand-to-metal charge transfer (LMCT) absorption(s) which involve promotion of an electron from the filled  $\pi$  orbitals of the ligands to the vacancy in the ruthenium  $d\pi$  orbitals. [19, 20, 22]

Triplicate sets of single wavelength kinetics collected at 400, 470 and 650 nm were used to track, in detail, the temporal evolution of the <sup>3</sup>MLCT of (1). Representative data are shown in Figure 7.3. In contrast to the spectral data discussed above, the kinetics were collected using excitation pulses centered at 520 nm. Further detuning of the excitation pulse was undertaken to minimizes the likelihood of charge transfer to the bpy ligand (and possible ILET dyanimcs, vide supra) as well as the amplitude of vibrational cooling dynamics in the transient data.[23] Global fitting of the triplicate sets of data returned a dominant decay of  $270 \pm 18$  ps present at all probe wavelengths (Table 7.1). The data collected at 470, and to a lesser degree 650 nm, was found to contain an additional  $2 \pm 1$  ps component at early times.

To gain insight into the spectral behavior of the weak 2 ps dynamic additional chirp corrected spectra were collected probing the blue side of the spectral window (Figure 7.4). In agreement with the single

<sup>&</sup>lt;sup>‡</sup> The reduction potential of tpy in  $[Ru(tpy)_2]^{2+}$  is -1.31 V vs. SCE (see Chapter 2) while bpy reduction in  $[Ru(bpy)_3]^{2+}$  is -1.38 V vs. SCE.[17]



Figure 7.3: Magic angle transient kinetics of  $[\text{Ru}(\text{bpy})(\text{tpy})(\text{OH}_2)]^{2+}$  in room temperature H<sub>2</sub>O collected at  $\lambda_{\text{probe}} = 400 \text{ nm} (top), \lambda_{\text{probe}} = 470 \text{ nm} (middle)$ , and  $\lambda_{\text{probe}} = 650 \text{ nm} (bottom)$ . The solid red line represent global fits to the data. A common decay component of  $270 \pm 18$  ps was found at each probe wavelength with a weak early time dynamic of  $2 \pm 1$  ps present at 470 and 650 nm.



Table 7.1: Global fitting results for  $[Ru(bpy)(tpy)(OH_2)]^{2+}$  kinetics collected in room temperature  $H_2O$ 

Figure 7.4: Early time chirp corrected magic angle transient spectra of  $[Ru(bpy)(tpy)(OH_2)]^{2+}$  collected in room temperature H<sub>2</sub>O. Data points were collected every 5 nm and are represented by the filled circles.

wavelength kinetics, these spectra show a slight decrease in absorptive intensity as time after excitation increases from 0.5 and 2 ps. We note that the observed increase in bleach intensity can only occur if the total signal interrogated includes absorptive components (i.e., is not exclusively bleach in nature) and that these components decrease in intensity as the system evolves. Stated differently, the increase in bleach intensity between 420 and 480 nm indicates that absorptive features are underlying the <sup>1</sup>MLCT  $\leftarrow$  <sup>1</sup>GS bleach at these wavelengths.

A similar suite of ultrafast pump-probe experiments were performed on the isotopologue (2). We remind the reader that the steady state absorption spectrum of both (1) and (2), Figure 7.1, are essentially identical suggesting isotopic substitution in both the coordination and solvent environment does not significantly perturb the <sup>1</sup>MLCT  $\leftarrow$  <sup>1</sup>GS excitation process. We note here that the liable nature of the OH<sub>2</sub> and



Figure 7.5: Scaled and overlaid chirp corrected magic angle transient spectra of  $[Ru(bpy)(tpy)(OH_2)]^{2+}$  in room temperature  $H_2O$  (blue) and  $[Ru(bpy)(tpy)(OD_2)]^{2+}$  in room temperature  $D_2O$  (green) collected 100 ps after excitation. Data points were collected every 5 nm and are represented by the filled circles. The portion of the spectrum contained between the dashed line has been omitted due to contamination by pump scatter

 $OD_2$  ligands precluded conducting experiments with a heterogeneous protected/deuterated ligand and solvent environment. Studies involving other weakly coordinating solvent such as DMSO, acetone,[24–26] and  $CH_2Cl_2$  were also avoided. Dissolving  $[Ru(bpy)(tpy)(OH_2)]^{2+}$  in DMSO resulted in complete substitution of the bound  $OH_2$  with a DMSO molecule (see Appendix F). <sup>1</sup>H-NMR studies with d-acetone and  $CD_2Cl_2$  showed evidence of mixed solvent and  $D_2O$  coordinated species.

The magic angle chirp corrected transient spectrum of (2) collected 100 ps after excitation, Figure 7.5, overlays nicely with that of the (1) verifying the same electronic excited state is populate in both, namely the <sup>3</sup>MLCT. Again, the shape and peak absorption of the reduced ligand feature in the near-UV indicates the tpy-localized <sup>3</sup>MLCT species is dominant (vide supra). Early time spectra of (2) were also collected and agrees with those of (1) (see Appendix F). Details of the temporal evolution of the <sup>3</sup>MLCT in (2) were monitored via single wavelengths kinetics collected at 400, 470, and 650 nm. Representative data are shown in Figure 7.6. These data were collected with pump pulses centered at 520 nm thereby duplicating the experimental set up used to collect kinetics for (1). Global fitting of the triplicate sets of the single



Figure 7.6: Magic angle transient kinetics of  $[Ru(bpy)(tpy)(OD_2)]^{2+}$  in room temperature  $D_2O$  collected at  $\lambda_{probe} = 400 \text{ nm} (top), \lambda_{probe} = 470 \text{ nm} (middle), \text{ and } \lambda_{probe} = 650 \text{ nm} (bottom)$ . The solid black line represent global fits to the data. A common decay component of  $220 \pm 12$  ps was found at each probe wavelength with a weak early time dynamic of  $1.4 \pm 0.5$  ps present at 470 and 650 nm.

Wavelength/nm	Tau Values/ps (± $2\sigma)$	Average pre-exponential values (± $2\sigma)$
400	$ au_1 = 220 \; (12)$	$A_1 = 1.00 \ (0.02)$
470	$ au_1 = 220 \ (12), \  au_2 = 1.4 \ (0.5)$	$A_1 = -1.00 \ (0.02), \ A_2 = 0.06 \ (0.02)$
650	$\tau_1{=}\ 220\ (12),\ \tau_2{=}\ 1.4\ (0.5)$	$A_1 = 0.99 \ (0.06), A_2 = -0.03 \ (0.04)$

Table 7.2: Global fitting results for  $[Ru(bpy)(tpy)(OD_2)]^{2+}$  kinetics collected in room temperature  $D_2O$ 

wavelength data returned a decay of  $220 \pm 12$  ps present at all the probe wavelengths. Similar to (1) the data collected at 470 and 650 nm was also found to contain an additional weak, early time dynamic of 1.4  $\pm$  0.5 ps (Table 7.2).

A discussion of the early time decay component in both species will follow later and we begin first with assignment of the longer ground state recovery. Considering (1), the dominant 270 ps decay timescale is comparable to the 250 ps MLCT lifetime of  $[\text{Ru}(\text{tpy})_2]^{2+}$  in H<sub>2</sub>O reported by Weaver.[27] This is not surprising given the similarity of the MLCT excited states, both have a reduced tpy ligand proximal to a Ru(III) metal center. The energetics of the MLCT state in both are also similar with (1) and  $[\text{Ru}(\text{tpy})_2]^{2+}$  having nearly identical peak emission wavelengths in room temperature water.[10] As is the case in  $[\text{Ru}(\text{tpy})_2]^{2+}$ , the hindered bite angle of the tpy ligand[28, 29] is expected to weaken the ligand field in (1) and (2) causing the <sup>3</sup>MLCT and <sup>3</sup>MC states to becoming energetically proximal.[10] Therefore, drawing on the work detailed in Chapter 2, we have assumed the simplified excited state decay shown in Equation 7.1 for both (1) and (2) with  $(k_1 + k_2) >> k_2$ . The excited state population is assumed to be equilibrated between the <sup>3</sup>MLCT and <sup>3</sup>MC states with ground state recovery rate limited by thermal activation from the <sup>3</sup>MC to the <sup>1</sup>GS. The observed rate of ground state recovery is a product of the <sup>3</sup>MLCT-<sup>3</sup>MC equilibrium constant and the <sup>3</sup>MC  $\rightarrow$  <sup>1</sup>GS intersystem crossing rate such that  $k_{obs} = \frac{k_1}{k_{-1}} \cdot k_2 = K_{EQ} \cdot k_2$ .

$${}^{3}MLCT \underset{k_{-1}}{\overset{k_{1}}{\rightleftharpoons}} {}^{3}MC \xrightarrow{k_{2}} {}^{1}GS \tag{7.1}$$

Comparing the lifetime of (1) and (2), it is striking that an *inverse* kinetic isotope effect (*i*-KIE) is observed with  $k_{H_2O}/k_{D_2O} = 0.81$ . To highlight this fact the single wavelength transient kinetics of (1) and (2) collected at 470 nm have been overlaid in Figure 7.7. This is especially surprising given that normal isotope



Figure 7.7: Single wavelength kinetics of  $[Ru(bpy)(tpy)(OH_2)]^{2+}$  collected in room temperature  $H_2O$  (blue) and  $[Ru(bpy)(tpy)(OD_2)]^{2+}$  in room temperature  $D_2O$  (green) at 470 nm. The global fits to the data are shown as the solid red and black line.

effects—i.e. longer lifetime in D<sub>2</sub>O versus H<sub>2</sub>O—have been reported<sup>§</sup> for a number of different Ru(II) and Os(II) polypyridyl complexes.[30–34] Elongation of the MLCT lifetime in these systems has been ascribed to quantum mechanical effects where overtones of high-frequency solvent O-H or O-D vibrational modes act as energy transfer acceptors with a higher overtone needed for D<sub>2</sub>O.[33, 35] The lions share of these studies, however, have focused on  $[M(bpy)_3]^{2+}$ -like tris-bidentate complexes. In these types of complexes the <sup>3</sup>MC is much higher in energy than the <sup>3</sup>MLCT[36, 37], therefore, it is conceivable the low energy nature of the <sup>3</sup>MC in (1) and (2) could be leading to the *i*-KIE. Presumably, such a mechanism would rely on differences in the <sup>3</sup>MC-solvent coupling for H<sub>2</sub>O versus D<sub>2</sub>O. To test this hypothesis single wavelength kinetics of  $[Ru(tpy)_2]^{2+}$  with both H<sub>2</sub>O and D<sub>2</sub>O as the solvent were collected. This study was not exhaustive and we report only bleach recovery dyanimes, nonetheless, fitting revealed ground state recovery takes slightly longer in D<sub>2</sub>O as compared to H<sub>2</sub>O ( $\tau_{obs H_2O} = 232 \pm 4$  ps,  $\tau_{obs D_2O} = 254 \pm 5$  ps; See Appendix F) yielding a normal KIE of 1.09. The KIE observed in  $[Ru(tpy)_2]^{2+}$  is weaker than those reported for tris-bidentate complexes ( $\approx 1.2$  to 1.8)[30, 33] and is presumably a result of the higher rate of non-radiative decay in the former, which

 $<sup>\</sup>frac{1}{8}$  To best of this authors knowledge no reports of *i*-KIE exist in the literature for Ru(II), Fe(II), or Os(II) polypyridyl complexes.

competes more effectively with resonance energy transfer to the solvent overtones. Therefore, explaining the i-KIE observed here via arguments involving solvent dependent differences in electronic coupling between the <sup>3</sup>MC and <sup>1</sup>GS state seems unlikely.¶

Another possible explanation would build on recent work by Hammes-Schiffer and co-works, which has shown that a weak *i*-KIE can manifest in proton-coupled electron transfer (PCET) reactions when there is a large free energy difference between the reactant and product.[39] In the context of (1) and (2), a direct <sup>3</sup>MLCT  $\rightarrow$  <sup>1</sup>GS mechanism could be expected to have significant PCET character due to the increased proton-donor quality (vide infra) of the coordinated water when coordinated to a Ru(III)–i.e. the <sup>3</sup>MLCT– vs. the Ru(II) oxidation state of the GS. However, given that <sup>3</sup>MC  $\rightarrow$  <sup>1</sup>GS intersystem crossing is the rate limiting step, with the oxidation state of the ruthenium metal center being Ru(II) for both the <sup>3</sup>MC and the <sup>1</sup>GS, the PCET nature of the ground state recovery is expected to be minimal making such an explanation of the *i*-KIE unlikely.

In the context of Equation 7.1, an *i*-KIE would result if a greater portion of the excited state population in (2) was shifted towards the <sup>3</sup>MC relative to (1)—i.e if  $K_{EQ_{D_2O}} > K_{EQ_{H_2O}}$ . Such shifting as a result of electrostatic (Born) effects can be ruled out given that the dielectric constants of H<sub>2</sub>O and D<sub>2</sub>O are nearly identical as well as the coefficients that determine their temperature dependence.[40] On the other hand, appropriate shifting of  $K_{EQ}$  can be predicted from the work of Weaver and coworker[27] which show that the redox couples of transition metals are sensitive to isotopic substitution of the solvent. Briefly, metal complexes containing aquo ligands were found to undergo a large positive shift in the n/n+1 redox couple upon moving from H<sub>2</sub>O to D<sub>2</sub>O. For example, the  $E_{\frac{1}{2}}$  for  $[Fe(OH_2)_6]^{3+/2+}$  shifts from 495 mV (vs. SCE) to 538 mV for  $[Fe(OD_2)_6]^{3+/2+}$ . In terms of the 1-electron half reactions this means that the oxidized form of the complex is relatively more stable in H<sub>2</sub>O compared to D<sub>2</sub>O. These effects are born out in a number of electron transfer cross reactions such as that between  $[Co(NH_3)_6]^{2+}$  and  $Cr_{(aq)}^{2+}$  where the equilibrium constant in H<sub>2</sub>O and D<sub>2</sub>O differ by a factor of 10, with reaction proceeding further in H<sub>2</sub>O. We note that if the coordination sphere of the metal is saturated with ligands that do not engage in hydrogen bonding with the solvent these couples are largely invariant to solvent isotopic substitution.[27]

<sup>&</sup>lt;sup>¶</sup> Such an argument would, presumably, take advantages of the know differences in the spectral density of  $H_2O$  and  $D_2O$  for higher-frequency librational and/or stretching motions.[38]

Analogous to Wavers work, or observation are also dependent on the presence of a ligand that engages in hydrogen bonding with the solvent (the aqua ligand) as a normal KIE was observed in  $[Ru(tpy)_2]^{2+}$ . Although there is no formal electron transfer reaction in Equation 7.1 the ruthenium metal center does undergo an oxidation state change from Ru(III) to Ru(II) upon moving from the <sup>3</sup>MLCT to the <sup>3</sup>MC. Therefore, in (2) compared to (1) the <sup>3</sup>MC would be favored relative to the <sup>3</sup>MLCT causing  $K_{EQ_{D_2Q}} >$  $K_{EQ_{H_2O}}$  and, accordingly  $k_{obs_{D_2O}} > k_{obs_{D_2O}}$  (recalling  $k_{obs} = K_{EQ} \cdot k_2$ ). The physical origin of this effect can be understood in the following way. As the formal oxidation state of the ruthenium center shifts from Ru(II) (<sup>3</sup>MC) to Ru(III) (<sup>3</sup>MLCT) the vibrational frequency of the bound  $H_2O$  (or  $D_2O$ ) will decrease due to increased electron donation to the metal center. [41] This results in a decrease in the zero-point energy difference between the H<sub>2</sub>O and D<sub>2</sub>O bond species in the <sup>3</sup>MLCT relative to the <sup>3</sup>MC. In enthalpic terms then the  ${}^{3}MC$  is lower in energy in (2) then in (1) shifting, relatively speaking, population towards the  ${}^{3}MC$ in (2). Entropic contributions are also expected to have a similar effect, namely shifting population towards the <sup>3</sup>MC in (2) relative to (1). Work by Hupp and Weaver [42] has shown that increasing the oxidation state of a transition metal complex in solution decreases the entropy of the solution with the effect being larger in  $D_2O$  than  $H_2O$ . This is attributed to increased hydrogen (deuteron) donation in the oxidized form which induces increased ordering of the solvent shell. That the effect is larger in  $D_2O$  than  $H_2O$  is thought to be a result of the formers more extensive hydrogen bonding.[43] Therefore, both enthalpic and entropic contributions are expected to push a larger fraction of the excited state population in (2) into the <sup>3</sup>MC relative to (1), thereby resulting in the observed *i*-KIE.

We return now to a discussion of the early time (sim 2 ps) dynamic observed at 470 and 650 nm. At the outset we have ruled out vibrational cooling[23] and interligand ET[20] (bpy<sup>--</sup>  $\longrightarrow$  tpy) within the MLCT manifold as possible sources because both processes would be expected to manifest as an increase in absorption near 400 nm, which does not agree with our experimental observations. A scenario that is consistent with the observed dyanimcs is solvent induced shifting of the LMCT transitions in response to the increased proton (deuteron) donation of the <sup>3</sup>MLCT discussed above. Berlinguette and co-workers[44] as well as Sakai and co-workers[45] have measured the absorption spectrum of the one electron oxidized species [Ru(bpy)(tpy)(OH<sub>2</sub>)]<sup>3+</sup> and observe two spectral features in our probe window. The first is a weak and broad absorption feature centered near 700 nm that is attributable to LMCT from the filled  $\pi$  orbitals of the terpyridine ligand.[20] The second feature is relatively stronger with a tail extending from the UV to

the terpyridine ligand.<sup>[20]</sup> The second feature is relatively stronger with a tail extending from the UV to approximately 480 nm and is assigned to LMCT from the bpy  $\pi$  orbitals.[45] These transitions are expected to be quite sensitive to the ligand field strength as they involve promotion of an electron to metal center  $d\pi$  orbitals. Therefore, as the solvent responds to the increased proton donating nature of the ligated H<sub>2</sub>O (or  $D_2O$ ) hydroxyl character will develop in the coordination sphere decreasing the ligand field splitting,  $OH^{-}$  is a weaker field ligand than  $H_2O$ , causing the energy difference between the ligand  $\pi$  orbitals and the metal center  $d\pi$  orbitals to increase and, accordingly, the LMCT transitions to blue shift. Consistent with this we observe an increase in absorption at 650 nm, ascribed to blue shifting of the 700 nm absorbance feature, and a decrease in absorption-i.e. an increase in the bleach intensity-near 480 nm attributed to blue shifting of the bpy LMCTs. This is highlighted in the early time spectra shown in Figure 7.4. We note the 2 ps timescale we observe agrees with the reorientational timescale of  $H_2O$  at room temperature[46–51], and would seem to support this assignment. Along these lines, one might expect to also observe an increase in absorption near 400 nm due to the aforementioned blue shifting of the bpy LMCT. Such dyanimes, however, are not observed. We suspect this is a result of the reduced ligand IL absorption decreasing at these colors upon equilibration of the excited state population between the <sup>3</sup>MLCT-<sup>3</sup>MC [20] (see Chapter 2). Thus, it would seem that counterbalancing spectral shifts resulting from proton (deuteron) motion of the coordinated  $H_2O(D_2O)$  and <sup>3</sup>MLCT-<sup>3</sup>MC equilibration are leading to the absence of early time dyanimous at 400 nm.

#### 7.4 Conclusion

We have investigated the MLCT excited state dyanimes of  $[Ru(bpy)(tpy)(OH_2)]^{2+}$  in H<sub>2</sub>O and  $[Ru(bpy)(tpy)(OD_2)]^{2+}$  in D<sub>2</sub>O using steady state and ultrafast pump-probe techniques. The steady state absorption spectrum of both complexes were found to be quite similar (Figure 7.1) and suggests that deuteration of the ligand and solvent has little effect on the initial MLCT excitation process. An inverse kinetic isotope effect was observed with the lifetime of the <sup>3</sup>MLCT excited state in H<sub>2</sub>O, 270 ± 18 ps, being longer than that observed in D<sub>2</sub>O, 220 ± 12 ps. This effect has been ascribed to fast proton (or deuteron) donation to solvent which causes the excited state population of  $[Ru(bpy)(tpy)(OD_2)]^{2+}$  in D<sub>2</sub>O to preferentially

partition towards the ground state reactive <sup>3</sup>MC. Based on these results is seem that proton motion and the response of the solvent can be used to both preserve the electronic character of the <sup>3</sup>MLCT excited state and increase its lifetime. Therefore, it is conceivable that future synthetic architectures building on this scaffold where attention is paid to the MLCT and MC energies while also incorporating endogenous or exogenous bases may allow for enhanced photo-redox capabilities due to increased time available for excited state redox reactions.

### Chapter 7 Addendum Bibliography

- K. J. Takeuchi, M. S. Thompson, D. W. Pipes, and T. J. Meyer, *Inorganic Chemistry*, 1984, 23, 1845–1851.
- (2) H.-W. Tseng, R. Zong, J. T. Muckerman, and R. Thummel, *Inorganic Chemistry*, 2008, 47, 11763–11773.
- (3) Z. Deng, H.-W. Tseng, R. Zong, D. Wang, and R. Thummel, *Inorganic Chemistry*, 2008, 47, 1835– 1848.
- (4) J. J. Concepcion, J. W. Jurss, J. L. Templeton, and T. J. Meyer, Journal of the American Chemical Society, 2008, 130, 16462–.
- (5) J. J. Concepcion, J. W. Jurss, M. K. Brennaman, P. G. Hoertz, A. O. T. Patrocinio, N. Y. Murakami Iha, J. L. Templeton, and T. J. Meyer, Accounts of Chemical Research, 2009, 42, 1954–1965.
- (6) D. J. Wasylenko, C. Ganesamoorthy, M. A. Henderson, B. D. Koivisto, H. D. Osthoff, and C. P. Berlinguette, *Journal of the American Chemical Society*, 2010, **132**, 16094–16106.
- (7) D. J. Wasylenko, C. Ganesamoorthy, B. D. Koivisto, M. A. Henderson, and C. P. Berlinguette, *Inor-ganic Chemistry*, 2010, 49, 2202–2209.
- (8) L. L. Duan, Y. H. Xu, P. Zhang, M. Wang, and L. C. Sun, *Inorganic Chemistry*, 2010, 49, 209–215.
- (9) L. Duan, C. M. Araujo, M. S. G. Ahlquist, and L. Sun, Proceedings of the National Academy of Sciences, 2012, 109, 15584–15588.
- E. Jakubikova, W. Z. Chen, D. M. Dattelbaum, F. N. Rein, R. C. Rocha, R. L. Martin, and E. R. Batista, *Inorganic Chemistry*, 2009, 48, 10720–10725.
- (11) D. H. Oh and S. G. Boxer, Journal of the American Chemical Society, 1989, 111, 1130–1131.
- (12) M. A. Webb, F. J. Knorr, and J. L. McHale, Journal of Raman Spectroscopy, 2001, 32, 481–485.
- (13) E. M. Kober, B. P. Sullivan, and T. J. Meyer, *Inorganic Chemistry*, 1984, 23, 2098–2104.
- (14) S. A. Miller and A. M. Moran, Journal of Physical Chemistry A, 2010, 114, 2117–2126.

- (15) S. Wallin, J. Davidsson, J. Modin, and L. Hammarström, *Journal of Physical Chemistry A*, 2005, 109, 4697–4704.
- (16) S. M. Scott, A. K. Burrell, P. A. Cocks, and K. C. Gordon, Journal of the Chemical Society-Dalton Transactions, 1998, 3679–3684.
- (17) E. H. Yonemoto, R. L. Riley, Y. I. Kim, S. J. Atherton, R. H. Schmehl, and T. E. Mallouk, Journal of the American Chemical Society, 1992, 114, 8081–8087.
- (18) J. Winkler, T. L. Netzel, and N. Sutin, Journal Of The American Chemical Society, 1987, 109, 2381–2392.
- (19) S. Záliš, C. Consani, A. El Nahhas, A. Cannizzo, M. Chergui, F. Hartl, and A. Vlček, *Inorganica Chimica Acta*, 2011, **374**, 578–585.
- (20) J. T. Hewitt, P. J. Vallett, and N. H. Damrauer, The Journal of Physical Chemistry A, 2012, 116, 11536–11547.
- (21) W. Henry et al., Journal of Physical Chemistry A, 2008, 112, 4537–4544.
- (22) R. Berger and D. Mcmillin, *Inorganic Chemistry*, 1988, 27, 4245–4249.
- (23) G. B. Shaw, D. J. Styers-Barnett, E. Z. Gannon, J. C. Granger, and J. M. Papanikolas, Journal of Physical Chemistry A, 2004, 108, 4998–5006.
- (24) T. Ishizuka, T. Sawaki, S. Miyazaki, M. Kawano, Y. Shiota, K. Yoshizawa, S. Fukuzumi, and T. Kojima, *Chemistry-A European Journal*, 2011, **17**, 6652–6662.
- (25) D. Powell and P. Lay, *Inorganic Chemistry*, 1992, **31**, 3542–3550.
- (26) T. Sugaya and M. Sano, *Inorganic Chemistry*, 1993, **32**, 5878–5879.
- (27) M. J. Weaver and S. M. Nettles, *Inorganic Chemistry*, 1980, 19, 1641–1646.
- (28) K. Lashgari, M. Kritikos, R. Norrestam, and T. Norrby, Acta Crystallographica Section C: Crystal Structure Communications, 1999, 55, 64–67.
- (29) L. Hammarström and O. Johansson, Coordination Chemistry Reviews, 2010, 254, 2546–2559.
- (30) J. Van Houten and R. J. Watts, Journal of the American Chemical Society, 1975, 97, 3843–3844.

- (31) R. Sriram and M. Z. Hoffman, Chemical Physics Letters, 1982, 85, 572–575.
- (32) M. L. Fetterolf and H. W. Offen, Journal Of Physical Chemistry, 1986, 90, 1828–1830.
- (33) A. Masuda and Y. Kaizu, Inorganic Chemistry, 1998, 37, 3371–3375.
- (34) M. Kovács and A. Horváth, Inorganica Chimica Acta, 2002, 335, 69–76.
- (35) P. Y. Chen and T. J. Meyer, *Chem. Rev*, 1998, **98**, 1439–1477.
- (36) D. W. Thompson, J. F. Wishart, B. S. Brunschwig, and N. Sutin, Journal of Physical Chemistry A, 2001, 105, 8117–8122.
- (37) E. M. Kober, J. L. Marshall, W. J. Dressick, B. P. Sullivan, J. V. Caspar, and T. J. Meyer, *Inorganic Chemistry*, 1985, 24, 2755–2763.
- (38) J.-J. Max and C. Chapados, The Journal of Chemical Physics, 2009, 131, 184505.
- (39) A. Hazra, A. V. Soudackov, and S. Hammes-Schiffer, Journal of Physical Chemistry Letters, 2011, 2, 36–40.
- (40) E. M. Arrnett and D. R. McKelvey, in *Solute-Solvent Interactions*, ed. J. F. Coetzee and C. D. Ritchie, Marcel Dekker, New York, 1969, pp. 343–399.
- (41) J. Bigeleisen, The Journal of Chemical Physics, 1960, 32, 1583.
- (42) J. T. Hupp and M. J. Weaver, Inorganic Chemistry, 1984, 23, 3639–3644.
- (43) A. Soper and C. Benmore, *Physical Review Letters*, 2008, **101**, 065502.
- (44) D. J. Wasylenko, C. Ganesamoorthy, M. A. Henderson, B. D. Koivisto, H. D. Osthoff, and C. P. Berlinguette, *Journal Of The American Chemical Society*, 2010, **132**, 16094–16106.
- (45) A. Kimoto, K. Yamauchi, M. Yoshida, S. Masaoka, and K. Sakai, *Chemical Communications*, 2012, 48, 239–241.
- (46) K. Winkler, J. Lindner, H. Bürsing, and P. Vöhringer, The Journal of Chemical Physics, 2000, 113, 4674.
- (47) C. P. Lawrence and J. L. Skinner, The Journal of Chemical Physics, 2003, 118, 264.

- (48) Y. L. A. Rezus and H. J. Bakker, The Journal of Chemical Physics, 2005, 123, 114502.
- (49) D. Laage and J. T. Hynes, *Science*, 2006, **311**, 832–835.
- (50) K. J. Tielrooij, C. Petersen, Y. L. A. Rezus, and H. J. Bakker, *Chemical Physics Letters*, 2009, 471, 71–74.
- R. A. Nicodemus, S. A. Corcelli, J. L. Skinner, and A. Tokmakoff, *Journal Of Physical Chemistry B*, 2011, 115, 5604–5616.

## Thesis Bibliography

### **Chapter 1 References**

- (1) G. Wald, *Science*, 1968, **162**, 230.
- (2) R. W. Schoenlein, L. A. Peteanu, R. A. Mathies, and C. V. Shank, *Science*, 1991, 254, 412.
- (3) L. A. Peteanu, R. W. Schoenlein, Q. Wang, R. A. Mathies, and C. V. Shank, Proceedings of the National Academy of Sciences of the United States of America, 1993, 90, 11762.
- (4) A. H. Zewail, Pure and Applied Chemistry, 2000, 72, 2219–2232.
- (5) A. H. Zewail, *Physics Today*, 1980, **33**, 27–33.
- (6) D. J. Tannor and S. A. Rice, *Journal of Chemical Physics*, 1985, 83, 5013–5018.
- (7) D. J. Tannor, R. Kosloff, and S. A. Rice, Journal of Chemical Physics, 1986, 85, 5805–5820.
- (8) T. Baumert, M. Grosser, R. Thalweiser, and G. Gerber, *Physical Review Letters*, 1991, 67, 3753–3756.
- (9) T. Baumert, B. Bühler, M. Grosser, R. Thalweiser, V. Weiss, E. Wiedenmann, and G. Gerber, *Journal Of Physical Chemistry*, 1991, 95, 8103–8110.
- (10) E. D. Potter, J. L. Herek, S. Pedersen, Q. Liu, and A. H. Zewail, *Nature*, 1992, **355**, 66–68.
- R. Kosloff, S. A. Rice, P. Gaspard, S. Tersigni, and D. J. Tannor, *Chemical Physics*, 1989, 139, 201–220.
- (12) C. J. Bardeen, Q. Wang, and C. V. Shank, Physical Review Letters, 1995, 75, 3410–3413.
- (13) C. J. Bardeen, J. Che, K. R. Wilson, V. V. Yakovlev, P. Cong, B. Kohler, J. L. Krause, and M. Messina, *The Journal of Physical Chemistry A*, 1997, **101**, 3815–3822.
- (14) P. Brumer and M. Shapiro, *Chemical Physics*, 1986, **126**, 541–564.
- (15) P. Brumer and M. Shapiro, Accounts of Chemical Research, 1989, 22, 407–413.
- (16) M. Shapiro, J. W. Hepburn, and P. Brumer, *Chemical Physics*, 1988, 149, 451–454.
- M. Shapiro and P. Brumer, *Principles of the Quantum Control of Molecular Processes*, Wiley, Hoboken, 2003.

- (18) M. Shapiro and P. Brumer, Journal of Physical Chemistry A, 2001, 105, 2897–2902.
- (19) A. M. Weiner, D. E. Leaird, J. S. Patel, and J. R. Wullert, *Optics Letters*, 1990, 15, 326–328.
- (20) A. M. Weiner, Progress in Quantum Electronics, 1995, 19, 161–237.
- (21) A. M. Weiner and A. M. Kan'an, *IEEE Journal of Selected Topics in Quantum Electronics*, 1998, 4, 317–331.
- (22) A. M. Weiner, Optical Communications, 2011, 284, 3669–3692.
- (23) S. Shi, A. Woody, and H. Rabitz, Journal of Chemical Physics, 1988, 88, 6870-6883.
- (24) H. Rabitz and W. Zhu, Accounts of Chemical Research, 2000, 33, 572–578.
- (25) H. Rabitz, R. de Vivie-Riedle, M. Motzkus, and K. Kompa, Science, 2000, 288, 824–828.
- (26) Q. Ren and G. G. Balint-Kurti, The Journal of Physical Chemistry A, 2009, 113, 14255–14260.
- (27) R. S. Judson and H. Rabitz, *Physical Review Letters*, 1992, 68, 1500–1503.
- (28) R. J. Levis, G. M. Menkir, and H. Rabitz, Science, 2001, 292, 709-713.
- (29) C. J. Bardeen, V. V. Yakovlev, K. R. Wilson, S. D. Carpenter, P. M. Weber, and W. S. Warren, *Chemical Physics Letters*, 1997, 280, 151–158.
- (30) J. L. Herek, W. Wohlleben, R. J. Cogdell, D. Zeidler, and M. Motzkus, Nature, 2002, 417, 533-535.
- (31) C. Brif, R. Chakrabarti, and H. Rabitz, New Journal of Physics, 2010, 12, 075008.
- (32) W. Wohlleben, T. Buckup, J. L. Herek, and M. Motzkus, ChemPhysChem, 2005, 6, 850–857.
- (33) V. I. Prokhorenko, A. M. Nagy, S. A. Waschuk, L. S. Brown, R. R. Birge, and R. J. D. Miller, *Science*, 2006, **313**, 1257–1261.
- (34) V. I. Prokhorenko, A. M. Nagy, L. S. Brown, and R. J. Dwayne Miller, *Chemical Physics*, 2007, 341, 296–309.
- (35) T. Buckup, J. Hauer, J. Voll, R. Vivie-Riedle, and M. Motzkus, *Faraday Discussions*, 2011, 153, 213–225.
- (36) E. M. Grumstrup, J. C. Johnson, and N. H. Damrauer, *Physical Review Letters*, 2010, 105, 257403.

- (37) B. Brüggemann, J. Organero, T. Pascher, T. Pullerits, and A. Yartsev, *Physical Review Letters*, 2006, 97, 208301.
- (38) D. Kuciauskas, J. E. Monat, R. Villahermosa, H. B. Gray, N. S. Lewis, and J. K. McCusker, Journal of Physical Chemistry B, 2002, 106, 9347–9358.
- (39) B. O'Regan and M. Grätzel, Nature, 1991, 353, 737–740.
- (40) V. Balzani, L. Moggi, M. F. Manfrin, F. Bolletta, and M. Gleria, *Science*, 1975, 189, 852–856.
- (41) M. Grätzel, in *Energy Resources through Photochemistry and Catalysis*, Academic Press Inc., New York, 1983, 71 and references therein.
- (42) M. Grätzel and K. Kalyanasundaram, in Photosensitization and Photocatalysis Using Inorganic and Organometallic Compounds, Kluwer Academic Publishers, Dordrecht, 1993, 247 and references therein.
- (43) J. J. Concepcion, J. W. Jurss, M. K. Brennaman, P. G. Hoertz, A. O. T. Patrocinio, N. Y. Murakami Iha, J. L. Templeton, and T. J. Meyer, Accounts of Chemical Research, 2009, 42, 1954–1965.
- (44) J. W. Tucker and C. R. J. Stephenson, Journal of Organic Chemistry, 2012, 77, 1617–1622.
- (45) N. H. Damrauer, G. Cerullo, A. Yeh, T. R. Boussie, C. V. Shank, and J. K. McCusker, *Science*, 1997, 275, 54–57.
- (46) A. C. Bhasikuttan, M. Suzuki, S. Nakashima, and T. Okada, *Journal of the American Chemical Society*, 2002, **124**, 8398–8405.
- (47) S. Yoon, P. Kukura, C. M. Stuart, and R. A. Mathies, *Molecular Physics*, 2006, **104**, 1275–1282.
- (48) A. Cannizzo, F. van Mourik, W. Gawelda, G. Zgrablic, C. Bressler, and M. Chergui, Angewandte Chemie-International Edition, 2006, 45, 3174–3176.
- (49) W. Henry et al., Journal of Physical Chemistry A, 2008, 112, 4537–4544.
- (50) S. Wallin, J. Davidsson, J. Modin, and L. Hammarström, *Journal of Physical Chemistry A*, 2005, 109, 4697–4704.
- (51) A. Yeh, C. V. Shank, and J. K. McCusker, *Science*, 2000, **289**, 935–938.

- (52) G. B. Shaw, C. L. Brown, and J. M. Papanikolas, Journal of Physical Chemistry A, 2002, 106, 1483–1495.
- (53) G. B. Shaw, D. J. Styers-Barnett, E. Z. Gannon, J. C. Granger, and J. M. Papanikolas, Journal of Physical Chemistry A, 2004, 108, 4998–5006.
- (54) S. A. Miller and A. M. Moran, Journal of Physical Chemistry A, 2010, 114, 2117–2126.
- M. A. Montgomery, R. R. Meglen, and N. H. Damrauer, Journal of Physical Chemistry A, 2006, 110, 6391–6394.
- (56) M. A. Montgomery, R. R. Meglen, and N. H. Damrauer, Journal of Physical Chemistry A, 2007, 111, 5126–5129.
- (57) G. Vogt, G. Krampert, P. Niklaus, P. Nuernberger, and G. Gerber, *Physical Review Letters*, 2005, 94, 068305.
- (58) V. I. Prokhorenko, A. M. Nagy, and R. J. D. Miller, Journal of Chemical Physics, 2005, 122, 184502.
- (59) J. Savolainen, R. Fanciulli, N. Dijkhuizen, A. L. Moore, J. Hauer, T. Buckup, M. Motzkus, and J. L. Herek, Proceedings of the National Academy of Sciences of the United States of America, 2008, 105, 7641–7646.
- (60) M. Joffre, *Science*, 2007, **317**, 453b–453b.
- (61) A. C. Han and M. Shapiro, *Physical Review Letters*, 2012, **108**, 183002.
- (62) P. Brumer and M. Shapiro, *Chemical Physics*, 1989, **139**, 221.
- (63) V. I. Prokhorenko, A. M. Nagy, S. A. Waschuk, L. S. Brown, R. R. Birge, and R. J. Dwayne Miller, Science, 2007, 317, 453c–453c.
- (64) T. Buckup, J. Hauer, C. Serrat, and M. Motzkus, Journal of Physics B: Atomic, Molecular and Optical Physics, 2008, 41, 074024.
- (65) P. van der Walle, M. T. W. Milder, L. Kuipers, and J. L. Herek, Proceedings of the National Academy of Sciences of the United States of America, 2009, 106, 7714–7717.

- (66) J. Roslund, M. Roth, L. Guyon, V. Boutou, F. Courvoisier, J.-P. Wolf, and H. Rabitz, Journal of Chemical Physics, 2011, 134, pages.
- (67) G. Katz, M. A. Ratner, and R. Kosloff, New Journal of Physics, 2010, 12, 015003.
- (68) M. Spanner, C. A. Arango, and P. Brumer, The Journal of Chemical Physics, 2010, 133, 151101.
- (69) C. A. Arango and P. Brumer, The Journal of Chemical Physics, 2013, 138, 071104.
- (70) S. Campagna, F. Puntoriero, F. Nastasi, G. Bergamini, and V. Balzani, Photochemistry and Photophysics of Coordination Compounds I, 2007, 280, 117–214.
- (71) R. J. Watts, Journal of Chemical Education, 1983, 60, 834–842.
- (72) N. C. Fletcher, M. Nieuwenhuyzen, and S. Rainey, Journal of the Chemical Society-Dalton Transactions, 2001, 2641–2648.
- E. Holder, G. Trapp, J. C. Grimm, V. Schurig, and E. Lindner, *Tetrahedron: Asymmetry*, 2002, 13, 2673–2678.
- (74) H. A. Meylemans, Ph.D. Thesis, 2010.
- (75) M. Abdelhaq, Physical Chemistry, University of Colorado at Boulder, 2012.
- (76) M. Heller and U. S. Schubert, European Journal of Organic Chemistry, 2003, 2003, 947–961.
- (77) J. P. Sauvage, J. P. Collin, J. C. Chambron, S. Guillerez, C. Coudret, V. Balzani, F. Barigelletti, L. Decola, and L. Flamigni, *Chemical Reviews*, 1994, 94, 993–1019.
- J. Winkler, T. L. Netzel, and N. Sutin, Journal Of The American Chemical Society, 1987, 109, 2381–2392.
- (79) U. Siemeling et al., Chemistry A European Journal, 2003, 9, 2819–2833.
- (80) G. D. Scholes, Annual Review of Physical Chemistry, 2003, 54, 57–87.
- (81) G. Albano, V. Balzani, E. C. Constable, M. Maestri, and D. R. Smith, *Inorganica Chimica Acta*, 1998, 277, 225–231.
- (82) R. Passalacqua, F. Loiseau, S. Campagna, Y. Q. Fang, and G. S. Hanan, Angewandte Chemie-International Edition, 2003, 42, 1608–1611.

- (83) H. Y. Ding, X. S. Wang, L. Q. Song, J. R. Chen, J. H. Yu, Chao-Li, and B. W. Zhang, Journal of Photochemistry and Photobiology A: Chemistry, 2006, 177, 286–294.
- (84) J. R. Schoonover, D. M. Dattelbaum, A. Malko, V. I. Klimov, T. J. Meyer, D. J. Styers-Barnett, E. Z. Gannon, J. C. Granger, W. S. Aldridge, and J. M. Papanikolas, *Journal of Physical Chemistry A*, 2005, **109**, 2472–2475.
- (85) K. Hutchison, J. C. Morris, T. A. Nile, J. L. Walsh, D. W. Thompson, J. D. Petersen, and J. R. Schoonover, *Inorganic Chemistry*, 1999, **38**, 2516–2523.
- (86) J. P. Collin, S. Guillerez, J. P. Sauvage, F. Barigelletti, L. Decola, L. Flamigni, and V. Balzani, *Inorganic Chemistry*, 1991, **30**, 4230–4238.
- (87) O. Johansson, M. Borgström, R. Lomoth, M. Palmblad, J. Bergquist, L. Hammarström, L. C. Sun, and B. Åkermark, *Inorganic Chemistry*, 2003, 42, 2908–2918.
- (88) P. P. Laine, F. Bedioui, F. Loiseau, C. Chiorboli, and S. Campagna, Journal of the American Chemical Society, 2006, 128, 7510–7521.
- (89) E. A. Alemán, C. D. Shreiner, C. S. Rajesh, T. Smith, S. A. Garrison, and D. A. Modarelli, *Dalton Transactions*, 2009, 6562–6577.

#### Chapter 2 References

- (1) C. Brif, R. Chakrabarti, and H. Rabitz, New Journal of Physics, 2010, 12, 075008.
- (2) M. Dantus and V. V. Lozovoy, Chemical Reviews, 2004, 104, 1813–1859.
- (3) S. A. Rice and M. Zhao, Optical Control of Molecular Dynamics, Wiley, New York, 2000.
- (4) T. Brixner, N. H. Damrauer, and G. Gerber, Advances in Atomic, Molecular, and Optical Physics, 2001, 46, 1–54.
- (5) M. L. Stone and G. A. Crosby, *Chemical Physics Letters*, 1981, 79, 169–173.
- (6) J. R. Kirchhoff, D. R. McMillin, P. A. Marnot, and J. P. Sauvage, Journal of the American Chemical Society, 1985, 107, 1138–1141.

- J. Winkler, T. L. Netzel, and N. Sutin, Journal Of The American Chemical Society, 1987, 109, 2381–2392.
- (8) R. Berger and D. Mcmillin, Inorganic Chemistry, 1988, 27, 4245–4249.
- (9) C. R. Hecker, A. K. I. Gushurst, and D. R. McMillin, *Inorganic Chemistry*, 1991, **30**, 538–541.
- (10) J. P. Collin, S. Guillerez, J. P. Sauvage, F. Barigelletti, L. Decola, L. Flamigni, and V. Balzani, *Inorganic Chemistry*, 1991, **30**, 4230–4238.
- (11) E. Amouyal, M. Mouallem-Bahout, and G. Calzaferri, *Journal of Physical Chemistry*, 1991, 95, 7641–7649.
- (12) J. P. Sauvage, J. P. Collin, J. C. Chambron, S. Guillerez, C. Coudret, V. Balzani, F. Barigelletti, L. Decola, and L. Flamigni, *Chemical Reviews*, 1994, 94, 993–1019.
- (13) K. Hutchison, J. C. Morris, T. A. Nile, J. L. Walsh, D. W. Thompson, J. D. Petersen, and J. R. Schoonover, *Inorganic Chemistry*, 1999, **38**, 2516–2523.
- (14) O. Johansson, M. Borgström, R. Lomoth, M. Palmblad, J. Bergquist, L. Hammarström, L. C. Sun, and B. Åkermark, *Inorganic Chemistry*, 2003, 42, 2908–2918.
- (15) U. Siemeling et al., Chemistry A European Journal, 2003, 9, 2819–2833.
- (16) E. A. Medlycott and G. S. Hanan, Coordination Chemistry Reviews, 2006, 250, 1763–1782.
- (17) T. Österman, M. Abrahamsson, H. C. Becker, L. Hammarström, and P. Persson, Journal of Physical Chemistry A, 2012, 116, 1041–1050.
- (18) K. Lashgari, M. Kritikos, R. Norrestam, and T. Norrby, Acta Crystallographica Section C: Crystal Structure Communications, 1999, 55, 64–67.
- (19) K. Kalyanasundaram, S. M. Zakeeruddin, and M. K. Nazeeruddin, Coordination Chemistry Reviews, 1994, 132, 259–264.
- (20) A. Islam, N. Ikeda, A. Yoshimura, and T. Ohno, *Inorganic Chemistry*, 1998, **37**, 3093–3098.
- (21) F. Neve, A. Crispini, S. Campagna, and S. Serroni, *Inorganic Chemistry*, 1999, 38, 2250–2258.
- (22) B. P. Sullivan, J. M. Calvert, and T. J. Meyer, *Inorganic Chemistry*, 1980, 19, 1404–1407.

- (23) H. Hofmeier, E. Herdtweck, and U. S. Schubert, Zeitschrift Fur Anorganische Und Allgemeine Chemie,
  2004, 630, 683–688.
- (24) K. J. Takeuchi, M. S. Thompson, D. W. Pipes, and T. J. Meyer, *Inorganic Chemistry*, 1984, 23, 1845–1851.
- (25) V. V. Pavlishchuk and A. W. Addison, Inorganica Chimica Acta, 2000, 298, 97–102.
- (26) H. A. Meylemans, J. T. Hewitt, M. Abdelhaq, P. J. Vallett, and N. H. Damrauer, Journal of the American Chemical Society, 2010, 132, 11464–11466.
- (27) A. Shirakawa and T. Kobayashi, Applied Physics Letters, 1998, 72, 147.
- (28) T. Wilhelm, J. Piel, and E. Riedle, Optics Letters, 1997, 22, 1494–1496.
- (29) U. Megerle, I. Pugliesi, C. Schriever, C. F. Sailer, and E. Riedle, Applied Physics B, 2009, 96, 215–231.
- (30) R. J. Watts, Journal of Chemical Education, 1983, 60, 834–842.
- (31) S. Campagna, F. Puntoriero, F. Nastasi, G. Bergamini, and V. Balzani, Photochemistry and Photophysics of Coordination Compounds I, 2007, 280, 117–214.
- (32) M. Maestri, N. Armaroli, V. Balzani, E. C. Constable, and A. M. W. C. Thompson, *Inorganic Chem-istry*, 1995, 34, 2759–2767.
- (33) C. C. Phifer and D. R. McMillin, Inorganic Chemistry, 1986, 25, 1329–1333.
- (34) N. H. Damrauer, G. Cerullo, A. Yeh, T. R. Boussie, C. V. Shank, and J. K. McCusker, *Science*, 1997, 275, 54–57.
- (35) M. Presselt, B. Dietzek, M. Schmitt, S. Rau, A. Winter, M. Jager, U. S. Schubert, and J. Popp, Journal of Physical Chemistry A, 2010, 114, 13163–13174.
- (36) M. K. DeArmond and C. M. Carlin, Coordination Chemistry Reviews, 1981, 36, 325–355.
- (37) D. Braun, P. Huber, J. Wudy, J. Schmidt, and H. Yersin, Journal of Physical Chemistry, 1994, 98, 8044–8049.
- (38) H. Riesen and E. Krausz, Journal of Chemical Physics, 1993, 99, 7614–7618.

- (39) H. Riesen, L. Wallace, and E. Krausz, Journal of Physical Chemistry, 1996, 100, 17138–17144.
- (40) H. Riesen and E. Krausz, Chemical Physics Letters, 1996, 260, 130–135.
- (41) C. Turro, Y. C. Chung, N. Leventis, M. E. Kuchenmeister, P. J. Wagner, and G. E. Leroi, *Inorganic Chemistry*, 1996, **35**, 5104–5106.
- (42) P. W. Hansen and P. W. Jensen, Spectrochimica Acta Part a-Molecular and Biomolecular Spectroscopy, 1994, 50, 169–183.
- (43) R. F. Dallinger and W. H. Woodruff, Journal of the American Chemical Society, 1979, 101, 4391–4393.
- (44) P. G. Bradley, N. Kress, B. A. Hornberger, R. F. Dallinger, and W. H. Woodruff, Journal of the American Chemical Society, 1981, 103, 7441–7446.
- M. E. Moret, I. Tavernelli, M. Chergui, and U. Rothlisberger, *Chemistry A European Journal*, 2010, 16, 5889–5894.
- (46) D. A. Hoff, R. Silva, and L. G. C. Rego, Journal Of Physical Chemistry C, 2011, 115, 15617–15626.
- (47) D. H. Oh and S. G. Boxer, Journal of the American Chemical Society, 1989, 111, 1130–1131.
- (48) L. Karki and J. T. Hupp, Inorganic Chemistry, 1997, 36, 3318–3321.
- (49) M. A. Webb, F. J. Knorr, and J. L. McHale, Journal of Raman Spectroscopy, 2001, 32, 481–485.
- (50) E. M. Kober, B. P. Sullivan, and T. J. Meyer, *Inorganic Chemistry*, 1984, 23, 2098–2104.
- (51) S. Wallin, J. Davidsson, J. Modin, and L. Hammarström, Journal of Physical Chemistry A, 2005, 109, 4697–4704.
- (52) A. Yeh, C. V. Shank, and J. K. McCusker, Science, 2000, 289, 935–938.
- (53) J. K. McCusker, Accounts of Chemical Research, 2003, 36, 876–887.
- (54) A. Juris, V. Balzani, F. Barigelletti, S. Campagna, P. Belser, and A. von Zelewsky, *Coordination Chemistry Reviews*, 1988, 84, 85–277.
- (55) J. C. Curtis, B. P. Sullivan, and T. J. Meyer, *Inorganic Chemistry*, 1983, 22, 224–236.
- (56) F. Tessore, D. Roberto, R. Ugo, M. Pizzotti, S. Quici, M. Cavazzini, S. Brun, and F. De Angelis, *Inorganic Chemistry*, 2005, 44, 8967–8978.

- (57) N. H. Damrauer and J. K. McCusker, Journal of Physical Chemistry A, 1999, 103, 8440–8446.
- (58) M. K. Nazeeruddin, S. M. Zakeeruddin, and K. Kalyanasundaram, Journal of Physical Chemistry, 1993, 97, 9607.
- (59) J. F. Michalec, S. A. Bejune, and D. R. McMillin, Inorganic Chemistry, 2000, 39, 2708-.
- (60) K. Nakamura, Bulletin of the Chemical Society of Japan, 1972, 45, 1943.
- (61) P. S. Braterman, J. I. Song, and R. D. Peacock, *Inorganic Chemistry*, 1992, **31**, 555–559.
- (62) S. Záliš, C. Consani, A. El Nahhas, A. Cannizzo, M. Chergui, F. Hartl, and A. Vlček, *Inorganica Chimica Acta*, 2011, **374**, 578–585.
- (63) P. A. Anderson, F. Richard Keene, T. J. Meyer, J. A. Moss, G. F. Strouse, and J. A. Treadway, Journal of the Chemical Society-Dalton Transactions, 2002, 3820–3831.
- (64) A. C. Bhasikuttan, M. Suzuki, S. Nakashima, and T. Okada, *Journal of the American Chemical Society*, 2002, **124**, 8398–8405.
- (65) A. Cannizzo, F. van Mourik, W. Gawelda, G. Zgrablic, C. Bressler, and M. Chergui, Angewandte Chemie-International Edition, 2006, 45, 3174–3176.
- (66) S. Yoon, P. Kukura, C. M. Stuart, and R. A. Mathies, *Molecular Physics*, 2006, **104**, 1275–1282.
- (67) A. Cannizzo, C. J. Milne, C. Consani, W. Gawelda, C. Bressler, F. van Mourik, and M. Chergui, *Coordination Chemistry Reviews*, 2010, **254**, 2677–2686.
- (68) A. C. Albrecht, Journal of Molecular Spectroscopy, 1961, 6, 84.
- (69) H. S. Tan, I. R. Piletic, and M. D. Fayer, Journal Of The Optical Society Of America B-Optical Physics, 2005, 22, 2009–2017.
- (70) G. B. Shaw, D. J. Styers-Barnett, E. Z. Gannon, J. C. Granger, and J. M. Papanikolas, Journal of Physical Chemistry A, 2004, 108, 4998–5006.
- (71) W. Henry et al., Journal of Physical Chemistry A, 2008, 112, 4537–4544.
- (72) P. S. Braterman, A. Harriman, G. A. Heath, and L. J. Yellowlees, Journal of the Chemical Society-Dalton Transactions, 1983, 1801–1803.

- (73) A. Yoshimura, M. Z. Hoffman, and H. Sun, Journal of Photochemistry and Photobiology A: Chemistry, 1993, 70, 29–33.
- (74) A. Amini, A. Harriman, and A. Mayeux, Physical Chemistry Chemical Physics, 2004, 1157–1164.
- (75) E. Jakubikova, W. Z. Chen, D. M. Dattelbaum, F. N. Rein, R. C. Rocha, R. L. Martin, and E. R. Batista, *Inorganic Chemistry*, 2009, 48, 10720–10725.
- (76) A. O. Borg, S. S. M. C. Godinho, M. J. Lundqvist, S. Lunell, and P. Persson, Journal of Physical Chemistry A, 2008, 112, 4470–4476.
- (77) M. K. DeArmond, Accounts of Chemical Research, 1974, 7, 309–315.
- (78) M. Rae and M. N. Berberan-Santos, Journal of Chemical Education, 2004, 81, 436–440.
- (79) O. A. Borg, S. Godinho, M. J. Lundqvist, S. Lunell, and P. Persson, Journal of Physical Chemistry A, 2008, 112, 4470–4476.
- (80) H. A. Meylemans, C. F. Lei, and N. H. Damrauer, *Inorganic Chemistry*, 2008, 47, 4060–4076.
- L. Hammarström, F. Barigelletti, L. Flamigni, M. T. Indelli, N. Armaroli, G. Calogero, M. Guardigli,
  A. Sour, J. P. Collin, and J. P. Sauvage, *Journal of Physical Chemistry A*, 1997, 101, 9061–9069.
- (82) P. P. Laine, F. Bedioui, F. Loiseau, C. Chiorboli, and S. Campagna, Journal of the American Chemical Society, 2006, 128, 7510–7521.
- (83) M. T. Indelli, M. Orlandi, C. Chiorboli, M. Ravaglia, F. Scandola, F. Lafolet, S. Welter, and L. De Cola, Journal of Physical Chemistry A, 2012, 116, 119–131.
- (84) P. P. Laine, F. Bedioui, E. Amouyal, V. Albin, and F. Berruyer-Penaud, Chemistry A European Journal, 2002, 8, 3162–3176.
- (85) M. Beley, J. P. Collin, J. P. Sauvage, H. Sugihara, F. Heisel, and A. Miehé, Journal of the Chemical Society-Dalton Transactions, 1991, 11, 3157–3159.
- (86) R. A. Malone and D. F. Kelley, Journal of Chemical Physics, 1991, 95, 8970.
- (87) J. L. Pogge and D. F. Kelley, Chemical Physics Letters, 1995, 238, 16.
- (88) J. P. Cushing, C. Butoi, and D. F. Kelley, Journal of Physical Chemistry A, 1997, 101, 7222–7230.
- (89) G. B. Shaw, C. L. Brown, and J. M. Papanikolas, Journal of Physical Chemistry A, 2002, 106, 1483– 1495.
- (90) S. A. Miller and A. M. Moran, Journal of Physical Chemistry A, 2010, 114, 2117–2126.
- (91) A. C. Benniston and A. Harriman, Chemical Society Reviews, 2006, 35, 169–179.
- W. B. Davis, M. A. Ratner, and M. R. Wasielewski, Journal of the American Chemical Society, 2001, 123, 7877–7886.
- J. Kallioinen, G. Benko, P. Myllyperkio, L. Khriachtchev, B. Skårman, R. Wallenberg, M. Tuomikoski,
   J. Korppi-Tommola, V. Sundstrom, and A. P. Yartsev, *Journal of Physical Chemistry B*, 2004, 108, 6365–6373.
- (94) C. Consani, M. Prémont-Schwarz, A. ElNahhas, C. Bressler, F. van Mourik, A. Cannizzo, and M. Chergui, Angewandte Chemie International Edition, 2009, 48, 7184–7187.
- (95) J. N. Schrauben, K. L. Dillman, W. F. Beck, and J. K. McCusker, *Chemical Science*, 2010, 1, 405.
- (96) R. M. van der Veen, A. Cannizzo, F. van Mourik, A. Vlček, and M. Chergui, Journal of the American Chemical Society, 2011, 133, 305–315.
- (97) M. Iwamura, H. Watanabe, K. Ishii, S. Takeuchi, and T. Tahara, Journal of the American Chemical Society, 2011, 133, 7728–7736.
- (98) P. J. Vallett and N. H. Damrauer, "To be submitted for publication", 2012.

#### Chapter 3 References

- C. Weinheimer, Y. Choi, T. Caldwell, P. Gresham, and J. Olmsted, Journal Of Photochemistry And Photobiology A-Chemistry, 1994, 78, 119–126.
- (2) G. Wilson, W. Sasse, and A. Mau, Chemical Physics Letters, 1996, 250, 583-588.
- G. Albano, V. Balzani, E. C. Constable, M. Maestri, and D. R. Smith, *Inorganica Chimica Acta*, 1998, 277, 225–231.

- (4) B. Maubert, N. McClenaghan, M. Indelli, and S. Campagna, *The Journal of Physical Chemistry A*, 2003, 107, 447–455.
- (5) R. Passalacqua, F. Loiseau, S. Campagna, Y. Q. Fang, and G. S. Hanan, Angewandte Chemie-International Edition, 2003, 42, 1608–1611.
- (6) J. Wang, G. Hanan, F. Loiseau, and S. Campagna, *Chemical Communications*, 2004, 2068–2069.
- (7) J. R. Schoonover, D. M. Dattelbaum, A. Malko, V. I. Klimov, T. J. Meyer, D. J. Styers-Barnett, E. Z. Gannon, J. C. Granger, W. S. Aldridge, and J. M. Papanikolas, *Journal of Physical Chemistry A*, 2005, **109**, 2472–2475.
- (8) H. Y. Ding, X. S. Wang, L. Q. Song, J. R. Chen, J. H. Yu, Chao-Li, and B. W. Zhang, Journal of Photochemistry and Photobiology A: Chemistry, 2006, 177, 286–294.
- (9) J. H. Wang, E. A. Medlycott, G. S. Hanan, F. Loiseau, and S. Campagna, *Inorganica Chimica Acta*, 2007, **360**, 876–884.
- (10) D. L. Dexter, Journal of Chemical Physics, 1953, 21, 836–850.
- (11) R. Passalacqua, F. Loiseau, S. Campagna, Y. Fang, and G. Hanan, Angewandte Chemie International Edition, 2003, 42, 1608–1611.
- (12) Y. Fang, N. Taylor, G. Hanan, F. Loiseau, R. Passalacqua, S. Campagna, H. Nierengarten, and A. Van Dorsselaer, *Journal Of The American Chemical Society*, 2002, **124**, 7912–7913.
- (13) A. M. McDaniel, H. W. Tseng, N. H. Damrauer, and M. P. Shores, *Inorganic Chemistry*, 2010, 49, 7981–7991.
- (14) Y. H. Meyer, R. Astier, and J. Leclercq, The Journal of Chemical Physics, 1972, 56, 801.
- (15) T. T. Goodnow and A. E. Kaifer, Journal Of Physical Chemistry, 1990, 94, 7682–7683.
- (16) M. Presselt, B. Dietzek, M. Schmitt, S. Rau, A. Winter, M. Jager, U. S. Schubert, and J. Popp, Journal of Physical Chemistry A, 2010, 114, 13163–13174.
- (17) E. Amouyal, M. Mouallem-Bahout, and G. Calzaferri, *Journal of Physical Chemistry*, 1991, 95, 7641–7649.

- (18) H. A. Meylemans, Ph.D. Thesis, 2010.
- (19) H. A. Meylemans and N. H. Damrauer, Inorganic Chemistry, 2009, 48, 11161–11175.
- (20) C. C. Phifer and D. R. McMillin, *Inorganic Chemistry*, 1986, **25**, 1329–1333.
- (21) N. Damrauer, T. Boussie, M. Devenney, and J. K. McCusker, Journal Of The American Chemical Society, 1997, 119, 8253–8268.
- (22) V. V. Pavlishchuk and A. W. Addison, Inorganica Chimica Acta, 2000, 298, 97–102.
- (23) V. D. Parker, Journal Of The American Chemical Society, 1976, 98, 98–103.
- (24) N. H. Damrauer, G. Cerullo, A. Yeh, T. R. Boussie, C. V. Shank, and J. K. McCusker, *Science*, 1997, 275, 54–57.
- (25) A. C. Bhasikuttan, M. Suzuki, S. Nakashima, and T. Okada, *Journal of the American Chemical Society*, 2002, **124**, 8398–8405.
- (26) A. Cannizzo, F. van Mourik, W. Gawelda, G. Zgrablic, C. Bressler, and M. Chergui, Angewandte Chemie-International Edition, 2006, 45, 3174–3176.
- (27) S. Yoon, P. Kukura, C. M. Stuart, and R. A. Mathies, *Molecular Physics*, 2006, **104**, 1275–1282.
- (28) L. X. Xiao, Y. Q. Xu, M. Yan, D. Galipeau, X. J. Peng, and X. Z. Yan, Journal of Physical Chemistry A, 2010, 114, 9090–9097.
- (29) D. H. Oh and S. G. Boxer, Journal of the American Chemical Society, 1989, 111, 1130–1131.
- (30) H. Riesen, L. Wallace, and E. Krausz, Journal of Physical Chemistry, 1996, 100, 17138–17144.
- (31) H. Riesen and E. Krausz, *Chemical Physics Letters*, 1996, 260, 130–135.
- (32) L. Karki and J. T. Hupp, Inorganic Chemistry, 1997, 36, 3318–3321.
- (33) M. A. Webb, F. J. Knorr, and J. L. McHale, Journal of Raman Spectroscopy, 2001, 32, 481–485.
- (34) E. M. Kober, B. P. Sullivan, and T. J. Meyer, *Inorganic Chemistry*, 1984, 23, 2098–2104.
- (35) G. B. Shaw, D. J. Styers-Barnett, E. Z. Gannon, J. C. Granger, and J. M. Papanikolas, Journal of Physical Chemistry A, 2004, 108, 4998–5006.

- (36) S. Wallin, J. Davidsson, J. Modin, and L. Hammarström, Journal of Physical Chemistry A, 2005, 109, 4697–4704.
- (37) W. Henry et al., Journal of Physical Chemistry A, 2008, 112, 4537–4544.
- (38) N. H. Damrauer and J. K. McCusker, Journal of Physical Chemistry A, 1999, 103, 8440–8446.
- (39) J. T. Hewitt, P. J. Vallett, and N. H. Damrauer, The Journal of Physical Chemistry A, 2012, 116, 11536–11547.
- (40) J. Winkler, T. L. Netzel, and N. Sutin, Journal Of The American Chemical Society, 1987, 109, 2381–2392.
- (41) R. Berger and D. Mcmillin, *Inorganic Chemistry*, 1988, 27, 4245–4249.
- (42) P. S. Braterman, J. I. Song, and R. D. Peacock, *Inorganic Chemistry*, 1992, **31**, 555–559.
- (43) G. Porter and M. W. Windsor, Proceedings of the Royal Society of London Series A-Mathematical and Physical Sciences, 1958, 245, 238–258.
- (44) T. G. Pavlopoulos, Spectrochimica Acta Part A-Molecular and Biomolecular Spectroscopy, 1991, 47, 517–518.
- (45) G. Jackson, R. Livingston, and A. C. Pugh, Transactions of the Faraday Society, 1960, 56, 1635–1639.
- (46) S. Záliš, C. Consani, A. El Nahhas, A. Cannizzo, M. Chergui, F. Hartl, and A. Vlček, *Inorganica Chimica Acta*, 2011, **374**, 578–585.
- (47) R. Katoh, Y. Tamaki, and A. Furube, Journal of Photochemistry and Photobiology A: Chemistry, 2006, 183, 267–272.
- (48) M. R. Padhye, S. P. McGlynn, and M. Kasha, *The Journal of Chemical Physics*, 1956, 24, 588.
- (49) A. Amini, A. Harriman, and A. Mayeux, *Physical Chemistry Chemical Physics*, 2004, 1157–1164.
- (50) M. Maestri, N. Armaroli, V. Balzani, E. C. Constable, and A. M. W. C. Thompson, *Inorganic Chem-istry*, 1995, 34, 2759–2767.
- (51) R. D. Harcourt, G. D. Scholes, and K. P. Ghiggino, Journal of Chemical Physics, 1994, 101, 10521– 10525.

- (52) D. L. Andrews, C. Curutchet, and G. D. Scholes, Laser and Photonics Reviews, 2011, 5, 114–123.
- (53) R. A. Marcus, Annual Review of Physical Chemistry, 1964, 15, 155–196.
- (54) P. F. Barbara, T. J. Meyer, and M. A. Ratner, Journal of Physical Chemistry, 1996, 100, 13148–13168.
- (55) F. Emmerling, M. Lettenberger, and A. Laubereau, Journal of Physical Chemistry, 1996, 100, 19251– 19256.
- (56) Z. Wang, S. J. Weininger, and W. G. Mcgimpsey, Journal of Physical Chemistry, 1993, 97, 374–378.
- (57) G. Jackson and R. Livingston, Journal of Chemical Physics, 1961, 35, 2182–2186.

#### Chapter 4 References

- J. P. Collin, S. Guillerez, J. P. Sauvage, F. Barigelletti, L. Decola, L. Flamigni, and V. Balzani, *Inorganic Chemistry*, 1991, **30**, 4230–4238.
- L. F. Cooley, S. L. Larson, C. M. Elliott, and D. F. Kelley, Journal of Physical Chemistry, 1991, 95, 10694–10700.
- (3) E. Yonemoto, G. Saupe, R. Schmehl, S. Hubig, R. Riley, B. Iverson, and T. E. Mallouk, *Journal Of The American Chemical Society*, 1994, **116**, 4786–4795.
- (4) J. P. Sauvage, J. P. Collin, J. C. Chambron, S. Guillerez, C. Coudret, V. Balzani, F. Barigelletti, L. Decola, and L. Flamigni, *Chemical Reviews*, 1994, 94, 993–1019.
- (5) F. Barigelletti and L. Flamigni, Chemical Society Reviews, 2000, 29, 1–12.
- (6) H. Durr and S. Bossmann, Accounts of Chemical Research, 2001, 34, 905–917.
- R. Lomoth, T. Häupl, O. Johansson, and L. Hammarström, *Chemistry-A European Journal*, 2002, 8, 102–110.
- (8) O. Johansson, M. Borgström, R. Lomoth, M. Palmblad, J. Bergquist, L. Hammarström, L. C. Sun, and B. Åkermark, *Inorganic Chemistry*, 2003, 42, 2908–2918.
- (9) Y. Xu et al., Chemistry-A European Journal, 2005, 11, 7305–7314.
- (10) M. Falkenström, O. Johansson, and L. Hammarström, *Inorganica Chimica Acta*, 2007, **360**, 741–750.

- (11) S. Karlsson, J. Modin, H.-C. Becker, L. Hammarström, and H. Grennberg, *Inorganic Chemistry*, 2008, 47, 7286–7294.
- (12) M. R. Hartings, I. V. Kurnikov, A. R. Dunn, J. R. Winkler, H. B. Gray, and M. A. Ratner, *Coordination Chemistry Reviews*, 2010, **254**, 248–253.
- (13) J. Hankache and O. S. Wenger, Physical Chemistry Chemical Physics, 2012.
- (14) A. C. Benniston and A. Harriman, Chemical Society Reviews, 2006, 35, 169–179.
- (15) P. P. Laine, S. Campagna, and F. Loiseau, Coordination Chemistry Reviews, 2008, 2552–2571.
- (16) H. A. Meylemans, C. F. Lei, and N. H. Damrauer, Inorganic Chemistry, 2008, 47, 4060–4076.
- (17) A. Benniston, A. Harriman, P. Li, P. Patel, and C. Sams, *Chemistry A European Journal*, 2008, 14, 1710–1717.
- (18) H. A. Meylemans and N. H. Damrauer, Inorganic Chemistry, 2009, 48, 11161–11175.
- (19) H. A. Meylemans, J. T. Hewitt, M. Abdelhaq, P. J. Vallett, and N. H. Damrauer, Journal of the American Chemical Society, 2010, 132, 11464–11466.
- (20) N. S. Lewis and D. G. Nocera, Proceedings of the National Academy of Sciences of the United States of America, 2006, 103, 15729–15735.
- (21) M. I. Hoffert et al., Science, 2002, 298, 981–987.
- (22) K. Kalyanasundaram, Coordination Chemistry Reviews, 1982, 46, 159–244.
- (23) A. Juris, V. Balzani, F. Barigelletti, S. Campagna, P. Belser, and A. von Zelewsky, *Coordination Chemistry Reviews*, 1988, 84, 85–277.
- (24) S. Campagna, F. Puntoriero, F. Nastasi, G. Bergamini, and V. Balzani, Photochemistry and Photophysics of Coordination Compounds I, 2007, 280, 117–214.
- (25) J. P. Collin, S. Guillerez, and J. P. Sauvage, Journal of the Chemical Society-Chemical Communications, 1989, 776–778.
- (26) K. Hutchison, J. C. Morris, T. A. Nile, J. L. Walsh, D. W. Thompson, J. D. Petersen, and J. R. Schoonover, *Inorganic Chemistry*, 1999, **38**, 2516–2523.

- (27) M. Abdelhaq, Physical Chemistry, University of Colorado at Boulder, 2012.
- (28) H. A. Meylemans, Ph.D. Thesis, 2010.
- (29) F. Neve, A. Crispini, S. Campagna, and S. Serroni, Inorganic Chemistry, 1999, 38, 2250–2258.
- (30) B. P. Sullivan, J. M. Calvert, and T. J. Meyer, *Inorganic Chemistry*, 1980, **19**, 1404–1407.
- (31) K. J. Takeuchi, M. S. Thompson, D. W. Pipes, and T. J. Meyer, *Inorganic Chemistry*, 1984, 23, 1845–1851.
- (32) H. Hofmeier, E. Herdtweck, and U. S. Schubert, Zeitschrift Fur Anorganische Und Allgemeine Chemie,
   2004, 630, 683–688.
- (33) C. C. Phifer and D. R. McMillin, *Inorganic Chemistry*, 1986, **25**, 1329–1333.
- (34) C. R. Hecker, A. K. I. Gushurst, and D. R. McMillin, *Inorganic Chemistry*, 1991, **30**, 538–541.
- (35) M. Maestri, N. Armaroli, V. Balzani, E. C. Constable, and A. M. W. C. Thompson, *Inorganic Chem-istry*, 1995, 34, 2759–2767.
- M. Head-Gordon, A. M. Grana, D. Maurice, and C. A. White, *Journal of Physical Chemistry*, 1995, 1995, 14261–14270.
- (37) A. Vlček and S. Záliš, Coordination Chemistry Reviews, 2007, 251, 258–287.
- (38) J. D. Henrich, H. Y. Zhang, P. K. Dutta, and B. Kohler, Journal of Physical Chemistry B, 2010, 114, 14679–14688.
- (39) V. V. Pavlishchuk and A. W. Addison, Inorganica Chimica Acta, 2000, 298, 97–102.
- (40) A. Weller, Zeitschrift für Physikalische Chemie, 1982, 133, 93–98.
- (41) M. Abrahamsson et al., Inorganic Chemistry, 2005, 44, 3215–3225.
- (42) R. A. Marcus, Annual Review of Physical Chemistry, 1964, 15, 155–196.
- (43) I. Rips and J. Jortner, *Journal of Chemical Physics*, 1987, 87, 6513–6519.
- (44) P. F. Barbara, G. C. Walker, and T. P. Smith, Science, 1992, 256, 975.

- (45) E. H. Yonemoto, R. L. Riley, Y. I. Kim, S. J. Atherton, R. H. Schmehl, and T. E. Mallouk, Journal of the American Chemical Society, 1992, 114, 8081–8087.
- (46) J. K. McCusker, Accounts of Chemical Research, 2003, 36, 876–887.
- (47) F. Tessore, D. Roberto, R. Ugo, M. Pizzotti, S. Quici, M. Cavazzini, S. Brun, and F. De Angelis, *Inorganic Chemistry*, 2005, 44, 8967–8978.
- (48) J. F. Michalec, S. Bejune, D. Cuttell, G. Summerton, J. Gertenbach, J. Field, R. Haines, and D. Mcmillin, *Inorganic Chemistry*, 2001, 40, 2193–2200.
- (49) J. C. Curtis, B. P. Sullivan, and T. J. Meyer, *Inorganic Chemistry*, 1983, 22, 224–236.
- (50) M. K. Nazeeruddin, S. M. Zakeeruddin, and K. Kalyanasundaram, Journal of Physical Chemistry, 1993, 97, 9607.
- (51) K. Kalyanasundaram, S. M. Zakeeruddin, and M. K. Nazeeruddin, Coordination Chemistry Reviews, 1994, 132, 259–264.
- (52) N. H. Damrauer and J. K. McCusker, Journal of Physical Chemistry A, 1999, 103, 8440–8446.
- (53) T. Häupl, R. Lomoth, and L. Hammarström, Journal of Physical Chemistry A, 2003, 107, 435–438.
- (54) T. Watanabe and K. Honda, Journal Of Physical Chemistry, 1982, 86, 2617–2619.
- (55) P. M. S. Monk, The viologens : physicochemical properties, synthesis, and applications of the salts of 4,4'-bipyridine, Wiley, Chichester ; New York, 1998.
- (56) N. H. Damrauer, G. Cerullo, A. Yeh, T. R. Boussie, C. V. Shank, and J. K. McCusker, *Science*, 1997, 275, 54–57.
- (57) A. C. Bhasikuttan, M. Suzuki, S. Nakashima, and T. Okada, *Journal of the American Chemical Society*, 2002, **124**, 8398–8405.
- (58) A. Cannizzo, F. van Mourik, W. Gawelda, G. Zgrablic, C. Bressler, and M. Chergui, Angewandte Chemie-International Edition, 2006, 45, 3174–3176.
- (59) S. Yoon, P. Kukura, C. M. Stuart, and R. A. Mathies, *Molecular Physics*, 2006, 104, 1275–1282.
- (60) A. C. Albrecht, Journal of Molecular Spectroscopy, 1961, 6, 84.

- (61) H. S. Tan, I. R. Piletic, and M. D. Fayer, Journal Of The Optical Society Of America B-Optical Physics, 2005, 22, 2009–2017.
- (62) G. B. Shaw, D. J. Styers-Barnett, E. Z. Gannon, J. C. Granger, and J. M. Papanikolas, Journal of Physical Chemistry A, 2004, 108, 4998–5006.
- (63) B. S. Brunschwig and N. Sutin, Coordination Chemistry Reviews, 1999, 187, 233–254.
- (64) I. Rips and J. Jortner, Journal of Chemical Physics, 1987, 87, 2090-2104.
- (65) R. Siebert, A. Winter, M. Schmitt, J. Popp, U. S. Schubert, and B. Dietzek, Macromolecular Rapid Communications, 2012, 33, 481–497.

#### Chapter 5 References

- (1) B. P. Sullivan, J. M. Calvert, and T. J. Meyer, *Inorganic Chemistry*, 1980, 19, 1404–1407.
- (2) K. J. Takeuchi, M. S. Thompson, D. W. Pipes, and T. J. Meyer, *Inorganic Chemistry*, 1984, 23, 1845–1851.
- H. Hofmeier, E. Herdtweck, and U. S. Schubert, Zeitschrift Fur Anorganische Und Allgemeine Chemie, 2004, 630, 683–688.
- (4) M. Abdelhaq, Physical Chemistry, University of Colorado at Boulder, 2012.
- N. H. Damrauer, G. Cerullo, A. Yeh, T. R. Boussie, C. V. Shank, and J. K. McCusker, Science, 1997, 275, 54–57.
- (6) A. C. Bhasikuttan, M. Suzuki, S. Nakashima, and T. Okada, *Journal of the American Chemical Society*, 2002, **124**, 8398–8405.
- (7) A. Cannizzo, F. van Mourik, W. Gawelda, G. Zgrablic, C. Bressler, and M. Chergui, Angewandte Chemie-International Edition, 2006, 45, 3174–3176.
- (8) S. Yoon, P. Kukura, C. M. Stuart, and R. A. Mathies, *Molecular Physics*, 2006, **104**, 1275–1282.
- (9) A. C. Albrecht, Journal of Molecular Spectroscopy, 1961, 6, 84.

- (10) H. S. Tan, I. R. Piletic, and M. D. Fayer, Journal Of The Optical Society Of America B-Optical Physics, 2005, 22, 2009–2017.
- (11) G. B. Shaw, D. J. Styers-Barnett, E. Z. Gannon, J. C. Granger, and J. M. Papanikolas, Journal of Physical Chemistry A, 2004, 108, 4998–5006.
- J. T. Hewitt, P. J. Vallett, and N. H. Damrauer, The Journal of Physical Chemistry A, 2012, 116, 11536–11547.
- (13) G. Porter and M. W. Windsor, Proceedings of the Royal Society of London Series A-Mathematical and Physical Sciences, 1958, 245, 238–258.
- (14) Y. H. Meyer, R. Astier, and J. Leclercq, The Journal of Chemical Physics, 1972, 56, 801.
- (15) D. N. Dempster, T. Morrow, and M. F. Quinn, Journal of Photochemistry, 1974, 2, 329–341.
- (16) T. G. Pavlopoulos, Spectrochimica Acta Part A-Molecular and Biomolecular Spectroscopy, 1991, 47, 517–518.
- (17) R. Bonneau, I. Carmichael, and G. L. Hug, Pure and Applied Chemistry, 1991, 63, 290–299.
- (18) O. Johansson, M. Borgström, R. Lomoth, M. Palmblad, J. Bergquist, L. Hammarström, L. C. Sun, and B. Åkermark, *Inorganic Chemistry*, 2003, 42, 2908–2918.

#### Chapter 6 References

- (1) T. Brixner, N. H. Damrauer, P. Niklaus, and G. Gerber, *Nature*, 2001, **414**, 57–60.
- M. A. Montgomery, R. R. Meglen, and N. H. Damrauer, *Journal of Physical Chemistry A*, 2006, 110, 6391–6394.
- (3) M. A. Montgomery, R. R. Meglen, and N. H. Damrauer, Journal of Physical Chemistry A, 2007, 111, 5126–5129.
- (4) M. A. Montgomery and N. H. Damrauer, New Journal of Physics, 2009, 11, 105053.
- (5) M. A. Montgomery, E. M. Grumstrup, and N. H. Damrauer, Journal Of The Optical Society Of America B-Optical Physics, 2010, 27, 2518–2533.

- (6) B. Brüggemann, J. Organero, T. Pascher, T. Pullerits, and A. Yartsev, *Physical Review Letters*, 2006, 97, 208301.
- (7) E. M. Grumstrup, J. C. Johnson, and N. H. Damrauer, *Physical Review Letters*, 2010, 105, 257403.
- (8) E. Grumstrup, Ph.D. Thesis, University of Colorado at Boulder, 2011.
- (9) A. Shirakawa and T. Kobayashi, Applied Physics Letters, 1998, 72, 147.
- (10) T. Wilhelm, J. Piel, and E. Riedle, *Optics Letters*, 1997, **22**, 1494–1496.
- (11) A. M. Weiner, Review of Scientific Instrumentation, 2000, 71, 1929–1960.
- (12) A. M. Weiner, Optical Communications, 2011, 284, 3669–3692.
- (13) D. H. Reitze, A. M. Weiner, and D. E. Leaird, Applied Physics Letters, 1992, 61, 1260.
- (14) J. L. Herek, W. Wohlleben, R. J. Cogdell, D. Zeidler, and M. Motzkus, *Nature*, 2002, **417**, 533–535.
- (15) E. M. Grumstrup, S.-H. Shim, M. A. Montgomery, N. H. Damrauer, and M. T. Zanni, Optics Express, 2007, 15, 16681–16689.
- (16) J. Savolainen, R. Fanciulli, N. Dijkhuizen, A. L. Moore, J. Hauer, T. Buckup, M. Motzkus, and J. L. Herek, Proceedings of the National Academy of Sciences of the United States of America, 2008, 105, 7641–7646.
- (17) V. I. Prokhorenko, A. M. Nagy, S. A. Waschuk, L. S. Brown, R. R. Birge, and R. J. D. Miller, *Science*, 2006, **313**, 1257–1261.
- (18) V. I. Prokhorenko, A. M. Nagy, L. S. Brown, and R. J. Dwayne Miller, *Chemical Physics*, 2007, 341, 296–309.
- (19) P. van der Walle, M. T. W. Milder, L. Kuipers, and J. L. Herek, Proceedings of the National Academy of Sciences of the United States of America, 2009, 106, 7714–7717.
- (20) M. Spanner, C. A. Arango, and P. Brumer, The Journal of Chemical Physics, 2010, 133, 151101.
- (21) G. Katz, M. A. Ratner, and R. Kosloff, New Journal of Physics, 2010, 12, 015003.
- (22) C. A. Arango and P. Brumer, The Journal of Chemical Physics, 2013, 138, 071104.

#### Chapter 7 References

- K. J. Takeuchi, M. S. Thompson, D. W. Pipes, and T. J. Meyer, *Inorganic Chemistry*, 1984, 23, 1845–1851.
- (2) H.-W. Tseng, R. Zong, J. T. Muckerman, and R. Thummel, *Inorganic Chemistry*, 2008, 47, 11763–11773.
- (3) Z. Deng, H.-W. Tseng, R. Zong, D. Wang, and R. Thummel, *Inorganic Chemistry*, 2008, 47, 1835– 1848.
- (4) J. J. Concepcion, J. W. Jurss, J. L. Templeton, and T. J. Meyer, Journal of the American Chemical Society, 2008, 130, 16462–.
- (5) J. J. Concepcion, J. W. Jurss, M. K. Brennaman, P. G. Hoertz, A. O. T. Patrocinio, N. Y. Murakami Iha, J. L. Templeton, and T. J. Meyer, Accounts of Chemical Research, 2009, 42, 1954–1965.
- (6) D. J. Wasylenko, C. Ganesamoorthy, M. A. Henderson, B. D. Koivisto, H. D. Osthoff, and C. P. Berlinguette, *Journal of the American Chemical Society*, 2010, **132**, 16094–16106.
- (7) D. J. Wasylenko, C. Ganesamoorthy, B. D. Koivisto, M. A. Henderson, and C. P. Berlinguette, *Inor-ganic Chemistry*, 2010, 49, 2202–2209.
- (8) L. L. Duan, Y. H. Xu, P. Zhang, M. Wang, and L. C. Sun, *Inorganic Chemistry*, 2010, 49, 209–215.
- (9) L. Duan, C. M. Araujo, M. S. G. Ahlquist, and L. Sun, Proceedings of the National Academy of Sciences, 2012, 109, 15584–15588.
- E. Jakubikova, W. Z. Chen, D. M. Dattelbaum, F. N. Rein, R. C. Rocha, R. L. Martin, and E. R. Batista, *Inorganic Chemistry*, 2009, 48, 10720–10725.
- (11) D. H. Oh and S. G. Boxer, Journal of the American Chemical Society, 1989, 111, 1130–1131.
- (12) M. A. Webb, F. J. Knorr, and J. L. McHale, Journal of Raman Spectroscopy, 2001, 32, 481–485.
- (13) E. M. Kober, B. P. Sullivan, and T. J. Meyer, *Inorganic Chemistry*, 1984, 23, 2098–2104.
- (14) S. A. Miller and A. M. Moran, Journal of Physical Chemistry A, 2010, 114, 2117–2126.

- (15) S. Wallin, J. Davidsson, J. Modin, and L. Hammarström, *Journal of Physical Chemistry A*, 2005, 109, 4697–4704.
- (16) S. M. Scott, A. K. Burrell, P. A. Cocks, and K. C. Gordon, Journal of the Chemical Society-Dalton Transactions, 1998, 3679–3684.
- (17) E. H. Yonemoto, R. L. Riley, Y. I. Kim, S. J. Atherton, R. H. Schmehl, and T. E. Mallouk, Journal of the American Chemical Society, 1992, 114, 8081–8087.
- (18) J. Winkler, T. L. Netzel, and N. Sutin, Journal Of The American Chemical Society, 1987, 109, 2381–2392.
- (19) S. Záliš, C. Consani, A. El Nahhas, A. Cannizzo, M. Chergui, F. Hartl, and A. Vlček, *Inorganica Chimica Acta*, 2011, **374**, 578–585.
- J. T. Hewitt, P. J. Vallett, and N. H. Damrauer, The Journal of Physical Chemistry A, 2012, 116, 11536–11547.
- (21) W. Henry et al., Journal of Physical Chemistry A, 2008, 112, 4537–4544.
- (22) R. Berger and D. Mcmillin, *Inorganic Chemistry*, 1988, 27, 4245–4249.
- (23) G. B. Shaw, D. J. Styers-Barnett, E. Z. Gannon, J. C. Granger, and J. M. Papanikolas, Journal of Physical Chemistry A, 2004, 108, 4998–5006.
- (24) T. Ishizuka, T. Sawaki, S. Miyazaki, M. Kawano, Y. Shiota, K. Yoshizawa, S. Fukuzumi, and T. Kojima, *Chemistry-A European Journal*, 2011, **17**, 6652–6662.
- (25) D. Powell and P. Lay, *Inorganic Chemistry*, 1992, **31**, 3542–3550.
- (26) T. Sugaya and M. Sano, *Inorganic Chemistry*, 1993, **32**, 5878–5879.
- (27) M. J. Weaver and S. M. Nettles, *Inorganic Chemistry*, 1980, 19, 1641–1646.
- (28) K. Lashgari, M. Kritikos, R. Norrestam, and T. Norrby, Acta Crystallographica Section C: Crystal Structure Communications, 1999, 55, 64–67.
- (29) L. Hammarström and O. Johansson, Coordination Chemistry Reviews, 2010, 254, 2546–2559.
- (30) J. Van Houten and R. J. Watts, Journal of the American Chemical Society, 1975, 97, 3843–3844.

- (31) R. Sriram and M. Z. Hoffman, Chemical Physics Letters, 1982, 85, 572–575.
- (32) M. L. Fetterolf and H. W. Offen, Journal Of Physical Chemistry, 1986, 90, 1828–1830.
- (33) A. Masuda and Y. Kaizu, Inorganic Chemistry, 1998, 37, 3371–3375.
- (34) M. Kovács and A. Horváth, Inorganica Chimica Acta, 2002, 335, 69–76.
- (35) P. Y. Chen and T. J. Meyer, *Chem. Rev*, 1998, **98**, 1439–1477.
- D. W. Thompson, J. F. Wishart, B. S. Brunschwig, and N. Sutin, Journal of Physical Chemistry A, 2001, 105, 8117–8122.
- (37) E. M. Kober, J. L. Marshall, W. J. Dressick, B. P. Sullivan, J. V. Caspar, and T. J. Meyer, *Inorganic Chemistry*, 1985, 24, 2755–2763.
- (38) J.-J. Max and C. Chapados, The Journal of Chemical Physics, 2009, 131, 184505.
- (39) A. Hazra, A. V. Soudackov, and S. Hammes-Schiffer, Journal of Physical Chemistry Letters, 2011, 2, 36–40.
- (40) E. M. Arrnett and D. R. McKelvey, in *Solute-Solvent Interactions*, ed. J. F. Coetzee and C. D. Ritchie, Marcel Dekker, New York, 1969, pp. 343–399.
- (41) J. Bigeleisen, The Journal of Chemical Physics, 1960, 32, 1583.
- (42) J. T. Hupp and M. J. Weaver, Inorganic Chemistry, 1984, 23, 3639–3644.
- (43) A. Soper and C. Benmore, *Physical Review Letters*, 2008, **101**, 065502.
- (44) D. J. Wasylenko, C. Ganesamoorthy, M. A. Henderson, B. D. Koivisto, H. D. Osthoff, and C. P. Berlinguette, *Journal Of The American Chemical Society*, 2010, **132**, 16094–16106.
- (45) A. Kimoto, K. Yamauchi, M. Yoshida, S. Masaoka, and K. Sakai, *Chemical Communications*, 2012, 48, 239–241.
- (46) K. Winkler, J. Lindner, H. Bürsing, and P. Vöhringer, The Journal of Chemical Physics, 2000, 113, 4674.
- (47) C. P. Lawrence and J. L. Skinner, The Journal of Chemical Physics, 2003, 118, 264.

- (48) Y. L. A. Rezus and H. J. Bakker, The Journal of Chemical Physics, 2005, 123, 114502.
- (49) D. Laage and J. T. Hynes, *Science*, 2006, **311**, 832–835.
- (50) K. J. Tielrooij, C. Petersen, Y. L. A. Rezus, and H. J. Bakker, *Chemical Physics Letters*, 2009, 471, 71–74.
- R. A. Nicodemus, S. A. Corcelli, J. L. Skinner, and A. Tokmakoff, *Journal Of Physical Chemistry B*, 2011, 115, 5604–5616.

# Appendix A

#### Supporting Information for Chapter 2

#### A.1 Additional Information about the Ultrafast Spectrometer

Both the instrument response function (IRF) and temporal resolution of the spectrometer were characterized by cross-correlation of the pump and probe pulses in neat solvent. The temporal width of the IRF was quantified by fitting the absolute value of the pump probe cross-correlation envelop in neat acetonitrile to a Gaussian function.[1] Representative temporal FWHM value measured at 380, 400, 480, and 620 nm are  $300 \pm 24$  fs,  $280 \pm 30$  fs,  $190 \pm 25$  fs and  $210 \pm 23$  fs respectively with the error bars based on several independent measurements. The measured IRF is much longer than the pump pulse duration due to significant chirp of our probe pulse. The relative thickness of our sample cell (1.25 mm windows and 2 mm sample volume; NGS Precision Cells, 61UV2) also likely contribute to the temporal width of the IRF. Nonetheless, we are still able to resolve sub-50 fs dynamics as evidenced by the TA signal collected in neat chloroform (Figure A.1). Chirp correction of the spectral and kinetics data was accomplished by setting the positive peak of the pump-probe cross correlation at each wavelength to t = 0.[1]

## A.2 Details of Data Collection Procedures, Chirp Correction, and Fitting Practices Used For Collection of the Ultrafast Data

When calculating time points to visit in a single wavelength transient kinetics scans a quasi-logarithmic approach to time step spacing was employed.<sup>[2]</sup> This approach ensures that the time decades from -1 to 1 ps, 1 to 10 ps, 10 to 100 ps... all contain an equal number of data points and, therefore, when fitting routines



Figure A.1: Top: Magic angle TA of neat  $\text{CHCl}_3$  collected using a pump pulse centered at 525 nm and probing at 600 nm. The inset shows an enlarged picture of the observed beat pattern. Bottom: FFT of the data presented in the inset. The peaks at 260 cm<sup>-1</sup> (period = 127 fs), 366 cm<sup>-1</sup> (period = 91 fs), and 667 cm<sup>-1</sup> (period = 50 fs) all correspond to known modes of  $\text{CHCl}_3$ .

are applied each temporal decade receives equally weight.

Global fitting of the data was accomplished using IGOR Pro and consisted of simultaneously fitting

three spectrally distinct sets of kinetics data to an exponential model of the type shown in Eq A.1:

$$-\Delta T(t) = \sum_{i} A_i e^{-t/tau_i} + y_0 \tag{A.1}$$

Here,  $-\Delta T(t)$  refers to the negative change in transmittance as a function of time (t), which is the way the data were collected and presented, and  $y_0$  is a time independent offset. For  $[\operatorname{Ru}(\operatorname{tpy})(\operatorname{ttpy})]^{2+}$  and  $[\operatorname{Ru}(\operatorname{ttpy})_2]^{2+}$ , single wavelength kinetics were collected at 400, 480, and 620 nm while for  $[\operatorname{Ru}(\operatorname{tpy})_2]^{2+}$ kinetics were collected at 380, 475 and 620 nm. The time constants and pre-exponential values reported in the manuscript are an average of the results from global fitting three independent data sets. Thus, a total of nine independent data traces, three per wavelength, were collected for each complex. The uncertainties reported ( $2\sigma$ ) for data at any given wavelength are two times the standard deviation of the three independent data sets collected. To exclude artifacts of the pump-probe overlap in the fitting routine, only data points greater than  $\approx 400$  fs after t = 0 were included. For the data collected at 380 nm, where the IRF is significantly longer, only data points greater than  $\approx 500$  fs after t = 0 were included. Normalization of the raw - $\Delta T$  data was done by setting the value of the first data point used for fitting to 1 or -1 for absorptive or bleach signals respectively. The kinetics and spectra presented in this chapter represent an average of 4 scans.

# A.3 Deriving the <sup>3</sup>MLCT<sup>-3</sup>MC $K_{eq}$ and associated rate constants in [Ru(tpy)<sub>2</sub>]<sup>2+</sup> using a pre-equilibrium assumption

For clarity, we first restate Eq 2.1 from Chapter 2 below as Eq.

$${}^{3}\text{MLCT} \xrightarrow[k_{h}]{k_{h}} {}^{3}\text{MC} \xrightarrow{k_{h}} {}^{1}\text{GS}$$
 (A.2)

Making use of a pre-equilibrium (between the <sup>3</sup>MLCT and <sup>3</sup>MC) approximation, the equilibration timescale (referred to as  $\tau_{eq}$ , Eq. A.3) and the long-time behavior of population in each state can be expressed as follows:[3]

$$\tau_{eq} = \frac{1}{k_a + k_b} \tag{A.3}$$

$$[MLCT](t) = \frac{k_b}{k_a + k_b} [MLCT_0] e^{-kt}$$
(A.4)

$$[MC](t) = \frac{k_a}{k_a + k_b} [MLCT_0] e^{-kt}$$
(A.5)

$$[GS](t) = [MLCT_0](1 - e^{-kt})$$
(A.6)

Where 
$$k = \frac{k_a k_c}{k_a + k_b}$$
 (A.7)

The 2.3 ps dynamics observed in the data collected at 380 and 620 nm is a direct measurement of  $\tau_{eq}$  while the overall 124 ps decay component is equal to k. If one assumes that <sup>3</sup>MLCT-<sup>3</sup>MC equilibration is complete before any excited-state population is lost, the equilibrium amounts of <sup>3</sup>MLCT and <sup>3</sup>MC species, respectively, are given by:

$$[MLCT]_{eq} = \frac{k_b}{k_a + k_b} [MLCT_0] = k_b \times \tau_{eq} \times [MLCT]_0$$
(A.8)

$$[MC]_{eq} = \frac{k_b}{k_a + k_b} [MLCT_0] = k_a \times \tau_{eq} \times [MLCT]_0$$
(A.9)

Utilizing the measured equilibration time of 2.3 ps, the sum of the two pre-exponential components measured at 380 nm (1.08; which we assume directly reflects the initial <sup>3</sup>MLCT population  $[MLCT]_0$ ), and the preexponential of the long time component measured at 380 nm (0.92; reflecting  $[MLCT]_{eq}$ ), we can estimate  $k_b = 0.37 \text{ ps}^{-1}$  directly from Eq. A.8. With this value (and the equilibration time of 2.3 ps) we can determine  $k_a = 0.064 \text{ ps}^{-1}$  from Eq. A.3. The equilibrium constant  $K_{eq} = 0.17$  follows from the expression  $K_{eq} = k_a/k_b$ . Finally, from the expression for k (Eq. A.7) and its measure of 1/124 ps we can determine  $k_c = 0.054 \text{ ps}^{-1}$ , corresponding to the <sup>3</sup>MC  $\rightarrow$  <sup>1</sup>GS intersystem crossing rate constant.

# A.4 Estimating the Molar Absorptivity of $[Ru^{III}(tpy^{-})(ttpy)]^{2+}$ and $[Ru^{III}(tpy)(ttpy^{-})]^{2+}$ using the Isoabsorptive Transient Absorption Spectra

To develop a deeper understanding of the spectro-temporal dynamics of  $[Ru(tpy)(ttpy)]^{2+}$  following <sup>1</sup>MLCT excitation, we devised an analysis scheme to estimate the excited-state molar absorptivity of the tpy-localized ( $[\operatorname{Ru}^{\operatorname{III}}(\operatorname{tpy}^{\neg})(\operatorname{ttpy})]^{2^+}$ ) and ttpy-localized ( $[\operatorname{Ru}^{\operatorname{III}}(\operatorname{tpy})(\operatorname{ttpy}^{\neg})]^{2^+}$ ) species at 400 nm. At the outset it should be noted that measuring the absolute excited-state molar absorptivity of a complex using TA methods is difficult and requires, amongst other things, a detailed knowledge of the number of excited molecules in the sample, a homogenous transverse distribution of excited-states within the sample volume, and minimal amounts of scattering, fluorescence and phosphorescence.[4] Accordingly, the values reported herein are meant for comparative purposes only and should not be regarded as an accurate measurement of the true excited-state molar absorptivity of these complexes. The transient signal at 400 nm in each complex is assumed to be composed of both excited-state absorption and ground state bleaching contributions. Therefore, the measured  $-\Delta T/T$  signal can be approximated by Eq. A.10 where  $\epsilon_{ex}$  and  $\epsilon_{gs}$  are the molar absorptivity of the ground and excited-states at 400 nm, respectively, l is the excitation path length, and  $N_{ex}$  is the number of excited states.

$$-\Delta T/T \approx (\varepsilon_{ex} - \varepsilon_{gs}) * (l) * (N_{ex}) \tag{A.10}$$

This expression ignores scattering and emission, which occurs at much redder wavelengths in these complexes. Homogenous distribution of excited-states within the sample volume is also assumed. Using the isoabsoprtive transient spectra collected at 10 ps (See Chapter 2), the values for  $\epsilon_{gs}$  from our ground state molar absorption measurements, and the power and central frequency of the excitation laser pulse (needed to approximate the number excited-states), the  $\epsilon_{ex}$  of  $[\operatorname{Ru}(\operatorname{tpy})_2]^{2+}$ ,  $[\operatorname{Ru}(\operatorname{tpy})(\operatorname{ttpy})]^{2+}$ , and  $[\operatorname{Ru}(\operatorname{ttpy})_2]^{2+}$  at 400 nm are estimated to be 8,700 M<sup>-1</sup> cm<sup>-1</sup>, 13,200 M<sup>-1</sup> cm<sup>-1</sup>, and 22,200 M<sup>-1</sup> cm<sup>-1</sup>, respectively. For  $[\operatorname{Ru}(\operatorname{tpy})_2]^{2+}$ , the <sup>3</sup>MLCT absorption is thought to be primarily a result of reduced try ligand absorption. In  $[\operatorname{Ru}(\operatorname{tpy})(\operatorname{ttpy})]^{2+}$  absorption is attributed to the reduced ttpy ligand (i.e.- $[\operatorname{Ru}^{\mathrm{III}}(\operatorname{tpy})(\operatorname{ttpy})]^{2+}$ ). The <sup>3</sup>MLCT absorption of  $[\operatorname{Ru}(\operatorname{ttpy})_2]^{2+}$  is thought to have contributions from both reduced and neutral ttpy ligand absorption. Therefore, assuming a value of 13,200 M<sup>-1</sup> cm<sup>-1</sup> for the reduced ttpy ligand absorption, we estimate the neutral ttpy ligand molar absorptivity at 400 nm to be 9,000 M<sup>-1</sup> cm<sup>-1</sup>. With these values we are able to estimate the molar absorption at 400 nm for the tpy-localized ( $[\operatorname{Ru}^{\mathrm{III}}(\operatorname{tpy}^{--})(\operatorname{ttpy}^{--})]^{2+}$ ) and ttpy-localized ( $[\operatorname{Ru}^{\mathrm{III}}(\operatorname{tpy})(\operatorname{ttpy}^{--})]^{2+}$ ) and ttpy-localized configuration, absorption would result from both the reduced ttpy ligand and the neutral ttpy ligand configuration, absorption at 400 nm for the tpy-localized ( $[\operatorname{Ru}^{\mathrm{III}}(\operatorname{tpy}^{--})(\operatorname{ttpy}^{--})]^{2+}$ ) and ttpy-localized configuration, absorption would result from both the reduced ttpy ligand and the neutral ttpy ligand giving a total excitedstate molar absorption of  $\approx 17,800 \text{ M}^{-1} \text{ cm}^{-1}$ . The ttpy-localized configuration would be primarily reduced ttpy ligand absorption giving a total <sup>3</sup>MLCT molar absorption of only  $\approx 13,200 \text{ M}^{-1} \text{ cm}^{-1}$ . The tpy-localized <sup>3</sup>MLCT is, therefore, expected to be significantly more absorptive at 400 nm than the ttpy-localized <sup>3</sup>MLCT. Accordingly, as we predict that the initial <sup>3</sup>MLCT has a significant amount of both tpy-localized and ttpylocalized <sup>3</sup>MLCT configurations, the overall absorptive signal at 400 nm can be expected to decrease as the system thermalizes to the low energy ttpy-configuration via ILET of the type  $[\text{Ru}^{\text{III}}(\text{tpy}^{--})(\text{ttpy})]^{2+} \rightarrow$  $[\text{Ru}^{\text{III}}(\text{tpy})(\text{ttpy}^{--})]^{2+}$ . That this decrease in absorption is experimentally observed to be concomitant with an increase in the reduced ttpy absorption feature from 515 – 650 nm supports our assignment of the 3.3 ps dynamic to  $[\text{Ru}^{\text{III}}(\text{tpy}^{--})(\text{ttpy})]^{2+} \rightarrow [\text{Ru}^{\text{III}}(\text{tpy})(\text{ttpy}^{--})]^{2+}$  ILET.

#### Appendix A

- S. A. Kovalenko, A. L. Dobryakov, J. Ruthmann, and N. P. Ernsting, *Physical Review A*, 1999, 59, 2369–2384.
- (2) U. Megerle, I. Pugliesi, C. Schriever, C. F. Sailer, and E. Riedle, Applied Physics B, 2009, 96, 215–231.
- (3) M. Rae and M. N. Berberan-Santos, Journal of Chemical Education, 2004, 81, 436–440.
- (4) R. Bonneau, I. Carmichael, and G. L. Hug, Pure and Applied Chemistry, 1991, 63, 290-299.

# Appendix в

# Supporting Information for $[Ru(tpy-An)(tpy)]^{2+}$

# B.1 Calculating the redox potentials for the two steps in the Dexter energy transfer process

As discussed in Chapter 3, the <sup>3</sup>MLCT  $\rightarrow$  <sup>3</sup>An energy transfer process is thought to occur via a Dexter energy transfer process. This process can be conceptualized as a double electron transfer process with the first step being either oxidation of the anthracene and reduction of the Ru(III) center, see Equations B.1, or reduction of the anthracene and oxidation of the MLCT excited state, see Equation B.2.

$$[Ru^{III}(tpy^{-})(tpy)]^{2++}An \rightarrow [Ru^{II}(tpy^{-})(tpy)]^{++}An^{+}$$
(B.1)

$$[Ru^{III}(tpy^{-})(tpy)]^{2++}An \rightarrow [Ru^{III}(tpy)(tpy)]^{3++}An^{-}$$
(B.2)

Using the oxidation and reduction potentials reported in Chapter 3, the MLCT  $E_{00}$  value, and the oxidation and reduction potentials for anthracene the free energy change for the reactions given in Equation B.1 and Equation B.2 can be calculated. The redox reaction involving the  $[Ru(tpy)(tpy-An)]^{2+}$  are shown below:

Reductive Quenching: 
$$[\operatorname{Ru}^{\operatorname{III}}(\operatorname{tpy}^{-})(\operatorname{tpy})]^{2+} + e^{-} \longrightarrow [\operatorname{Ru}^{\operatorname{III}}(\operatorname{tpy}^{-})(\operatorname{tpy})]^{+}$$
  
Oxidative Quenching:  $[\operatorname{Ru}^{\operatorname{III}}(\operatorname{tpy})(\operatorname{tpy})]^{3+} + e^{-} \longrightarrow [\operatorname{Ru}^{\operatorname{III}}(\operatorname{tpy}^{-})(\operatorname{tpy})]^{2+}$ 

The potential for both of these half reactions can be calculated as follows:

$$Reductive \, Quenching = E_{red^{2+/+}} + E_{00} = -1.31 + 2.1 \, eV = 0.79 \, V \, (SCE)$$

$$Oxidative \, Quenching = E_{red^{3+/2+}} - E_{00} = 1.25 - 2.1 \, eV = -0.85 \, V \, (SCE)$$

Using these values and the oxidation and reduction potentials for anthracene (1.07 and -1.97 V vs SCE) the  $E_{rxn}$  for Equations B.1 and B.2 can be calculated as follows:

$$E_{rxn 1} = \underbrace{0.79 V}_{cathode} - \underbrace{(1.37 V)}_{anode} = -0.58 V$$
$$E_{rxn 2} = \underbrace{-1.97 V}_{cathode} - \underbrace{(-0.85 V)}_{anode} = -1.12 V$$

These results show that the first steps is a possible mechanism involving double electron transfer are quite endergonic (recall  $\Delta G \propto -E_{rxn}$ ). Therefore, we do not expect such a mechanism to be contributing to the observed dyanimes.

# B.2 <sup>1</sup>H-NMR spectrum of $[Ru(tpy-An)(tpy)]^{2+}$



Figure B.1: <sup>1</sup>H-NMR of  $[Ru(tpy-An)(tpy)]^{2+}$  in d-acetonitrile.

# Appendix c

#### Supporting Information for Chapter 4

#### C.1 <sup>1</sup>H-NMR spectra

#### $C.2 \qquad A \rightarrow B \rightarrow C \text{ Kinetics Model}$

In deriving a fitting model for the two ET dyads characterized we relied on the simple three state picture shown in Figure C.3. Based on this model the change in population of each state can be expressed



Figure C.1: <sup>1</sup>H-NMR spectra of  $[Ru(tpy)(tpy-p-MV)]^{4+}$  in d-acetonitrile.



Figure C.2: <sup>1</sup>H-NMR spectra of  $[Ru(ttpy)(tpy-p-MV)]^{4+}$  in d-acetonitrile.

as:

$$\frac{\partial^{3}MLCT}{\partial t} = -k_{ET} \cdot [^{3}MLCT] \tag{C.1}$$

$$\frac{\partial^3 ET}{\partial t} = k_{ET} \cdot [^3 MLCT] - k_{BET} \cdot [^3 ET]$$
(C.2)

$$\frac{\partial GS}{\partial t} = k_{BET} \cdot [{}^{3}ET] \tag{C.3}$$

Integrating these expression the total transient signal can be expressed as

$$\begin{aligned} Signal(\lambda, t) &= A_{\lambda} \cdot e^{-k_{ET} \cdot t} + B_{\lambda} \cdot \frac{k_{ET}}{k_{BET} - k_{ET}} \cdot \left(e^{-k_{ET} \cdot t} - e^{-k_{BET} \cdot t}\right) \\ &- C_{\lambda} \cdot \left(\frac{k_{BET}}{k_{BET} - k_{ET}} \cdot e^{-k_{ET} \cdot t} - \frac{k_{ET}}{k_{BET} - k_{ET}} \cdot e^{-k_{BET} \cdot t}\right) + y_{0} \end{aligned}$$

where A, B, and C are the molar absorptivity of the  ${}^{3}MLCT$ ,  ${}^{3}ET$ , and GS at a given wavelength,  $\lambda$ , convolved with the effective experimental path length.



Figure C.3: The three state picture used to derive the fitting model employed for fitting the kinetics data collected at 420 and 620 nm for  $[\text{Ru}(\text{tpy})(\text{tpy}-\text{p}-\text{MV})]^{4+}$  and  $[\text{Ru}(\text{tpy})(\text{tpy}-\text{p}-\text{MV})]^{4+}$ . The initial intersystem crossing (ISC) has been omitted because it occurs on a sub-100 fs timescale, which is shorter than the time resolution of the spectrometer. The two processes shown in black,  $k_o$  and  $k_{REV}$  have also been ignored as they are orders of magnitude smaller than  $k_{ET}$  and  $k_{BET}$ .

	Average $A \ (\pm 2\sigma)$	Average $B \ (\pm 2\sigma)$	Ratio $(B/A)$
Case 1	1.17(0.021)	3.3(0.16)	2.8
$Case \ 2$	1.7(0.1)	9.07(0.3)	5.3

Table C.1: A and B coefficients from fitting the kinetics collected 415 nm for  $[Ru(tpy)(tpy-p-MV)]^{4+}$  to either case 1 ( $\tau_1 = ET$  and  $\tau_2 = BET$ ) or case 2 ( $\tau_1 = BET$  and  $\tau_2 = ET$ )

## C.3 Assigning the ET and BET timescale based on Analysis of the Pre-Exponential Values

As commented on in Chapter 4, fitting the rise and decay dynamics observed in  $[Ru(tpy)(tpy-p-MV)]^{4+}$  and  $[Ru(ttpy)(tpy-p-MV)]^{4+}$  with the model given in Equation ?? results in an ambiguous situation where equally good fits result from assuming  $\tau_1 = ET$  and  $\tau_2 = BET$  (case 1) or  $\tau_1 =$ BET and  $\tau_2$ =ET (case 2). If the loss of population from the <sup>3</sup>MLCT could be independently measured then differentiation between case 1 and case 2 would be possible, however, no such experimental technique is currently available in our lab. The absorption spectrum of the  ${}^{3}MLCT$  and  ${}^{3}ET$  overlap at all the probe colors accessible with our current current ultrafast spectrometer set-up and the time correlated single photon counting instrument in lab has a time resolution that is too long to be of any use ( $\approx 60$  ps). Therefore, to assign  $\tau_1$  and  $\tau_2$  to ET and BET we have relied on an analysis of the magnitude of the A and B coefficients at 415 nm, which are proportional to the molar absorptivity of the  ${}^{3}MLCT$  and  ${}^{3}ET$ , that result from assuming case 1 and case 2. As shown in Table C.1, when assuming case 1 the magnitude of B is almost three times that of A while in case 2 B is 5.33 times larger. The molar absorptivity of the <sup>3</sup>ET species at 415 nm,  $B_{415}$ , is estimated to be approximately 40,000 cm<sup>-1</sup> M<sup>-1</sup> based on comparison with the molar absorption of the one-electron reduced  $MV^{2+}$ . The molar absorption the <sup>3</sup>MLCT is approximated as 13,000 cm<sup>-1</sup> M<sup>-1</sup>based on the analysis of reduced ttpy ligand absorption detailed in Appendix A. Based on these values the B/A ratio is expected to be 3.1, which is quite close to the ratio observed in case 1. Based on this analysis we, therefore, have assigned  $\tau_1 = \text{ET}$  and  $\tau_2 = \text{BET}$  (case 1). We note that these results also agree with the ET and BET assignment made in Ru(II) tris-bidentate analogs. [1–3]

#### Appendix C Bibliography

- (1) M. Abdelhaq, Physical Chemistry, University of Colorado at Boulder, 2012.
- (2) H. A. Meylemans, C. F. Lei, and N. H. Damrauer, *Inorganic Chemistry*, 2008, 47, 4060–4076.
- (3) H. A. Meylemans, J. T. Hewitt, M. Abdelhaq, P. J. Vallett, and N. H. Damrauer, Journal of the American Chemical Society, 2010, 132, 11464–11466.

# Appendix D

# Supporting Information for Photophysical Characterization of $[Ru(tpy-An)(tpy-\phi-MV)]^{4+}$ Pulse Shaping Experiments



Figure D.1: <sup>1</sup>H-NMR of  $[Ru(tpy-An)(tpy-p-MV)]^{4+}$  in d-acetonitrile. Residual DMF solvent from the synthesis is indicated with the red arrow.

# Appendix E

#### Supporting Information for AFC Pulse Shaping Experiments

#### E.1 Power Dependent Study

The power dependence of the kinetics observed in  $[Ru(tpy-An)(tpy-\phi-MV)]^{4+}$  were characterized for pulse energies ranging from 16 nJ/pulse to 120 nJ/pulse. The attentive reader will have recognized these pulse energies are much smaller than those used for characterization in Chapters 2 through 5. The discrepancy is a result a much smaller pump-pulse spot size for the AFC pulse shaping experiments. Representative kinetics collected at 650 nm are shown in Figure E.1. As is evident, the molecular response is unchanged over this range of excitation energies. The AFC experiments conducted typically used excitation pulses with energies between 80 and 100 nJ/pulse, which is within the linear excitation regime.

# E.2 Experimental Signal Simulations for Single Versus Pulse Train Excitation

In effort understand photoinduced observed anto  $_{\mathrm{the}}$ dyanimes when exciting  $[Ru(tpy-An)(tpy-\phi-MV)]^{4+}$  with a train of pulses we have simulated the transient signal at 607 nm. We have considered only dynamics resulting from population in the MLCT and ET states because the anthracene  $T_1$  has minimal absorption and dyanimes at this probe wavelength. The ground state also has minimal absorptive intensity at 607 nm and has, therefore, been omitted as well. The differential equations governing the excited state population are given in Equations E.1 and E.2. The values of  $k_{ET}$  and  $k_{BET}$ were set to  $\frac{1}{1.1 ps}$  and  $\frac{1}{5.5 ps}$ , respectively, in accordance with timescales reported in Chapter 5. In these



Figure E.1: Normalized magic angle transient kinetics of  $[Ru(tpy-An)(tpy-\phi-MV)]^{4+}$  collected at a variety of excitation pulse energies.

expressions Erf corresponds to the error function and is used to impulsively populate the MLCT akin to excitation with a laser pulse. For the simulations detailed herein the derivative of the Erf used gave a Gaussian shape with a temporal FWHM of about 43 fs. The divisor y is used control the population excited by each pulse.

$$\frac{\partial[MLCT]}{\partial t} = -k_{ET}[MLCT]; \ [MLCT]_0 = \frac{(1 + Erf[x \cdot 25])}{y}$$
(E.1)

$$\frac{\partial [ET]}{\partial t} = k_{ET}[MLCT] - k_{BET}[ET]; \ [ET]_0 = 0 \tag{E.2}$$

To replicate the data presented in Chapter 6 we have simulated the excited state dynamics resulting from excitation with the pulse train created when  $\alpha = 1.5$  and  $\tau = 0.5 \, ps$ . This corresponds to a pulse train of approximately 7 pulses with an intensity profile like the auto-correlation shown in the Chapter. The MLCT population dynamics resulting from each pulse is shown in Figure E.2. The signal predicted at 607 nm,  $-\Delta T_{607nm}(t)$ , is given in Equation E.3 and is simply the sum of the population created by each pulse in the train. To account for the ET state being more absorptive than the MLCT at this probe wavelength a



Figure E.2: MLCT population created by each pulse in the pulse train.

multiplier of 2.2 was aded to the ET population.

$$-\Delta T_{607nm}(t) = \sum_{all \ pulses} MLCT_{population} + 2.2 \cdot \sum_{all \ pulses} ET_{population}$$
(E.3)

The signal predicted for the above pulse train, as well as for a single pulse, is given in Figure E.3. Both qualitatively agree with the observed dyanimes. The pulse train excitation results in a lower maximum absorptive signal that converge at sufficiently long times after excitation with that of the single pulse excitation case. Therefore, as discussed in Chapter 6, the early time dyanimes observed in  $[Ru(tpy-An)(tpy-\phi-MV)]^{4+}$ upon pulse train excitation should not be construed as evidence of control over the EnT or ET yield.



Figure E.3: Simulated transient signal measured at 607 nm for  $[Ru(tpy-An)(tpy-\phi-MV)]^{4+}$  when excited with a single pulse (red) and a train of pulses (blue) with inter-pulse spacing of 0.5 ps.

# Appendix **F**

## Supporting Information for $[Ru(bpy)(tpy)(OH_2)]^{2+}$

# F.1 <sup>1</sup>H-NMR spectra of $[Ru(bpy)(tpy)(OH_2)]^{2+}$ and $[Ru(bpy)(tpy)(OD_2)]^{2+}$ species

To establish if substitution of the bound  $OH_2$  for  $OD_2$  in  $[Ru(bpy)(tpy)(OH_2)]^{2+}$  occurs upon dissolution of  $[Ru(bpy)(tpy)(OH_2)](OTf)_2$  in  $D_2O$  <sup>1</sup>H-NMR spectra were collected in a variety of solvents. To determine the chemical shift of the bound water  $[Ru(bpy)(tpy)(OH_2)](OTf)_2$  was first dissolved in d-DMSO (Figure F.1). In agreement with the assignments of Berlinguette and co-workers[1] we observe the bound water proton resonance at  $\approx 5.89$  ppm. We note that complete substitution of the bound  $OH_2$  for a d-DMSO



Figure F.1: <sup>1</sup>H-NMR of  $[Ru(bpy)(tpy)(OH_2)](OTf)_2$  dissolved in d-DMSO. This spectrum was collected immediately after dissolution because the bound  $OH_2$  is completely replaced by DMSO after about 8 hours.



Figure F.2: <sup>1</sup>H-NMR of  $[Ru(bpy)(tpy)(OH_2)](OTf)_2$  collected 5 minuets (blue) and 8 hours (red) after being dissolved in d-DMSO. The resonance near 5.89 ppm, corresponding to a bound water, is clearly lost after prolonged exposure to the weakly coordinating DMSO solvent. The resonance at 10 ppm, corresponding to the bpy proton pointing at the ligated water, also undergoes a considerable shift during this time period further supporting loss of the ligated OH<sub>2</sub>. The resulting complex is presumably  $[Ru(bpy)(tpy)(DMSO)]^{2+}$ . This assignment is supported by the marked shift in UV-vis spectrum also accompanying prolonged time in DMSO.

occurs after prolonged time in solution (Figure F.1). The <sup>1</sup>H-NMR spectrum of  $[Ru(bpy)(tpy)(OH_2)](OTf)_2$ collected immediately after dissolution in 99.99% D<sub>2</sub>O is shown in Figure F.3. As is clear, there is no evidence of a bound water resonance at or in the vicinity of 5.89 ppm. This is interpreted as full replacement of the bound OH<sub>2</sub> for OD<sub>2</sub>. Additional experiments undertaken using d-acetone and CD<sub>2</sub>Cl<sub>2</sub> as solvents (not shown) showed evidence of both OH<sub>2</sub> and solvent bound species. Because both of these solvents are, at best, weakly coordinating the bound OH<sub>2</sub> is thought to be extremely labial (in agreement with the fast replacement of OH<sub>2</sub> for OD<sub>2</sub>). The observation of mixed ligand species in d-acetone and CD<sub>2</sub>Cl<sub>2</sub> solvent systems precluded undertaking experiments with mixed ligand-solvent environments.

## F.2 Bleach recovery dyanimes of $[Ru(tpy)_2]^{2+}$ in H<sub>2</sub>O and D<sub>2</sub>O

To ascertain if inverse isotope effect on the excited state lifetime observed in  $[Ru(bpy)(tpy)(OH_2)]^{2+}$  in  $H_2O$  and  $[Ru(bpy)(tpy)(OD_2)]^{2+}$  in  $D_2O$  is common in these types of complexes or a result of the  $OH_2/OD_2$  ligand interacting with the solvent preliminary kinetics probing the bleach recovery dyanimes of  $[Ru(tpy)_2]^{2+}$


Figure F.3: <sup>1</sup>H-NMR of  $[Ru(bpy)(tpy)(OH_2)](OTf)_2$  dissolved in  $D_2O$ . No evidence of a bound water resonance is observed near 5.89 ppm.

in H<sub>2</sub>O and D<sub>2</sub>O were collected. These data were collected under experimental conditions identical to those detailed in Chapter 2 with the excitation pulse centered at 520 nm. Representative data are shown in Figure F.4. Fitting of the data to a single exponential model returned lifetimes of  $232 \pm 4$  ps and  $254 \pm 5$  ps for H<sub>2</sub>O and D<sub>2</sub>O as the solvent, respectively. The kinetic isotope effect  $(k_{H_2O}/k_{D_2O})$  is 1.09 indicating a weak normal isotope effect. This is contrary to the inverse isotope effect observed in  $[\text{Ru}(\text{bpy})(\text{tpy})(\text{OH}_2)]^{2+}$  and  $[\text{Ru}(\text{bpy})(\text{tpy})(\text{OD}_2)]^{2+}$ , which has a very similar MLCT energetics,[2] and suggests the coordinated water/deuterium oxide is responsible for the shorter excited state lifetime of  $[\text{Ru}(\text{bpy})(\text{tpy})(\text{OD}_2)]^{2+}$  relative to  $[\text{Ru}(\text{bpy})(\text{tpy})(\text{OH}_2)]^{2+}$ .



Figure F.4: Magic angle kinetics probing the bleach recovery dyanimes at 470 nm of  $[\text{Ru}(\text{tpy})_2]^{2+}$  in H<sub>2</sub>O (top) and D<sub>2</sub>O (bottom) following excitation with a sub-50 fs laser pulse centered at about 520 nm. Single exponential fits to the data (solid lines) returned lifetimes of 232 ± 4 ps and 254 ± 5 ps for H<sub>2</sub>O and D<sub>2</sub>O as the solvent, respectively.

**F.3** <sup>3</sup>MLCT Magic angle transient spectra of the excited  $[\mathrm{Ru(bpy)}_3]^{2+}$ of  $\mathbf{in}$ state room temperature acetonitrile and  $\left[\mathrm{Ru}(\mathrm{bpy})(\mathrm{tpy})(\mathrm{OD}_2)\right]^{2+} \text{ in } \mathrm{D}_2\mathrm{O}$ 



Figure F.5: Chirp corrected magic angle transient spectra of  $[Ru(bpy)_3]^{2+}$  collected 10 ps after excitation. Spectral data points were collected every 5 nm and represented by the filled circles. The data contained between the dashed grey lines has been omitted due to contamination by pump scatter. The dip in the absorptive intensity near 620 nm is due to detected emission from the <sup>3</sup>MLCT as determined by collecting spectra at a variety of negative time points.



Figure F.6: Chirp corrected magic angle spectra of  $[Ru(bpy)(tpy)(OD_2)]^{2+}$  in  $D_2O$ . Data points were collected every 5 nm and are represented by solid dots. The data contained between the dashed lines has been omitted due to contamination from pump scatter.

## Appendix F Bibliography

- D. J. Wasylenko, C. Ganesamoorthy, M. A. Henderson, B. D. Koivisto, H. D. Osthoff, and C. P. Berlinguette, *Journal of the American Chemical Society*, 2010, **132**, 16094–16106.
- (2) E. Jakubikova, W. Z. Chen, D. M. Dattelbaum, F. N. Rein, R. C. Rocha, R. L. Martin, and E. R. Batista, *Inorganic Chemistry*, 2009, 48, 10720–10725.