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Experimental Verification of Photon Upconversion Via Cooperative Energy Pooling

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Experimental Verification of Photon Upconversion via Cooperative Energy Pooling

by

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B.A., University of California, Berkeley, 2008

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 Physics

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This thesis entitled:
Experimental Verification of Photon Upconversion via Cooperative Energy Pooling
written by D. H. Weingarten
has been approved for the Department of Physics

Prof. Sean E. Shaheen

Prof. Daniel S. Dessau

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.
Photon upconversion, the process of combining multiple low-energy photons into one higher-energy photon, is a fundamental interaction of light and matter that has applications in fields ranging from cancer therapy to solar energy. However, all photon upconversion methods demonstrated thus far involve challenging aspects, including requirements of high excitation intensities, degradation in ambient air, requirements of exotic materials or phases, or involvement of inherent energy loss processes.

In this thesis I present the first experimental observations and characterization of Cooperative Energy Pooling (CEP), a photon upconversion mechanism that provides a pathway towards overcoming the aforementioned disadvantages. This singlet-based process utilizes a sensitizer-acceptor design in which multiple photoexcited sensitizer chromophores resonantly and simultaneously transfer their energies to a higher-energy state on a single acceptor. This thesis presents two generations of CEP systems along with steady-state and time-resolved spectroscopies verifying the upconversion process. This work is expanded with theoretical calculations and numerical simulations modeling the CEP process, the results of which are used to derive design guidelines for optimized CEP systems.
Dedication

To my parents,
for being the ground beneath my feet.
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Throughout the seven years of this project I have had the assistance, support, and encouragement of a great many people. I never would have finished this research and certainly never would have accomplished anything nearly as valuable without the help of all of the people below, so the least I owe them is a brief expression of gratitude.

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Chapter 1

Introduction

Photon upconversion, the process of combining multiple low-energy photons into one higher-energy photon, has been modeled and studied in various forms since the 1960s [1, 2]. The known mechanisms for photon upconversion—namely excited-state absorption, two-photon absorption (2PA), photon avalanche, energy-transfer upconversion (ETU), second harmonic generation, and triplet–triplet annihilation (TTA)—have been observed in atomic, crystalline, nanoparticle and molecular systems [3], and recent work has demonstrated upconversion yields of up to 38% [4]. Such developments in upconversion have made the technique appealing for a wide range of applications such as deep-tissue photodynamic cancer therapies [5, 6], quantum cryptography [7, 8], three-dimensional data storage [9, 10] and enhanced solar cell devices [11, 12].

However, there are challenges that face the further development and application of these photon upconversion techniques, including requirements of high-intensity excitation sources, deterioration in ambient conditions, requisite use of exotic elements or phases, or fundamental energy loss steps during the upconversion process.

Cooperative energy pooling (CEP) is an energy transfer mechanism that provides an alternative route towards efficient and applicable photon upconversion. CEP is the process of two photoexcited sensitizer chromophores non-radiatively transferring their energy to a single higher-energy singlet state in an acceptor chromophore. Instead of dipole–dipole coupling between the emissive states of the sensitizers and the absorbing
state of the acceptor, as in the Förster resonance energy transfer process (FRET), CEP is carried out via a coupling of the emissive states of both sensitizers with the 2PA tensor of the acceptor [13, 14, 15]. In this way the sensitizers act as photon storage centers that relax the stringent temporal and spatial constraints for achieving 2PA in the acceptor, enabling upconversion with greater efficiency and at reduced excitation intensities.

This thesis introduces the underlying theoretical foundations of CEP and presents experimental observations of successful CEP upconversion in organic, solid-state systems. The thesis begins with a general explanation of the fundamental concepts underlying photon upconversion as an introduction for non-scientists. Chapter 3 then introduces the technical concepts underlying energy transfer among molecules, the various forms of photon upconversion, and the basic rate equations and energetic pathways governing the CEP process.

The remainder of the thesis presents my original work experimentally demonstrating cooperative energy pooling and numerically simulating its behavior. Chapter 4 details what we believe to be the first intentional design of a CEP system and the subsequent measurement of successful CEP upconversion. A review of upconversion literature [16, 17] suggests that CEP has been observed in the past, but that it was misidentified and described empirically. The work presented in this chapter represents the first intentional investigation of CEP upconversion and connection between the observed behavior of the system and its underlying fundamental physical properties. Data from this proof-of-concept implementation is then fit by a proposed model of the CEP process and design guidelines are presented to facilitate further research and development of more optimized CEP systems.

Having observed CEP, the next chapter goes on to develop improved theoretical and numerical tools for understanding and optimizing the CEP process. Chapter 5 begins by deriving the action distance of the CEP process, following a similar
methodology to that used in deriving the Förster radius of FRET. This understanding of the CEP radius is then incorporated into a numerical simulation of CEP. This simulation models the overall CEP efficiency as a function of excitation intensity, sensitizer exciton diffusivity, and CEP radius. The results of this simulation indicate that CEP yield is non-linearly dependent on each of these parameters and that while efficiencies can be improved most directly by increasing all three parameters there exists a threshold value for each individual parameter that must be surpassed in order to achieve appreciable CEP yields.

Finally, chapter 6 presents a second generation of CEP systems utilizing the properties of polymers to yield improved rates of CEP upconversion. Two different polymer-based systems are presented along with preliminary internal quantum yield measurements on one of the systems. This project culminates with femtosecond transient absorption measurements of the CEP film that conclusively demonstrate CEP energy transfer occurring on a tens-to-hundreds of picoseconds timescale. The thesis ends with a brief presentation of promising future directions for CEP research and a summary of the conclusions from this work.
Chapter 2

A general introduction to photon upconversion and cooperative energy pooling

2.1 Introduction

This chapter is aimed towards a general audience and is intended to be a simple and enjoyable introduction to light and the tricks it can play, with an eye towards understanding the new experimental developments presented in this thesis. No science background is needed to understand this chapter and, consequently, all of the scientific work of impact will be presented in further chapters.

We will start with a broad introduction to the concept of light and photons in general. Since the main work in this thesis involves the complex behavior of light and its interactions with matter, it is worth beginning with a foundational approach to how light works and a description of the more simple interactions between light and matter -- absorption and emission.

One of the interesting tricks light can play with matter is called photon upconversion. This is the process of multiple low-energy photons of light getting combined into one higher-energy photon. Since this process plays a central role in the research presented here we will go into some detail about how photon upconversion works, when the process can occur and how to do it efficiently. We will also explain why photon upconversion is scientifically interesting as well as the numerous applications it has
been employed for in medicine, data transmission and storage, microfabrication, and other industries.

Finally, with all that out of the way we will get to the meat of this thesis: cooperative energy pooling. Cooperative energy pooling (CEP) is a form of upconversion that has been previously theorized but never positively identified in the lab. While there exist plenty of other methods for photon upconversion, CEP provides a new tool in the pocket of researchers hoping to play tricks with high-energy light and experimentally validating a novel form of photon upconversion widens the scope for future research. The final portion of this chapter will describe the process of photon upconversion and a brief history of how it came to be discovered, and finally provide a description of the experimental work carried out in verifying that CEP does, in fact, happen in the world. After discussing some of the experiments proving the existence of CEP, we will finish by explaining some computer simulation work that explores some of the finer details of CEP as well as directions for future research that could move the field forward.

2.2 Playing tricks with light

To understand a concept like “photon upconversion via cooperative energy pooling” we have to start with an understanding of light. Any beam of light can be thought of as a stream of many many particles of light. These particles are called photons. If the light is a single color then every photon has that exact same color. However, if the light has many colors in it – like white light, which contains all visible colors – then every photon will have a different color corresponding to the colors present in the light as a whole. Every color of light has a corresponding energy to it. Photons that we see as being the color blue have more energy than red photons. Similarly, invisible ultraviolet (UV) photons have more energy than blue photons and far more energy than invisible infrared (IR) photons.
2.2.1 Absorption and emission

Different materials are capable of absorbing and emitting different energies of light. When a photon comes into contact with a material it generally has three options: pass through the material unobstructed, bounce off the material, or get absorbed. When the photon is transmitted or reflected there is no change in the energy of the photon, though there is a change in its direction if it is reflected. It's when the photon gets absorbed that things get interesting.

When a material absorbs a photon it is the atoms or molecules that make up the material that actually absorb the photon. In these atoms or molecules (we will use the term molecule for the rest of the chapter, but the general process is the same) there are many electrons orbiting around with a particular energy like a tetherball on a string (but one which never slows down). When a photon is absorbed one of these electrons gains all of the energy from that photon and changes into a more energetic orbit, like a tetherball spinning faster and higher around the pole. The molecule is now considered to be in an excited state.

However, a molecule cannot absorb every energy of light. Different molecules can absorb different colors of photons, which is part of what gives objects their color. A particular molecule will be able to absorb light in a certain range of energies – various shades of green, for example – and within that range will be able to absorb some colors more strongly and others less so.

These absorption ranges tend to come in distinct bands. One can think of these bands as separate “shelves” for the electron getting excited – some shelves are lower down and require less energy to get to and some shelves are higher up and require more energy. However, between the shelves is just empty space that an electron can not rest on. This corresponds to a molecule that, for example, can absorb various shades of green but not blues or oranges, but perhaps can absorb some much-higher-
energy UV light. If an incoming photon has energy that is below the lowest “shelf”, or excited state, of the molecule then it will not be absorbed and will simply pass through. Similarly, if the incoming photon has an energy somewhere above the first shelf but with no energy shelves nearby then it can not be absorbed either. Only photons with energies approximately equal to the absorption bands, or shelves, of the molecule will be absorbed. The spacing and shapes of the different absorption bands are unique for each molecule. By measuring the absorption spectrum of a material we can get information that helps uniquely identify it.

**Figure 2.1 | An overview of measuring the absorption spectrum of a liquid.** On the left is a source of white light, illustrated by the different colored lightwaves displayed in the leftmost box. The beam of white light shines through a liquid sample where the green photon is absorbed to leave an electron in a higher-energy state, as shown in the middle box. Also shown in this middle box is how a red photon has too little energy to be absorbed and a blue photon has too much energy to be absorbed. Finally, the light that is not absorbed passes through the sample and is detected at the right. In the above right box is shown the spectrum of light transmitted through the sample, from which we can determine the absorption spectrum of the sample solution. (Image available via Creative Commons; originally by Jon Chui.)

After a molecule absorbs a photon it will not stay excited forever. If nothing else is around to interfere with it, an energized electron in an excited molecule will continue zipping around for a short time (usually a few nanoseconds, which is a few millionths of a millisecond) before it drops back down to the orbit it previously had. But in dropping down and losing that extra energy it will emit a photon with the same amount of energy
it loses. This is called emission and is the process responsible for light bulbs giving off light as well as fluorescent objects glowing.

However, between absorbing the photon and emitting the photon the electron typically loses a little bit of energy. This happens because some of the other electrons and protons in the molecule are shaken up by the change in energy of the excited electron, and in getting shaken up they steal a little bit of energy in the form of heat. When the excited electron drops back down to its original energy level and emits a photon, this photon consequently has less energy than the one that was originally absorbed, causing the emission spectrum of the molecule to look different and slightly redder (less energetic) than the absorption spectrum.

In figure 2.2 we can see an example of the absorption and emission spectra of the molecule Stilbene-420. This molecule is commonly used in laundry detergents as a fabric whitener because it absorbs UV light and emits blue light\(^1\). This means that the fabric does not change color, since the only colors of light this molecule absorbs are invisible, but it does look more white because now it gives off a bluer color that balances out with the yellow colors of older clothing to give the cloth an overall whiter appearance. Science!

One final point to note is that an excited electron will not stay excited forever. While the electron is excited it will interact with all the other electrons and nuclei in the molecule which will eventually jostle it enough to cause it to drop down and emit a photon. The exact way in which an excited electron gets jostled by the other components of the molecule is unique to every molecule, which means that the amount of time an electron stays excited after absorbing a photon is unique to a molecule. Additionally, if the molecule has other molecules nearby then the excited electron can get jostled by those too, causing the electron to lose its energy even quicker. Overall,

\(^1\) Stilbene-420 also has some interesting properties that let it absorb two-photons simultaneously, which will be discussed further below and form a central part of chapter 4.
measuring the absorption and emission spectra of a material gives us information that is relatively unique and helps to identify that molecule and even identify it when it is mixed into a larger material. By taking measurements of how long the material stays excited before it emits light we can get a further piece of identifying information about it as well as information about whether it is being crowded by other neighboring molecules or not.

2.2.2 Introduction to photon upconversion

Photon upconversion is what happens when molecules start playing fancier tricks with photons. Normally two photons can not interact in any way. Two photons that “collide” will actually just pass through each other without any interaction between them, regardless of what energies either of them have. However, certain materials have special properties that allow them to act as photon combiners.
Photon upconversion is the process of two photons being absorbed by a material, then having their energies combined and eventually emitted as a photon with a higher energy than either of the initial photons. In practice, this could look like shining a red light (low energy photons) on an object and seeing it glow blue (emitting high energy photons) – for a photon upconversion process within the visible range of light.

Most processes involving light – like absorption and emission – only deal with a single photon at a time, and hence are directly dependent on the amount of light involved in the process; e.g. the more excitation light the more photons gets absorbed. However, since photon upconversion involves absorbing two photons at a time this process is proportional to the square of the number of incoming photons, making it very inefficient at low light intensities but highly efficient at extreme light intensities. This is the main explanation for why photon upconversion was mostly overlooked by science until the invention of the laser in the late 1950s, which finally provided a means of creating extremely intense sources of light at very particular energies. This was precisely the tool needed to observe photon upconversion, and it is no accident that every form of photon upconversion known today was first observed in the 1960s via laser excitation.

There are a number of ways in which photon upconversion can occur, and we will briefly explain them here. The simplest methods involve one single molecule absorbing two photons. This molecule can absorb two photons simultaneously and get excited to the lowest available energy state in the molecule, and this process is appropriately called Two-Photon Absorption (2PA). This process was first proposed in 1931 by Maria Göppert-Mayer in her doctoral dissertation, but it was not until the invention of lasers that experiment caught up to her theory and 2PA was first observed. Unfortunately, 2PA is generally incredibly inefficient in most molecules and tends to only occur with a few percent efficiency at light intensities equal to about a trillion (1,000,000,000,000) times the light from the sun on a sunny day. The other one-molecule form of upconversion is
called excited state absorption (ESA), which is when a molecule absorbs two photons sequentially to excite an electron up to the first energy “shelf” and from there up to the second. While this process can occur under light sources far less intense than those required for 2PA, it still requires intense light because the second photon must be absorbed before the electron excited from the first photon can decay. This provides only a short window of a few nanoseconds in which the second photon must arrive, and hence requiring both molecules with long-lived excited states and intense excitation sources. However, excited states above the lower-energy excited state tend to live for much shorter times than the first excited state and also tend to let their excited electrons drop down to the first excited state without releasing a photon (i.e. they lose all their excess energy to heat). This means that even after all the work of absorbing two photons and getting to a highly-excited state, most of the time we will simply lose half of that energy to heat and only a very small portion of molecules that absorb two photons will actually emit a photon from the highly excited state, making ESA relatively inefficient.

The final form of photon upconversion that we will discuss is called energy transfer upconversion (ETU). This process involves two different types of molecules: one that is especially good at absorbing light of a particular energy (the donor) and one that steals that energy from the first molecule (the acceptor). For ETU to occur the donor first absorbs a photon to achieve an excited state. If an acceptor is close enough, generally physically next to the donor, then it can steal the energy from the donor to get into its own first excited state, which has nearly the same energy but in a more stable configuration. The acceptor molecule is specially chosen to be able to stay in its first excited state for a long time – thousands or millions of times longer than the donor could – while it waits for the donor to absorb another photon. Once the donor absorbs a second photon the acceptor proceeds to steal that energy as well, boosting it to its second excited state from whence it can drop all the way back to the ground state and emit an upconverted photon.
Within this upconversion category of ETU is a particular type of upconversion called triplet-triplet annihilation (TTA). Traditionally ETU upconversion has been achieved in nanoparticles made out of rare earth elements called lanthanides. These are heavy elements found on the bottom of the periodic table that have special properties that make them suitable for ETU. However, they are only mined from particular parts of the globe and are relatively complicated to refine. TTA is a type of ETU that can be accomplished using organic molecules that can be (relatively) easily synthesized in a lab. These organic molecules achieve the same long-lived excited states as the
lanthanides by using a special type of excited state known as a triplet. TTA can achieve very high efficiency photon upconversion, up to 38% efficiency \([4]\), which is efficient enough to be visible by eye when excited by a normal lamp. However, triplet states lose their long lifetime when exposed to oxygen and can only be used by sacrificing some of the energy of each absorbed photon, resulting in a final upconverted photon with less than two times the energy of the excitation light.

![Image](image.png)

**Figure 2.4 | Demonstration of triplet-triplet annihilation photon upconversion.** This image shows a standard commercial laser pointer exciting TTA photon upconversion from green to purple light strongly enough to be visible by eye. This image taken from work by Singh-Rachford and Castellano \([19]\).

### 2.2.3 Applications of photon upconversion

Since there are so many different manners in which photon upconversion can occur, the process has been experimented on in a large number of different materials and has been observed in atomic, crystalline, nanoparticle, and molecular systems\([3]\).
Such developments in upconversion have made the technique appealing for a wide range of applications, both scientific as well as industrial.

Photon upconversion has promising applications in solar energy. The vast majority of solar panels available today function by absorbing light only up to the first excited state (“energy shelf”) of the solar panel material. This first excited state is called a band gap. All photons with energies less than the energy band gap of the solar panel are simply not absorbed, and all photons with energies above the band gap are successfully absorbed but give up all of their excess energy as heat. This means that there is a trade-off in choosing the band gap of a solar panel material. The higher the band gap the more energy the solar panel will create for every photon absorbed, but the fewer photons there are with enough energy to be absorbed in the first place. On the other hand, the lower the band gap the more photons the solar panel can absorb, but the less energy it will receive from each one. In 1961 William Shockley and Hans Quiesser calculated that, given the solar spectrum and trade-offs in raising or lowering the band gap of a solar panel, the absolute maximum efficiency a solar panel can achieve is 33.7%. That means that with a standard solar panel there will never be a way to harvest two thirds of the sun’s energy. However, adding photon upconversion to a solar cell enables the photons with energies below the band gap to combine together into a photon with enough energy to be absorbed. Adding a photon upconversion component to a solar cell allows us to break the 33.7% limit and build solar panels with efficiencies of up to 51%. Upconversion can essentially function as a turbocharger for solar energy – a slight modification to the panel itself enables far more efficient use of the same energy source it is already receiving.

In the medical world researchers have been applying photon upconversion to treating cancer. Normally, in order to remove cancer surgeons must cut a person

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2 Which is the main reason I was interested in this project in the first place.
3 This maximum efficiency point occurs when the band gap of the solar panel is ~ 1.34 electron Volts, which corresponds to infrared light that we can not see.
open to expose the cancer and then cut it out with a laser. However, deep-tissue photodynamic therapies [5, 6] allow a patient to swallow a pill containing photon upconverting molecules that bind only to the cancer. Doctors then shine infrared laser light onto the patient which passes harmlessly through the body until it encounters the upconversion molecules. The laser light is then upconverted to a much more energetic energy capable of destroying the cancer, but only in the exact location where the infrared laser intersects with the upconversion molecules inside the body. This eliminates the need to surgically cut open a patient as well as allowing for precise targeting of the cancer without putting the rest of the body at risk due to medically dangerous anti-cancer medicines.
In research labs photon upconversion has been used to improve the resolution of microscopes for observing biological materials [20, 21]. Upconversion allows scientists to shine an invisible IR onto a sample and only observe the upconverted glow from precise locations in the sample, allowing microscope measurements to be far more precise and less blurry. Additionally, specific types of upconversion allow the resolution of these microscopes to increase beyond the limits that light would normally allow, enabling scientists to visually see features as small as 30 nanometers [20].

Photon upconversion also has applications in tech with ongoing research into uses in micro-fabrication [22], 3D data storage [9, 10], and quantum cryptography [8, 7]. However, there are challenges that face the further development and application of these photon upconversion techniques. Most of these techniques require very high intensity light sources, which are not economical or convenient in many commercial applications. The materials use in upconversion methods like TTA tend to deteriorate rapidly when exposed to oxygen, which is an obstacle for use in non-laboratory conditions. Lanthanide materials are rare and expensive to mine and nanoparticles generally require expensive laboratories to properly synthesize, making these materials somewhat expensive and hence undesirable for large-scale use.

With the goal of overcoming these challenges, this thesis presents the first experimental observation of a new photon upconversion technique called cooperative energy pooling.

### 2.3 Teaching old photons new tricks: Cooperative Energy Pooling

Cooperative energy pooling (CEP) is a photon upconversion process that puts a new twist on a number of previously discovered upconversion methods. CEP begins with a molecule that is good at 2PA upconversion, allowing it to simultaneously absorb two low-energy photons to achieve a higher-energy excited state, as discussed above.
However, since 2PA is a very inefficient process CEP introduces a second molecule to improve things. Analogously to ETU, where a donor molecule transfers its energy to an already-excited acceptor molecule, this second molecule functions as a donor molecule and efficiently absorbs low-energy light. However, unlike ETU the acceptor molecule cannot steal the energy from an excited donor because it does not have an excited state of its own at that energy. The lowest energy “shelf” in the acceptor is nearly twice the energy of the donor.

The key feature of CEP is that the donor emits light at the same energies that the 2PA molecule (the acceptor) can two-photon absorb at. When two excited donors are near the same acceptor, the acceptor can simultaneously steal the energy from both donors to become excited itself. The acceptor can stay excited for a few nanoseconds on its own and then will drop back down to its ground state, emitting a photon of upconverted light.

Since the acceptor is excited in its lowest energy excited state (i.e. its lowest energy shelf) there is no worry about it decaying down to a lower excited state and losing energy to heat, like in ESA. Since the donors are each absorbing a single photon at a time (rather than absorbing two photons simultaneously) we do not have to worry about the low efficiency of two-photon absorption, like in 2PA. And since the acceptor ends up being in its lowest-energy excited state we do not need to use special lanthanide nanoparticles (like in ETU) or triplet states (like in TTA) in order to preserve the intermediate energy state for a long time. Thus, CEP upconversion has higher emission efficiency than ESA, absorbs light better than 2PA, and can be made out of easier-to-obtain molecules than ETU, and does not have the energy losses or sensitivity to oxygen of TTA systems.

This thesis presents research experimentally demonstrating cooperative energy pooling upconversion. We believe this to be the first experimental work to design a material specifically for CEP upconversion and successfully observe it. The theoretical
work describing how CEP functions was carried out in the 1990s by Jenkins and Andrews [13] but, as far as we are aware, has not been experimentally implemented until now.

However, that does not mean that we are the first experimenters to have measured CEP upconversion. Researchers have been observing upconversion in crystalline materials with trace concentrations of lanthanide elements embedded in them since the 1960s [16]. However, in each of these experiments the upconversion process was either misidentified as ETU or described in broad, observational terms without an understanding of the underlying mechanism. As late as the 1990s groups like Nickoleit et al. [17] were synthesizing custom donor-acceptor molecule pairs and observing upconversion, but misidentifying the upconversion process. With the benefit of hindsight and a careful study of the work of Jenkins and Andrews [13] and LaCount et al. [15], we are able to conclusively identify that the upconversion effect they were observing was due to CEP.

By beginning our experiment with an understanding of the theory behind CEP, we were able to carefully choose our triumvirate of donor and acceptor molecules in order to conclusively demonstrate the efficacy of CEP upconversion. Of particular benefit in these experiments was the fact that CEP does not require particularly complex donor or acceptor molecules. Instead of asking chemists to synthesize complex chemicals for us and carefully using the few milligrams of material that resulted from their months of labor, and instead of spending our entire budget on specially-made rare-earth-element-doped crystals, we were able to order standard dyes from standard commercial companies and observe CEP upconversion in these everyday materials. In fact, the first system in which we measured CEP upconversion was composed of Stilbene-420, the fabric whitener mentioned above in figure 2.2, and a standard low-cost laser dye.

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4 Though not photon upconversion. In this experiment they actually used the upconverted energy to perform a chemical reaction rather than to emit a higher-energy photon, but the upconversion process is similar.
Rhodamine 6G. The easy availability of the molecules used for CEP indicates that CEP might potentially be economically scalable should one of the industrial applications mentioned above become commercializable.

2.3.1 On chance and happenstance: an experimental anecdote

Finally, it is worth mentioning one of the so-stereotypical-I-can’t-believe-it-actually-happened accidents that enabled this whole experiment to succeed.

Early in the project we were attempting to make samples to experiment on by coating a thin glass slide with a mixture of our donor and acceptor molecules. All the theory and models we were aware of at that time indicated that if we were going to be able to see CEP upconversion at all, we were likely to need a sample with a blend of ten donor molecules for every one acceptor molecule. I gave the stock solutions of these molecules to our newest undergrad in the lab, Victor Palacios, and asked him to make these samples at the 10:1 ratio of donors to acceptors. Victor absent-mindedly reversed the ratio, resulting in a nearly clear molecular film when it should have been a deep red. Nonetheless, I put it in the spectrometer and decided to take an experimental measurement.

And immediately witnessed our first observation of CEP upconversion.

We were all very excited by our first breakthrough in the project and immediately asked Victor to go back to the lab and make a sample with the “correct” blend of donor and acceptor molecules so that we could see even more efficient CEP upconversion. He did so, resulting in the rich red-colored films we expected. I eagerly took these samples to the lab and measured...

...absolutely nothing.

Many measurements, a few instances of coprolalia⁵, and many many many samples later we realized that unexpected secondary effects prevented CEP upconversion.

⁵ Coprolalia: the involuntary and repetitive use of obscene language.
from happening in the “good” films, but allowed it to happen in “incorrectly” made films. If Victor had not made the simple mistake of accidentally switching the ratio of our molecular ingredients we would never have seen cooperative energy pooling and I would be presenting a very different, and much less exciting thesis.

Thank you Victor.
Chapter 3

A technical introduction to cooperative energy pooling

3.1 Introduction

This chapter lays out the historical and theoretical foundations of photon upconversion and cooperative energy pooling (CEP) in order to introduce the concepts that will be referenced throughout the rest of this work.

The chapter will begin with a review of the various forms of energy transfer between molecules or ions in a material. Energy transfer is important both as a fundamental mechanism enabling a number of photon upconversion processes as well as enabling long-range diffusion of excitons within a material, effects that are important in CEP. Förster resonance energy transfer (FRET) relies on an overlap of the emission spectrum of a sensitizer chromophore with the absorbance spectrum of an acceptor chromophore, which shares a similar fundamental mechanism to the reliance of CEP on the overlap between a sensitizer’s emission spectrum and the two-photon absorption (2PA) spectrum of an acceptor chromophore. This similarity in function enables us to build off of the techniques used to find the length-scales of FRET to find formulations of the action distance of CEP. Both of these topics are explored more fully in chapter 5. Here we will introduce FRET as well as another form of localized energy transfer, Dexter electron transfer, and review the technical details of their functionality.
The chapter will then proceed to review of the technical background of photon upconversion as a process, including the various upconversion mechanisms studied historically. While cooperative energy pooling as a process is unique in its method of energy transfer, it bears a number of similarities to well-studied upconversion mechanisms that can help place CEP in a more understandable context than an entirely novel phenomenon would be. The first studies of the CEP mechanism were undertaken in the mid 1990s by Robert Jenkins and David Andrews [14, 13] and developed a number of the fundamental ideas underlying the process. We will discuss these papers in the context of previously explored upconversion mechanism.

Finally, having discussed the mechanisms underlying photon upconversion in molecular system, we will examine the theoretical formulation of CEP. While “cooperative sensitization” upconversion had been observed since the late 1960s [23] it was generally explained phenomenologically and without a full understanding of the coupling between the sensitizer and acceptor chromophores. It was not until the 1990s that Jenkins and Andrews [14, 13] were able to lay a robust theoretical foundation underneath the previous experimental observations by deriving the theory of Cooperative Energy Pooling. We will briefly describe this history and then expand on the details of the CEP mechanism as proposed by Jenkins and Andrews, including some of the limitations of the theory as it currently stands and the ways in which it could be expanded. The chapter will conclude with a brief discussion of the advantages of CEP over other upconversion mechanisms as motivation for the work presented in the body of this thesis.

3.2 Energy transfer in photon upconversion systems

Energy transfer plays a key role in a number of photon upconversion systems and in CEP in particular, making it worthwhile to discuss here. There are three energy
transfer processes most pertinent to the systems in question that will be discussed here: radiative energy transfer, Förster resonance energy transfer, and Dexter energy transfer.

### 3.2.1 Radiative energy transfer

The first distinction to make among energy transfer mechanisms is between radiative and non-radiative mechanisms. An energy transfer process that involves a real, measurable photon is inherently a radiative process. This process involves a sensitizer emitting a photon of energy, that photon propagating through space, and the photon subsequently being absorbed by an acceptor. Since the photon must propagate for some duration between emission and absorption events radiative energy transfer is affected by the spatial characteristics of the system. Changes to the spatial configuration of a system can have significant effects on the radiative coupling between sensitizer and acceptor. The overlap of the emission spectra of the sensitizer and acceptor plays a key role in the ability for energy to be transferred from the one to the other and thus radiative energy transfer can be improved by careful selected of matching chromophores. This feature also implies that a characteristic feature of radiative energy transfer is an alteration of the observed far-field emission spectrum of the sensitizer, since the portion of its spectrum that overlaps with the acceptor will be reduced before leaving the material. However, since this interaction is in the far-field and there is no direct coupling between the two chromophores the lifetime of the sensitizer will be unaltered, indicating that the rate of radiative energy transfer is entirely determined by the emissivity of the sensitizer and providing another identifying feature. Combining the features listed and following the presentation of Auzel [3] we find the probability for radiative energy transfer to be

\[
P_{RT} = \frac{\sigma_A}{4\pi r^2 \tau_S} \int g_S(\lambda)g_A(\lambda) d\lambda \tag{3.1}
\]
where $\sigma_A$ is the integrated absorption cross-section of the acceptor, $r$ is the distance between the sensitizer and acceptor chromophores, $\tau_S$ is the radiative lifetime of the sensitizer, and the integral represents the spectral overlap between the emission spectrum of the sensitizer $g_S(\lambda)$ and the absorption spectrum of the acceptor $g_A(\lambda)$. Since the acceptor can not distinguish between the absorption of a photon due to radiative energy transfer versus a photon from an external light source, radiative energy transfer can function as a form of energy trapping since the lifetime of the acceptor excited state will be effectively reset after each radiative transfer event. If a chromophore has significant overlap between its absorption and emission spectra then substantial amounts of radiative energy transfer may occur among the chromophore population, enabling energy migration with a significantly longer lifetime than that of a single excited state.

### 3.2.2 Förster resonance energy transfer

Dipole-dipole coupling may also occur in the near-field, resulting in non-radiative energy transfer. This form of energy transfer was first explored theoretically by Theodor Förster and is known as Förster Resonance Energy Transfer, or FRET, in his honor. In FRET no photon is emitted. Instead, a virtual photon mediates a direct resonance between the emission of the sensitizer and the absorption of the acceptor. Once the dipoles of the sensitizer and acceptor are resonant the excited state of the sensitizer decays simultaneously with an electron being promoted into an excited state of identical energy in the acceptor. This process was shown by Förster to have a rate of

$$
\Gamma_{\text{FRET}}(r) = \frac{\Phi_S k^2}{\tau_S r^6} \left( \frac{9000(\ln 10)}{128 \pi^5 N_A r^4} \right) \int_0^{\infty} F_S(\lambda) \epsilon_A(\lambda) \lambda^4 d\lambda
$$

(3.2)

where $\Phi_S$ is the fluorescent quantum yield of the sensitizer, $k$ is a factor for the relative orientation between sensitizer and acceptor, $\tau_S$ is the lifetime of the excited sensitizer.

---

1 This formulation styled after that of Lakowicz [24].
in the absence of the acceptor, \( r \) is the distance between sensitizer and acceptor chromophores, \( n \) is the refractive index of the medium, and \( N_A \) is Avogadro’s number. \( F_S(\lambda) \) is the fluorescence intensity of the sensitizer in the wavelength range \( \lambda \) to \( \lambda + \Delta \lambda \) with the total intensity normalized to unity. \( \epsilon_A(\lambda) \) is the extinction coefficient of the acceptor a wavelength \( \lambda \).

In can be informative to find the distance at which half of the excited states of a chromophore transfer via the FRET process, a distance generally referred to as the Förster radius \( R_0 \). This distance is found by setting \( \Gamma_{\text{FRET}} \) equal to \( \tau_S \) and solving for \( r \), which yields

\[
R_0^6 = \frac{9000(\ln 10)k^2\Phi_S}{128\pi^5Nn^4} \int_0^\infty F_S(\lambda)\epsilon_A(\lambda)\lambda^4 d\lambda
\]

Since all of the parameters in equation (3.3) are either physical constants or fundamental properties of the sensitizer and acceptor, this formulation allows us to express the FRET rate in much simpler terms:

\[
\Gamma_{\text{FRET}}(r) = \frac{1}{\tau_S} \left( \frac{R_0}{r} \right)^6
\]

From this we can see that if the separation distance is shorter than \( R_0 \) then \( \Gamma_{\text{FRET}} \) will be faster than the decay rate and FRET will be significant, and vice versa for separation distances longer than the Förster radius. Equation (3.4) can be solved to find the overall efficiency of the FRET process, yielding

\[
\Phi_{\text{FRET}} = \frac{R_0^6}{R_0^6 + r^6}
\]

The strong \( r^6 \) dependence in (3.5) shows that small changes in the sensitizer-acceptor separation distance can have large effects on the overall FRET yield. A separation distance of 10% more than \( R_0 \) will yield only 36% efficiency of FRET while a separation 30% less than \( R_0 \) results in 89% of all energy getting transferred via FRET. Due to this strong distance dependence FRET is generally a short-range process with a typical operating range up to about 10 nm.
3.2.3 Dexter electron transfer

Whereas FRET transfers energy via a non-radiative dipole-dipole coupling, Dexter energy transfer utilizes a direct coupling between the electron orbitals of the sensitizer and acceptor to fully exchange electrons and thereby transfer energy. The electron exchange can only happen if the electrons each have access to the corresponding electronic orbitals of the corresponding chromophore and since wavefunctions tend have very short radii (i.e. the electron cloud is small) the range of Dexter electron transfer is
similarly limited to the the wavefunction overlap range – generally < 1 nm. This tends to limit Dexter energy transfer to nearest neighbor and collision-based interactions.

Since the extent of the overlap of the electron clouds is a key factor in Dexter energy transfer, the result is an exponential dependence on the separation distance between the two chromophores. The range of this distance is determined by the extent of the corresponding wavefunctions, and hence by the sum of the van der Waals radii of the chromophores. The rate of Dexter electron exchange is generally given by

\[ \Gamma_{\text{Dex}} \propto \exp \left( -\frac{2r}{L} \right) \int_0^\infty F_S(\lambda) c_A(\lambda) \lambda^4 d\lambda \]

where \( r \) is the separation distance between sensitizer and acceptor chromophores, \( L \) is the sum of the van der Waals radii of the chromophores, and the spectral overlap integral is the same as was present in (3.2).

The exponential dependence the Dexter electron transfer as well as its characteristic length scale being set by such a short distance as the van der Waals radii ensures that Dexter energy transfer will only function at distances shorter than FRET, but that at those length scales Dexter will be the dominant energy transfer mechanism. Finally, it is worth noting that Dexter electron transfer is capable of exchanging electrons in both singlet and triplet excited states, whereas due to spin conservation FRET is only able to effect energy transfer between singlet states as shown in figure 3.1.

\[^2\text{Note that some form a resonance energy transfer can effect energy transfer between triplet states, as discussed in detail by Scholes [25]. However, this energy transfer is not the simple dipole-dipole coupling generally referred to as FRET but rather a superexchange coupling through an extended chain of molecules with the (virtual) electronic states of “bridger” molecules connecting the donor and acceptor. If some of the bridging molecules have some degree of spin-orbit coupling than spin conservation rules may be preserved and allow Coulombic coupling of triplet energy states from the donor to the acceptor. However, this process is estimated to be approximately } \sim 10^{-6} \text{ times as strong a typical FRET and hence is not discussed in detail here.}\]
3.3 Theory of photon upconversion

When a photon is absorbed by a material its energy is fully transferred to the various energetic modes available in that material. If the excited material immediately releases a photon it may do so with the full original amount of energy imparted to it, emitting a photon of identical wavelength to the photon absorbed. However, after absorption it is often the case that some of the photon's energy will be dissipated in various manners through the material. For example, a photon might be absorbed via excitation an electron into the vibrational manifold of a particular excited electron state in a molecule. This vibrational manifold will then very quickly transfer its excess energy to the available phonon modes, leaving the electron in the lowest energy configuration of the state it was excited into. This state will have less energy than the photon original had, so any photon emitted from the molecule will be of a lower energy than the photon absorbed. This shift in energy from the excitation photon to the emitted photon is known as a Stokes shift.

The reverse process is also possible, in which the emitted photon has more energy than the absorbed photon. This process is called anti-Stokes emission. Conservation of energy requires that this excess energy must be extracted from some energy source within the emitting material and historically that source tended to be the phonon bath. Consequently, most anti-Stokes emission observed before the 1960s only had an energy increase of a few $k_B T$.

Photon upconversion is the process of combining multiple low-energy photons into one higher energy photon. Historically this process fell under the category of anti-Stokes emission. However, it was not until the discovery and observation of mechanisms more energetically efficient than phonon-based anti-Stokes emission that the process of photon upconversion became of applicable interest and wider study. The advent of the laser in the 1960s finally provided experimentalists with the photon fluxes required
to observe the non-linear photon upconversion mechanisms that had been theorized previously but had previously evaded observation. Here we will briefly introduce each of the known forms of photon upconversion.

The simplest form of photon upconversion is Excited state absorption (ESA). In this process a system absorbs a single photon to achieve an excited state, then subsequently absorbs a second photon to achieve a more energetic excited state. This process relies on the absorption cross-section of both the ground state and the first excited state, but as these are both linear absorption processes this product can be substantial. The main limiting factor in the observation of ESA is the requirement of the second absorption event occurring before the decay of the first excited state. The excitation flux must be intense enough for a second incident photon to encounter the same excited system before it decays by any other means available to it – radiative, non-radiative, or other. Thus, ESA is proportional to the product of the first-excited-state lifetime and the excitation intensity.

Energy transfer upconversion (ETU) is only slightly more complex than ESA. ETU involves two chromophores, a donor and an acceptor, which may be the identical or distinct materials. Once both the sensitizer and the acceptor are excited, perhaps by optical excitation, the sensitizer may transfer its energy to a highly excited state in the acceptor via FRET or Dexter, thereby losing its own energy and resulting in a highly excited acceptor. Radiative decay of the acceptor to its ground state then results in emission of a photon with energy greater than that of either of the first excited states of the sensitizer or acceptor. The key feature of the ETU process is the lack of simultaneity, in that the sensitizer excitation, acceptor excitation, and S-A energy transfer events can all occur at different times, provided that none of those excited states decay before the ETU process is completed. This process may also lose or gain energy from the phonon bath, potentially resulting in a final photon energy that is not resonant with the sum of the energies of the two initial excited states.
Figure 3.2 | Diagram of upconversion processes. Figure (a) shows upconversion via excited state absorption (ESA), where one photon is absorbed by the chromophore in its ground state (ground state absorption - GSA), followed by another absorption event from its excited state (excited state absorption - ESA), finally followed by emission of a high-energy photon (upconverted luminescence - UCL). Figure (b) shows energy transfer upconversion (ETU), where a donor chromophore absorbs a photon and transfers it (energy transfer - ET) to the first excited state of the acceptor and returns to its own ground state. The donor then absorbs a second photon and transfers that energy to the acceptor as well, whereupon the acceptor may emit a high-energy photon (UCL). Figure (c) shows the two-photon absorption (2PA) process where a chromophore absorbs two photons simultaneously to achieve excitation into its first excited state. The molecule then emits an upconverted photon and drops back down to its ground state. Note that the dashed line is a virtual state and not an eigenstate of the chromophore. Figure borrowed from Chan [18].

Second harmonic generation (SHG) is a nonlinear process in which two photons combine while propagating through a material to form a photon with double the energy of the initial photons. This effect was first observed in 1961 by Franken et al. [1] and was later found to be a subset of the broader class of sum-frequency generation. SHG can occur in materials that have non-negligible even-order terms in the expansion for electric susceptibility and that do not have inversion symmetry. Since this effect requires precise alignment in the polarization and propagation directions of the two incident photons as they propagate through the SHG material it is generally only observed in crystals.
Two-photon absorption (2PA) was first proposed by Maria Goeppert-Meyer in 1931 as her doctoral thesis [26]. While it took another 30 years to experimentally validate her theory, this novel form of photon upconversion was eventually observed in lanthanide-doped crystals [27]. 2PA is the process of a single atom/molecule simultaneously absorbing two incident photons. The process is displayed in figure 3.2. A key feature of this process is that while the absorbing material can absorb two photons it can not absorb just one of the same photons. This is because 2PA makes use of a virtual state rather an energy eigenstate and virtual states are unable to be occupied and hence can not be the end result of an absorption process. However, by using the virtual state to mediate the absorption of two sub-bandgap photons the material is able to achieve an otherwise forbidden transition. Since the mediating virtual state has no effective lifetime the two excitation photons must be exactly coincident temporally in order for 2PA to occur. Additionally, since 2PA depends on absorbing two photons simultaneously from the incident photon flux the yield of this upconversion process will have a quadratic dependence on the the excitation intensity. Thus, 2PA generally only occurs at extremely high excitation intensities resulting in 2PA cross-sections typically being measured in units of $10^{-50} \text{cm}^4\text{s/photons}$, a unit named the GM in honor of Maria Göppert-Mayer. In addition to 2PA, there exists the closely related process of resonant 2PA, in which there exists a (non-virtual) energy state in the absorber corresponding to the energy of a single absorbed photon. This process is still 2PA, but with a resonance enhancement due to the first-order process of the absorption steps.

Triplet-triplet annihilation (TTA) was first observed by Parker and Hatchard [2] in 1962. This form of photon upconversion involves two different types of chromophores – a sensitizer to absorb the light and an emitter to collect and upconvert the excitations. The process begins with the sequential absorption of two incident photons by two distinct sensitizer molecules, each of which then undergoes rapid intersystem crossing into excited triplet states. These long-lived triplet states allow the sensitizer sufficient
time to encounter an emitter molecule whereupon a Dexter energy transfer event results in a ground state sensitizer and an emitter in a lowest excited triplet state. The emitter then may encounter a second emitter in an excited lower-level triplet state, enabling the two emitters to undergo TTA and leave one emitter in the ground state and the other in a highly-excited triplet state. This highly-excited triplet state will then undergo rapid intersystem crossing, resulting in an excited lowest-lying singlet state with more energy than either of the absorbed photons. TTA requires sensitizers and emitters with carefully selected properties such that both undergo efficient intersystem crossing and have triplet energy levels that match appropriately between them to allow for Dexter energy transfer. However, the long lifetimes of triplet states allows the energy of absorbed photons to be stored for appreciable amounts of time while “waiting” for a second incident photon, enabling TTA to occur at low – even sub-solar – excitation intensities.

The final form of photon upconversion is called the photon avalanche (PA) effect and was first discovered in 1979 by Chivian et al.[28]. PA has a rather unorthodox excitation scheme in that it utilizes an excitation source that is resonant not with ground-state absorption but with the transition from the first to the second excited states in the gain medium. This results in particularly weak ground state absorption and only a small number of first excited states being initially excited. However, once in their first excited state the molecule/ion will readily undergo ESA with the now-resonant excitation source to achieve the second excited state. In a properly tuned PA system the dominant decay mechanisms from this second excited state are emission to the ground state, resulting in upconverted emission, or cross-relaxation with a neighboring ground state molecule/ion which results in both molecules/ions ending up in their first excited states. This cross-relaxation process leads to an exponential increase in the number of molecules/ions in their first excited state, and hence an exponential increase in the material’s ability to absorb the excitation light as well as a self-balancing mechanism whereby the fewer ground state molecules/ions remaining in the material the less the likelihood of cross-
relaxation and hence the more efficient the upconverted emission process will be. The limiting factor in this process is that the excitation intensity must surpass a minimum threshold in order to maintain a sustainable population of first-excited states. Below this threshold and no upconversion will occur, but surpass this threshold and very efficient photon upconversion may be observed.

3.4 Theory of cooperative energy pooling

3.4.1 A brief history of cooperative energy pooling

The story of cooperative energy pooling begins back in the 1960s with the observation by Ovsyankin and Feofilov [16] that they termed “cooperative sensitization”. These researchers doped BaF$_2$ crystals with YbF$_3$ and TuF$_3$ and observed that when the system was excited with 960 nm light corresponding to the absorption maximum of Yb the could measure upconverted emission at 470 and 670 nm corresponding to emission from the Tu. They explained this result by suggesting that resonance between the sum of the energies of the excited states and that of the acceptor state could give rise to "a resonant process wherein the donors go over to the ground state and the acceptor is excited".

Their observations were quickly followed up by others observing similar phenomena in various other lanthanide-doped crystals [23, 29] but without any more details to explain the coupling process between the sensitizers and the acceptors. Later work would show that Tb, the acceptor used in the most successful lanthanide-based cooperative sensitization systems, has a sizable 2PA cross-section at the wavelength of the sensitizer emission used in the most effective systems [30], suggesting that CEP is the mechanism responsible for the upconversion observed in these experiments.
Further experimental work in the 1990s by Nickoleit et al. [17] demonstrated energy upconversion in organic multi-chromophore molecules, verifying that cooperative sensitization – or simultaneous energy excitation transfer (SEET) as they called it – could occur in a wider variety of materials than previously known, but misidentifying the underlying mechanisms. While the kinetics and energetics of this upconversion process were characterized, the process remained poorly understood from a fundamental standpoint and was frequently falsely identified when observing other photon upconversion phenomena.

In 1998 Jenkins and Andrews [13] published a paper acknowledging these previous observations and proposing a quantum electrodynamic (QED) theory that neatly encapsulated all the previous observations under one umbrella. The “energy pooling” process they proposed is the three-body photon upconversion process that forms the basis for all the work of this thesis. In this work, and in our publications, we name the process “Cooperative Energy Pooling” out of deference to the initial work completed under the nomenclature of “cooperative sensitization” combined with the nomenclature of the theorists who properly identified the process. The remainder of this explanation of CEP generally follows the derivation and explanations of Jenkins and Andrews [13] as well as the computational expansion of that work carried out by LaCount et al. [15].

3.4.2 Theory of cooperative energy pooling

CEP is the process of two photoexcited sensitizer chromophores non-radiatively transferring their energy to a single higher-energy state in an acceptor chromophore. Instead of dipole-dipole coupling between the emissive states of the sensitizers and the absorbing state of the acceptor, as in the Förster Resonance Energy Transfer process.

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3 In their experiment there was no emission of upconverted photons, but rather isomerization at an energy above the energy of the excitation photons, so this experiment may perhaps better be categorized as photoisomerization upconversion.
(FRET), CEP is carried out via a coupling of the emissive states of both sensitizers with the two-photon absorption (2PA) tensor of the acceptor. In this way, the sensitizers act as photon storage centers that relax the stringent temporal and spatial constraints for achieving 2PA in the acceptor, enabling upconversion with greater efficiency and at reduced excitation intensities.

The kinetics diagram of CEP is shown schematically in figure 3.3. The sensitizers absorb low energy light and can transfer that energy to the acceptor via CEP while the acceptor absorbs high-energy light directly, resulting in a system capable of efficiently harvesting multiple wavelengths of light. Upconversion is observed via radiative emission from the acceptor under low-energy excitation. Though the work in this thesis demonstrates upconversion in the visible spectrum, the CEP mechanism is achievable with any chromophores that match sensitizer emission with acceptor 2PA energies, allowing this process to be tuned to any desired photon energy range in which suitable chromophores are available. If there is spectral overlap of sensitizer absorption with sensitizer emission bands (i.e. small Stokes shift) then FRET and Dexter energy transfer between sensitizers is enabled and exciton migration may occur in the film. Conversely, if there is overlap between the acceptor emission and sensitizer absorption spectra then FRET between acceptors and sensitizers is enabled and functions as a loss pathway by downconverting acceptor excitons into lower energy sensitizer excitons. Other energy loss pathways include non-radiative decay of the acceptor and both radiative and non-radiative decays of the sensitizer.

The key factors in efficient CEP are overlap of the sensitizer emission spectra with the 2PA cross-section of the acceptor and the geometry and distance considerations in the actual separation between the sensitizers and the acceptor. Just as in FRET, the more emissive the sensitizers are and the more (two-photon) absorptive the acceptor is the more efficient the energy transfer process will be. These factors are all evident in the theoretical formulation of CEP presented below, styled after LaCount et al.
We arrive at this formulation of CEP by investigating \( n^{th} \)-order perturbative couplings between initial and final states. Absorption and emission are first order couplings, FRET is a second order coupling, and CEP is a fourth order coupling. Using the electric dipole approximation for the interaction Hamiltonian and applying it to fourth-order perturbation theory yields the rates \( \Gamma \) of photoluminescence, FRET, CEP, and the related process of accretive energy transfer (AET, which is explained in more detail...
\[ \Gamma_{PL} = \frac{(E_i - E_f)^3 (\mu_0 a(S))^2}{3\pi \epsilon_0 \hbar^4 c^3} \]  \hspace{1cm} (3.6)

\[ \Gamma_{FRET} = \sum_{j,l=1}^{3} \frac{2\pi}{\hbar} \left| \mu_j^{a_i(S)} V_j(k, R) \mu_l^{b_j(A)} \right|^2 \]  \hspace{1cm} (3.7)

\[ \Gamma_{CEP} = \sum_{j,l,m,n=1}^{3} \frac{2\pi}{\hbar} \left| \mu_j^{a(S)} V_j(k, R') \alpha_{lm}^{b0(A)} (-k, -k) V_{mn}(k, R') \mu_n^{0a(S')} \right|^2 \]  \hspace{1cm} (3.8)

\[ \Gamma_{AET} = \sum_{j,l,m,n=1}^{3} \frac{2\pi}{\hbar} \left| \mu_j^{a(S)} V_j(k, R) \alpha_{lm}^{0a(S')} (2k, -k) V_{mn}(2k, R') \mu_n^{0a(A)} \right|^2 \]  \hspace{1cm} (3.9)

with the condition that \( E_f - E_i = 0 \) for all equations and with the electric dipole coupling tensor \( V \), and the 2PA tensor \( \alpha \) given by

\[ V_{mn}(k, R) = \frac{e^{\mp ikR}}{4\pi^2 \epsilon_0 R^3} \left[ (1 \pm ikR) \left( \delta_{mn} - 3\hat{R}_m\hat{R}_n \right) - k^2 R^2 \left( \delta_{mn} - \hat{R}_m\hat{R}_n \right) \right] \]  \hspace{1cm} (3.10)

\[ \alpha_{mn}^{(X)}(\pm k_1, \pm k_2) = \sum_{z} \frac{\mu_m^{iz(X)} \mu_n^{iz(X)}}{E_{iz} + i\gamma + \hbar ck_1} + \frac{\mu_n^{iz(X)} \mu_m^{iz(X)}}{E_{iz} + i\gamma + \hbar ck_2} \]  \hspace{1cm} (3.11)

In both sets of equations \( k \) is the magnitude of the wave vector associated with a photon emitted from the sensitizer, \( \mu^{ab(c)} \) represents the transition dipole moment from state \( b \) to state \( a \) on molecule \( c \). \( R(') \) is the displacement vector between the sensitizer \( S \) (\( S' \)) and the acceptor while \( R'' \) is the displacement vector between sensitizers \( S \) and \( S' \) in AET. Hats indicate units vectors and \( R \) is the magnitude of the \( R \) vector. \( \gamma \) is a broadening term assumed to have a value of \( k_B T = 25 - 100 \text{ meV} \). \( z \) is a summation over all the possible virtual states mediating the transition from initial to final states.

It is worth noting that CEP has a closely related form of energy transfer dubbed accretive energy transfer (AET), shown in equation (3.9). This process also involves two sensitizers and an acceptor, but involves energy transfer from one excited sensitizer to a high-energy virtual state in the second excited sensitizer – effectively functioning as a virtually-mediated ETU process, before transferring the energy of that highly excited state to the acceptor \[13, 15\]. This process is dependent on a resonance between

\[ ^4 \text{Following the formulations found in LaCount et al. [15].} \]
the ESA of the sensitizer with the energy of the sensitizer’s first excited state. Since the sensitizer-sensitizer energy transfer occurs non-radiatively it is also subject to the spatial dependence of FRET or Dexter energy transfer processes. Thus, the relative geometry of the sensitizers relative to the acceptor can determine whether CEP or AET is the dominant pathway. However, careful selection of sensitizers which have poor coupling between the first excited state energy and ESA will effectively shut down the AET pathway and avoid this energy loss mechanism.

3.4.3 Characteristics of cooperative energy pooling

Cooperative energy pooling has a number of unique features that make it an appealing pathway for energy upconversion but also indicate the need to expand our theoretical understanding of the process.

The CEP rates listed above inherently assume a system in which there are only two sensitizers, both of which are excited, and one ground state acceptor. However, in order to minimize the sensitizer-acceptor separation distance it is beneficial to create solid-state CEP systems in which all chromophores are tightly packed. Alternatively, one could synthesize chromophores with multiple sensitizers chemically bound to a single acceptor with dendritic structures designed to funnel the energies of multiple sensitizers towards a single acceptor as was suggested by Jenkins and Andrews [13]. In either case the initial excitation due to photon absorption in the sensitizers may lead to Frenkel excitons capable of probing more than one neighboring acceptor. The CEP rate formulated in equation (3.8) would no longer hold if multiple excitons were able to couple with a single acceptor, a situation likely to happen when chromophores are tightly packed or structured in dendritic geometries. Additionally, diffusion of sensitizer excitons would allow for excitonic channeling, which would further increase the likelihood of multiple excited sensitizers being available to a single acceptor.
Figure 3.4 | Schematic of possible energy transfer pathways in CEP system. From the ground state a donor can absorb a photon (Abs) and the resulting excited donor can photoluminesce back down to its ground state (PL). The second donor can also absorb a photon before PL decay of the first, leading to the dual excited state in the upper left. From there, CEP can occur to transfer the energy of both excited donors to the acceptor whereupon the energy from the excited acceptor may be harvested or emitted as a photon. Alternatively, ETU or AET can transfer the energy from one excited donor to a highly excited state on the second donor, leading to the scenario in the middle of the diagram. The highly excited donor state may then transfer its energy to the acceptor via FRET and complete the upconversion process, or decay via internal conversion (IC) back down to its first excited state, functioning as an energy loss mechanism.

While this scenario would seem to be beneficial to the overall CEP rate, it is nonetheless a more complex case not entirely covered by the theory derived thus far. In chapter 5 we treat this case numerically and derive data from simulations of mobile excitons. However, it must be remembered that a fundamental model for CEP with more
than two potential excited sensitizer donors would be highly beneficial and potentially reveal non-linear improvements to CEP rates in such a scenario.

From this basic understanding of the various photon upconversion methods and the mechanism of CEP one can identify a number of advantages of CEP over other forms of upconversion. CEP avoids inter-system crossing by utilizing only lowest-lying singlet excitations, allowing for less energy loss and potentially higher energy yield per upconversion event than processes like TTA. The exclusive use of singlet states also makes CEP unsusceptible to quenching by oxygen and hence more tolerant of environmental conditions than triplet-based mechanisms. While 2PA varies quadratically with excitation intensity and thus becomes negligible in low light conditions, CEP can achieve sub-quadratic intensity dependence by utilizing linearly-absorbing sensitizers as antennae to funnel excitations to the acceptor. All upconverted CEP emission occurs from the lowest-lying excited state of the acceptor, thus allowing the use of easily-produced organic chromophores as acceptors and avoiding the need for lanthanide nanoparticles typically required in ETU for their ability to emit from highly excited states. The use of organic chromophores also allows for strong absorption over a wide energy range, low environmental and biological toxicity, and the ability to relatively easily design and synthesize sensitizers and acceptors with optimized, arbitrarily tunable properties.

A final note may be made about the relationship between singlet fission (SF) and CEP. SF is the process of a single high-energy singlet splitting into two excited triplet states, one on the original excited chromophore and one on a neighboring chromophore. Since the two triplets together form a singlet excited state this process conserves overall spin-state and thus can be quite efficient, occurring on a picosecond or faster timescale. While SF is considered to be a reversing of the upconversion process in triplet-based TTA upconversion systems, and hence directly opposing the rate of TTA, the fact that CEP does not utilize triplet states causes SF to interact differently in a CEP system. If SF occurs in a CEP system it will result in two triplets, and since CEP does not utilize
triplets this results in a net loss of energy available for CEP upconversion. However, CEP acceptor chromophores may be designed with triplet state energies larger than half the energy of the excited singlet state. This would result in SF being an energetically uphill process with extremely low efficiencies, while not affecting the efficiency of CEP in any way.
Chapter 4

Initial experimental verification of cooperative energy pooling

4.1 Introduction

In this work, we demonstrate experimental observation of CEP photon upconversion. We measure the spectroscopic properties of pristine and blended sensitizer and acceptor chromophores and observe significant upconversion in the blended thin film. The mechanism of CEP is verified via measurements of control films with alternative chromophore blends. Further data on the intensity dependence of the observed upconversion process confirms the transition from quadratic towards linear dependence on the excitation intensity, as expected for a multi-chromophore upconversion process. We develop a kinetic model of the CEP process and find good fits to the measured data. This model is then used to present estimates of CEP performance under various conditions, showing that upconversion under solar excitation may be achievable with optimized chromophores. The results of this work are finally brought together to present guidelines for the selection of ideal chromophores for CEP and the development of improved CEP systems.
4.2 Results

4.2.1 CEP Upconversion with Stilbene-420 and Rhodamine 6G.

To experimentally demonstrate CEP we utilized well-known, commercially available organic chromophores. Stilbene-420 (Stilb420) was chosen as the acceptor due to its sizable 2PA cross-section [31] in the 500-600 nm range (figure 4.1) while Rhodamine 6G (Rhod6G) was selected as the sensitizer due to its high linear absorptivity, quantum yield near unity [32], and emission spectrum overlap with the 2PA spectrum of Stilb420.

Figure 4.1 | Spectral properties of the materials in this work. (a) Absorption, emission, and upconverted emission spectra of Rhod6G/Stilb420 blend CEP film. Upconverted emission was measured under 540 nm excitation. Normal emission was measured under excitation at 349 nm to avoid artifacts due to scattered excitation signal overlapping with emission spectrum. (b) Absorption, two-photon absorption, and emission spectra of pristine Stilbene-420 (acceptor) and absorption and emission spectra of pristine Rhodamine 6G (sensitizer) in thin films. Emission spectra were measured under excitation at 363 nm and 525 nm for Stilbene-420 and Rhodamine 6G, respectively. 2PA spectrum was observed in a 100 μmolar solution of Stilb420 in methanol and measured using the LaserStrobe system described in the Methods section.
To fabricate the CEP film, Rhod6G and Stilb420 were combined into solution and blade coated onto glass substrates to yield ~ 80 nm thick films. The resulting films had the spectral properties of a linear addition of the two components. Extensive overlap between Stilb420 emission and Rhod6G absorption indicates that any upconversion yields in this system will be strongly reduced by FRET losses from acceptor to sensitizer, as is further evidenced by the energy transfer over time from Stilb420 to Rhod6G (figure 4.2). Nonetheless, upon excitation with 545 nm light both a normal emission spectrum peaking at 572 nm, corresponding to Rhod6G, and an upconverted emission spectrum peaking at 445 nm, corresponding to Stilb420, were observed (figure 4.1). Trials with varying sensitizer/acceptor ratios to optimize upconversion yields revealed that Rhod6G exhibits strong self-quenching, necessitating an acceptor-heavy blend of 1:40 (sensitizer:acceptor) and further reducing upconversion yields.

The first evidence for CEP as the mechanism responsible for the observed upconversion is the similarity of the upconverted emission spectrum to the emission of pristine Stilb420. Excitation at photon energies corresponding to sensitizer absorption yielded fluorescence corresponding to acceptor emission, suggesting a multi-body process in which both chromophores play a role in upconversion. The alternative multi-body upconversion processes of ETU and photon avalanche processes may be immediately ruled out since the Stilb420 acceptor has no stable excited states at energies lower than the observed upconverted emission, a requirement of both of those processes.

4.2.2 Determining the Optimal Chromophore Blend Ratio

The counterintuitive blend ratio of 1:40 (sensitizer:acceptor) was found to be optimal due to strong self-quenching effects in Rhod6G when aggregated. In dilute solution Rhod6G is a very strong emitter with peak emission at 552 nm. However, at
Figure 4.2 | Prompt and time-integrated emission from CEP blend film. At prompt times (< 2 ns) the fluorescence spectrum is dominated by characteristic Stilb420 emission, as expected due to Stilb420 having over five times the absorption of Rhod6G at this excitation wavelength (60,000 M$^{-1}$cm$^{-1}$ for Stilb420 at 349 nm versus 11,500 M$^{-1}$cm$^{-1}$ for Rhod6G). Considering that the film is a 1:40 blend of Rhod6G/Stilb420 and that Stilb420 is a better absorber of the excitation light, the strength of Rhod6G emission at prompt times is beyond what one might expect for simple absorption and emission, suggesting energy transfer from Stilb420 to Rhod6G. The time averaged emission spectrum shows that total emission over time is dominated by the Rhod6G emission peak, suggesting that while most absorbed energy is concentrated in Stilb420 at short times it transitions to Rhod6G on a time-scale only slightly longer than the chromophores’ decay lifetimes. Taken together, this data suggests that the observed blend film exhibits FRET from Stilb420 to Rhod6G on a ns–μs timescale.

higher concentrations – both in solution and in film – the emission strength quickly decreases and redshifts. Blend films were fabricated at various ratios. It was found that as the Rhod6G concentration in the blend decreased its emission spectrum blue-shifted and approached the dilute solution emission spectrum with a concomitant increase in the CEP yield. Maximum upconverted (CEP) emission was found at a ratio of 1:40, at
which point the Rhod6G emission spectrum nearly matched the dilute solution emission spectrum. From this we conclude that Rhod6G self-quenching due to aggregation is the driving factor in determining the optimal blend ratio in this CEP system and that far greater CEP yields may be obtained with a donor chromophore that exhibits less self-quenching losses and allows the film to approach a more optimal blend ratio.

In order to more fully understand the effects of the chromophore blend ratio on the CEP mechanism, we modeled nearest neighbor distances between sensitizers using a Poisson distribution treatment [33] (figure 4.3). Included in the extended data is a figure of the average nearest-neighbor distance between sensitizer chromophores as a function of blend ratio, calculated assuming both acceptors and chromophores have spherical volumes of 1 nm$^3$. This calculation shows that at the 1:40 blend ratio used in this work the average distance between sensitizers is $\sim 1.91$ nm. Since all volume not taken up by sensitizers contains acceptor chromophores, the average distance between acceptor and sensitizers is thus closer to one half of the expected sensitizer-sensitizer distance, or $\sim 0.95$ nm. In reality Rhod6G and Stilb420 are closer to 2D discs than to 3D spheres, and the average sensitizer-acceptor distances may be even smaller. Such short separation distances are well within the range of RET, a similar $r^{-6}$-dependent process, in accord with our observation of CEP at this 1:40 blend ratio. This calculation also indicates that increased blend ratios (i.e. more sensitizers per acceptor) may lead to shorter average separation distances, potentially yielding dramatically improved CEP due to the $r^{-6}$ dependence.

Finally, the Stilb420/PVP control film – used to control for 2PA in pristine Stilb420 - was made at the same weight ratio (rather than molar ratio) as the Rhod6G/Stilb420 film in order to simulate disaggregation of the Stilb420 occurring in the CEP films.
Figure 4.3 | Nearest-neighbor distance as a function of blend ratio. Calculated average sensitizer-sensitizer nearest neighbor distance and average number of sensitizers in a 3 nm radius sphere as a function of chromophore blend ratio. These curves are calculated for a three-dimensional system of point particles whose centers are randomly (Poisson) distributed, following a solution originally by given by Hertz, as reproduced by Torquato [33].

4.2.3 Control Films to Verify CEP Mechanism.

To further verify the upconversion mechanism, control films were made by substituting alternative sensitizers or acceptors in the film. A blend film of neutral host polymer polyvinylpyrrolidone (PVP) and Rhod6G exhibited very strong fluorescence at 570 nm due to disaggregation of the Rhod6G [34], but no sign of upconversion (figure 4.4). This is expected due to both the negligible two-photon absorption of Rhod6G at the excitation wavelength [35] and the (sub-picosecond) thermalization of highly excited states down to the lowest lying excited state in organic chromophores.
(see Kasha’s rule [36]). Additionally, the excited state absorption spectrum of Rhod6G lies between 400 and 470 nm [37], indicating that Rhod6G cannot achieve a highly excited state via sequential excitation at the 540 nm excitation wavelength used in this work. Thus, two-photon excitation - either simultaneous or sequential - of the Rhod6G sensitizer and subsequent energy transfer to the Stilb420 acceptor can be eliminated as a potential cause of the observed upconverted emission. Blend films of Stilb420 with Rhodamine 800 (Rhod800), a NIR-emitting analogue of Rhod6G with no emission overlap with the 2PA spectrum of Stilb420, were compared against pristine Stilb420 films to test for doping-induced upconversion improvements. The modest 4-fold improvements in Rhod800/Stilb420 films (figure 4.4) indicates that the presence of a molecular dopant does moderately improve 2PA upconversion yields in Stilb420, likely by disaggregating the Stilb420 and hence reducing self-quenching losses. These control films demonstrate that the 160-fold upconversion enhancement in Rhod6G/Stilb420 films must be due to a multi-body, sensitizer-acceptor process and dependent on the spectral overlap between sensitizer emission and 2PA spectrum of the acceptor. Additionally, decay lifetimes for both upconverted and normal fluorescence from the CEP film are distinctly shorter than for the pristine films (figure 4.5), indicating strong interaction between sensitizers and acceptors and providing further evidence for energy transfer processes between chromophores – both CEP upconversion and FRET losses. Evidence for a multi-body upconversion process eliminates the possibility of Second Harmonic Generation, Excited State Absorption, or 2PA being responsible for the observed upconversion.

Strong evidence supports the conclusion that upconversion in Rhod6G/Stilb420 films is due solely to singlet excited states and is not due to TTA. Rhod6G has an inherently low triplet yield of $\Phi_T = 0.005$ [38] and all film preparation and measurement was carried out in air, thus ensuring that the low yield of triplets was quenched even further by the presence of atmospheric oxygen. Rhod6G has also been shown to increase triplet yield up to $\Phi_T \sim 0.3$ when aggregated [39], but decreased upconversion
Figure 4.4 | Upconverted Emission Spectra of CEP film and control films. Upconverted emission spectra of Rhod6G/Stilb420 blend film compared with control films of pristine Stilb420, Rhodamine 800/Stilb420, Rhod6G/PVP, and blank glass substrate. Emission from the Rhod6G/PVP film is due to PVP disaggregating Rhod6G and increasing the normal 590 nm emission enough to leak through both short-pass filter and monochromator filtering.

was observed at higher loadings of Rhod6G, indicating that an increase in sensitizer triplet population was not beneficial for improving upconversion as would be expected for a TTA system. Finally, lifetime data shows all fluorescence occurring on timescales <1 ns, suggesting that long-lived triplet states are not serving as intermediaries in the upconversion pathway.

Experiments with alternative sensitizer chromophores demonstrate that CEP is a robust process that is reproducible in a variety of chromophore systems. Rhodamine B and Merocyanine 540 have peak emission at 564 nm and 579 nm, respectively, and were selected as alternatives to Rhodamine 6G due to their reduced overlap with the
Figure 4.5 | Excited state lifetimes of pristine films and CEP blend film. Time-resolved single-photon counting data on pristine Stilbene-420, Rhodamine6G, and blended CEP film. The upconverted emission from the CEP film at 440 nm was excited with 545 nm light. All other lifetimes were measured using excitation at 400 nm and measuring emission at 440 nm (Stilb420) or 570 nm (Rhod6G and blend film normal emission). Decays were too curved to be accurately fit using mono-exponential lifetimes, but all decays visibly occur on timescales < 1 ns. The reduction in lifetime of both long- and short-wavelength emission from the blend film compared to pristine films indicates the opening of new decay pathways from both Rhod6G and Stilb420 - CEP upconversion and RET, respectively.

2PA spectrum of Stilb420. CEP models predict that reduced spectral overlap between sensitizer and acceptor chromophores should result in reduced upconversion, and this reduction was experimentally verified in blend films even after optimizing for different blend ratios and self-quenching properties. RhodB triplets at 2.05 eV have better overlap with the 2PA spectrum of Stilb420 than the 1.79 eV triplets of Rhod6G [40], yet Rhod6G/Stilb420 films exhibited better upconversion, further supporting the case for singlet-based CEP being responsible for the observed upconversion.
4.2.4 Intensity Dependence Measurements.

Since CEP is a three-body cooperative energy transfer mechanism involving the addition of two excitons, we expect it to exhibit a similar evolution from quadratic to linear intensity dependence with increasing excitation intensity as observed in TTA literature [41, 42, 43]. Measurements of excitation intensity dependence of the CEP film (figure 4.6a) reveal a progression from the quadratic regime into an intermediate regime, as expected. Film degradation at higher excitation intensities prevented measurement into the fully linear regime. Taking the double-logarithm of the intensity dependence data and performing a linear fit to consecutive subsets of neighboring data points allows for extraction of the instantaneous power law dependence of CEP upconversion versus excitation intensity (figure 4.6b). This analysis reveals a smooth transition from the quadratic toward the linear regime, analogous to what has been reported in TTA. This transition can be accurately replicated by a kinetic model of the complete CEP process, which is discussed below.

4.2.5 Modeling the CEP Process.

In order to more fully understand the intensity dependence of CEP and explore its feasibility at low excitation intensities we modeled the kinetics of a CEP system, taking into account each of the various possible excitonic pathways. Numerical solutions to the system of differential equations below allowed for simulations of CEP systems with
Figure 4.6 | Excitation intensity dependence of the CEP film. (a) Log-log plot of upconverted emission from the CEP film at 440 ± 20 nm as a function of 540 nm excitation intensity. The colored lines are quadratic (blue) and linear (red) fits to the first and last three data points, respectively. The green line is a fit to the CEP kinetic model, discussed below. Excitation-induced film degradation precluded the collection of data at higher excitation intensities. The inset shows the same figure but scaled linearly. (b) Instantaneous power-law dependence of measured and modeled excitation dependence curves, showing a progression toward linear power-law dependence at higher excitation intensities. The power-law dependence was determined by the slope of a linear fit to a sliding boxcar window of six data points from the log-log plot of intensity dependence in (a).

arbitrarily adjustable parameters, enabling us to optimize system parameters in silico.

\[
S' = -k_S (1 - \gamma) S^* + k_{FRET} A^* S - 2k_{CEP} S^* A^* + \frac{E}{d} (1 - 10^{-\epsilon d S^*}) \tag{4.1}
\]

\[
S'[t] = -S''[t] \tag{4.2}
\]

\[
A' = -k_A A^* - k_{FRET} A^* S^* + k_{CEP} S^* A^* \tag{4.3}
\]

\[
A'[t] = -A''[t] \tag{4.4}
\]

\[
S^*[0] = 0 \tag{4.5}
\]

\[
S[0] = R \tag{4.6}
\]

\[
A^*[0] = 0 \tag{4.7}
\]

\[
A[0] = 1 - R \tag{4.8}
\]
\(S^*[t]\) and \(S[t]\) are the population densities of the sensitizer in excited and ground states as a function of time \(t\), respectively, while \(A^*[t]\) and \(A[t]\) are the equivalents for acceptor populations. \(k_S\) and \(k_A\) are the rates of sensitizer and acceptor excited state decay, respectively. \(\gamma\) is the probability of radiative energy transfer between sensitizers as given in equation (3.1). \(k_{\text{FRET}}\) is the rate of FRET from acceptor to sensitizer, and \(k_{\text{CEP}}\) is the rate of the CEP process. \(E\) is the excitation flux intensity, \(d\) is the thickness of the blend film being modeled, \(\alpha\) is the molar attenuation coefficient of the sensitizer at the excitation wavelength, and \(R\) is the percentage of the film blend comprised of sensitizer chromophores. Ground state saturation effects are accounted for in this model by including terms for both excited and ground state populations in equations (4.2) and (4.4). Bleaching effects are accounted for by having the sensitizer absorption term (last term in equation (4.1)) include proportionality to the sensitizer ground state population.

Note that this model accounts for radiative coupling between sensitizers but not non-radiative couplings such as FRET and Dexter. This is due to the fact that exciton diffusion due to non-radiative coupling is a more complex effect which we were unable to effectively incorporate into this model. Exploration of exciton diffusion is carried out in more detail via numerical simulations in chapter 5 but for the sake of this model it is quasi-accounted for via somewhat generous estimations for values of \(\gamma\).

Experimental measurements of chromophore lifetime, film thickness, excitation flux, and sensitizer absorbance enable simulated excitation intensity dependence from this CEP model to be fitted quite closely to the experimentally measured data (figure 4.6), yielding estimates for the CEP and FRET rates within the film. Calculating the steady-state population of excited acceptors then allows for an estimate of the quantum yield of the CEP process, both as a function of absorbed photons (internal quantum yield) and incident photons (external QY). Further exploration of the parameters in this model verify that CEP may be achievable at low (near solar AM 1.5) flux intensities. Table 4.1 lists a number of notable parameter configurations.
Table 4.1 | Select CEP parameters and upconversion yields.

<table>
<thead>
<tr>
<th></th>
<th>$E^\dagger$</th>
<th>$k_{\text{CEP}}^\ddagger$</th>
<th>$k_{\text{FRET}}^\ddagger$</th>
<th>$k_S^\ddagger$</th>
<th>$k_A^\ddagger$</th>
<th>$\epsilon^\S$</th>
<th>$R$</th>
<th>$d^\¥$</th>
<th>$\gamma$</th>
<th>IQY</th>
<th>EQY</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solar flux</td>
<td>$1.7 \times 10^3$</td>
<td>$1.0 \times 10^{13}$</td>
<td>$1.0 \times 10^8$</td>
<td>$1.0 \times 10^9$</td>
<td>$1.0 \times 10^5$</td>
<td>0.50</td>
<td>79</td>
<td>0.50</td>
<td>9</td>
<td>7.0%</td>
<td></td>
</tr>
<tr>
<td>30× suns</td>
<td>$5.0 \times 10^4$</td>
<td>$6.3 \times 10^{12}$</td>
<td>$1.0 \times 10^8$</td>
<td>$1.6 \times 10^8$</td>
<td>$6.3 \times 10^4$</td>
<td>0.46</td>
<td>160</td>
<td>0.30</td>
<td>17%</td>
<td>14%</td>
<td></td>
</tr>
<tr>
<td>1,000× suns</td>
<td>$1.7 \times 10^6$</td>
<td>$3.2 \times 10^{12}$</td>
<td>$1.0 \times 10^8$</td>
<td>$2.5 \times 10^8$</td>
<td>$4.0 \times 10^4$</td>
<td>0.50</td>
<td>250</td>
<td>0.30</td>
<td>37%</td>
<td>32%</td>
<td></td>
</tr>
<tr>
<td>Best fit to data</td>
<td>$7.1 \times 10^7$</td>
<td>$9.3 \times 10^{11}$</td>
<td>$1.0 \times 10^{12}$</td>
<td>$4.0 \times 10^9$</td>
<td>$2.0 \times 10^9$</td>
<td>$7.6 \times 10^4$</td>
<td>0.025</td>
<td>160</td>
<td>3.1 - 36%</td>
<td>0.02 - 0.19%</td>
<td></td>
</tr>
</tbody>
</table>

The first three rows present internal and external quantum yield (IQY and EQY, respectively) for CEP systems with optimized, yet plausible, system parameters at varying excitation intensities, as calculated by the kinetic model presented in this work. The final row is a best-fit calculation of the quantum yields of the CEP blend film experimentally measured in this work at the range of excitation intensities used in measurement. In the final row the excitation intensity, acceptor decay rate, sensitizer absorption, chromophore blend ratio and film thickness are measured parameters while the CEP rate, FRET rate, sensitizer decay rate and sensitizer self-reabsorption rates are fitting parameters.

† Excitation in units of $\text{Einstems}^{\text{nm}}/\text{L.s}$.
‡ Units of s$^{-1}$.
§ Units of l/mol/cm.
¥ Units of nm.
# Calculated IQY and EQY values corresponding to the minimum and maximum excitation intensities listed in the first column.
* Fitted parameters.

It is worth briefly discussing the various terms in this model that may contribute to the overall excitation dependence or the model’s output. At high excitation intensities there will be sufficiently many excited sensitizers that the ground state will be depleted and sensitizer absorption will drop. This ground state bleaching will result in a weaker dependence of CEP upconversion on the excitation intensity and contribute to a transition from quadratic dependence at low excitation intensities towards a linear dependence and eventually a sub-linear dependence as the ground state becomes entirely bleached.

However, similar excitation intensity effects will result from the relationship between the effective CEP rate constant and the effective sensitizer decay rate constant, namely $k_{\text{CEP}}S^*[t]A[t] \approx k_S(1 - \gamma)$. Haefele et al. [42] present a clear argument detailing that when $k_{\text{CEP}}S^*[t]A[t] \gg k_S(1 - \gamma)$ the overall excitation dependence will be proportional to $S^*[t]$ and hence will have linear power law scaling, while the case of $k_{\text{CEP}}S^*[t]A[t] \ll k_S(1 - \gamma)$ results in excitation dependence proportional to $S^*[t]^2$ and hence will have
Figure 4.7 | Kinetic behavior of CEP model. This figure displays the occupation of the excited acceptor state ($A^*$), and excited sensitizer state ($S^*$), the acceptor ground state ($A$), and the sensitizer ground state ($S$) as a function of time after an excitation pulse. Figures (a)-(d) represent the kinetics of these states in systems corresponding to rows 1-4 of table 4.1. Note that the rapid fluctuation in figure (a) near $5 \times 10^{-8}$ s is due to aliasing in the Mathematica plotting code and not a real effect in the CEP system.

quadratic power law scaling. Thus, the ratio between the effective CEP and sensitizer decay rate constant will determine the contribution to the excitation dependence of CEP upconversion. However, unlike the excitation dependence contribution due to ground state bleaching, the excitation dependence contribution due to rate constants will never fall below linear.

Together, these contributions imply that an increase in either $k_{\text{CEP}}$ or $S^*[t]$ will result in a linearization of the excitation dependence of CEP. Since both linearization modes are proportional to $S^*[t]$, it is clear that both modes will play a role in the transition from quadratic to linear excitation dependence, and hence that ground state bleach is not the sole factor responsible for the observed excitation dependence. The key differentiating
factor between excitation dependence contributions due to ground state bleaching versus rate constants is the difference in their impacts on external quantum yield (EQY) versus the internal quantum yield (IQY). The EQY will be affected by both of these effects while the IQY will be insensitive to ground state bleaching and hence will only exhibit an excitation dependence reflective of the CEP and decay rate constants in the system.

4.3 Discussion

From the behavior of this model with respect to its various parameters, a number of conclusions can be drawn. Firstly, the optimal values for both chromophore blend ratio and film thickness vary as other system parameters are altered. As excitation intensity decreases or sensitizer absorbance increases, the optimal blend ratio skews toward increasingly acceptor-heavy blends and the optimal film thickness decreases. This trend indicates that optimal blend ratio and film thickness parameters are determined by the need for sufficient sensitizers to absorb the excitation light and that any excess sensitizers degrade performance by diluting the concentration of excited sensitizers. Thus, while one might expect a 2:1 blend ratio to be ideal, CEP model simulations suggest that this is only true at high excitation intensities and that blends of 1:1 or lower may be optimal for more typical excitation conditions and sensitizer absorbance values.

Secondly, CEP is very sensitive to the decay rate of the sensitizer, as any non-radiative decay of excited sensitizers reduces the concentration of sensitizer excitons, greatly reducing the overall CEP yield. However, a simple calculation assuming 1 nm$^3$ chromophores at the 1:40 blend ratio used in this work reveals that there are $> 30$ sensitizers within the 5.6 nm Förster radius for Rhod6G self-FRET [44], indicating that energy transfer among sensitizers before decay is likely and could potentially play a
role in counteracting the shortcomings of short-lived sensitizer excitons to boost the efficiency of CEP.

The excitation intensity required for a two-photon, multi-chromophore upconversion process can be roughly estimated using a simple equation: \( I_{\text{exc}} = \frac{2\hbar \omega}{\tau_S \sigma_S} \), where \( \tau_S \) is the lifetime of sensitizer excitons and \( \sigma_S \) is the cumulative absorption cross-section of all antenna sensitizers that can contribute energy to a common acceptor within an exciton lifetime. This equation suggests two basic pathways towards upconversion at low excitation intensities: long-lived sensitizer states and/or large (effective) absorption cross-sections. CEP provides a platform particularly suited for harnessing long-range energy transport to increase the effective \( \sigma_S \) and potentially achieve low-intensity upconversion. While CEP itself is a short-range process, the excitations it draws from need not originate from within the domain of CEP action, provided that they can simultaneously encounter an acceptor before decaying. Since nearly every sensitizer has a neighboring acceptor at optimized CEP blend ratios (especially at the acceptor-heavy blend ratio used in this work), this problem reduces to one of maximizing the probability that two sensitizer excitons encounter each other before they decay. The probability of an encounter between diffusing particles increases with their diffusion rate \([45]\), so higher exciton mobility yields higher CEP rates. The singlet nature of sensitizer excitons in a CEP system enables highly efficient hopping-type diffusion via both FRET and Dexter energy transfer processes, granting excitons diffusion lengths up to 100 nm \([46]\) despite their nanosecond-scale lifetimes. In short, CEP happens when two sensitizer excitons encounter each other and the singlet nature of these excitons allows for high mobilities that improve the probability of distant excitons encountering each other. The effective absorption cross-section for CEP therefore includes all of the molecules whose excitons are likely to encounter each other within their lifetimes, up to \( \sim 10^6 \) within a 100 nm radius, in the optimal case. This can improve \( \sigma_S \) far beyond typical
single-molecule absorption cross-sections and allow upconversion at lower excitation intensities than would be possible without the benefits of singlet exciton diffusion.

Incorporating the experimental results above into existing analyses of the CEP and 2PA processes suggests guidelines for optimizing the selection of sensitizer and acceptor chromophores in order to maximize the CEP rate ($k_{\text{CEP}}$), as follows: The acceptor should have a large 2PA cross-section ($k_{\text{CEP}} \propto \alpha_{2\text{PA}}^2$) as well as minimal FRET losses to the sensitizers, and it should exhibit minimal self-quenching in the solid state. The sensitizer chromophore should have strong absorbance and also exhibit minimal self-quenching in the solid state. The sensitizer's first excited state should have minimal Stokes shift, strong oscillator strength ($k_{\text{CEP}} \propto \mu^4$), and should overlap with 2PA of the acceptor. The morphology of the blended film should have minimal sensitizer-acceptor separation distance ($k_{\text{CEP}} \propto r^{-12}$).

Further gains can be envisioned through construction of macromolecular antennae assemblies, as recently demonstrated in chromophore-decorated nanoparticle ETU upconversion systems. An ideally designed system would direct excitons toward a common acceptor molecule, analogous to the antenna complex in natural photosynthesis systems that funnels excitations to a reaction center. This scheme would provide the acceptor with a locally concentrated population of sensitizer excitations, greatly improving the CEP rate over that of an “undirected” system at the same excitation intensity.

### 4.4 Conclusion

In conclusion, we have observed singlet-based Cooperative Energy Pooling upconversion in solid-state, air-exposed organic chromophore blends. The proof-of-concept Rhodamine 6G/Stilbene-420 system presented here yielded a 160-fold upconversion improvement over simple two-photon upconversion in Stilb420 and an
estimated 0.2% external quantum yield of upconversion under excitation $10^5 \text{W/cm}^2$.

The estimated internal quantum yield of CEP was 36%, indicating that addressing the numerous energy loss pathways identified in this work may enable dramatic improvements in upconversion. Further optimization of sensitizer-acceptor pairs according to the guidelines listed above can be expected to reveal the full potential of the CEP process to achieve greater and more practical upconversion yields.

4.5 Methods

4.5.1 CEP film-making procedures

Rhod6G was purchased from Santa Cruz Biotechnology. Stilb420 and Rhodamine 800 were purchased from Exciton (listed as LD800). M540 and RhodB were purchased from Sigma-Aldrich. All materials were used as received. To fabricate thin films Stilbene-420 and Rhodamine 6G were separately mixed into 50 mM solutions in dimethylsulfoxide solvent. These solutions were blended together in a ratio of 40 parts Stilb420 to one part Rhod6G. This blend solution was then coated onto a glass substrate using a Zehntner ZAA 2300 blade applicator with a platen temperature of 105°C, a blade height of 50 $\mu$m and a blade speed of 45 mm/s to produce films ~ 80 nm thick. Glass substrates were cleaned via sonication in acetone and methanol for 5min each and subsequent UV-ozone treatment for 2min before film deposition.

4.5.2 Spectroscopy methods

All absorption data was taken on a Varian Cary 500 spectrometer. Rhodamine 6G emission measurements were taken on a Horiba Scientific Fluorolog spectrofluorimeter using a monochromated Xe lamp as the excitation source. CEP blend film and Stilbene-420 emission spectra were taken on a LaserStrobe spectrometer from Photon Technology International using a GL-3300 nitrogen laser and GL-302 dye laser.
attachment, also from Photon Technology International. Upconverted emission spectra were measured with the emission filtered by a 500 nm short-pass filter from Thorlabs, model FES0500, to prevent reflected excitation light from interfering with the measured emission signal. Laser power was measured with a 919P-003-10 thermopile sensor from Newport. Time-Resolved Single Photon Counting Data was taken using excitation light generated by a Fianium SC400 supercontinuum fibre laser with wavelength selected by a Fianium AOTF system. Detection was measured via a photomultiplier tube connected to a Becker-Hickl SPC-130 system. All data was collected with signal count rate at < 2% of excitation rep rate to ensure proper TCSPC statistics. All spectra were corrected for the spectral responsivities of the systems used for data collection.
Chapter 5

Interaction distance and exciton diffusion in cooperative energy pooling systems

5.1 Introduction

While photon upconversion has been studied for a number of decades and is well understood in many respects, Cooperative Energy Pooling has unique aspects that differentiate it from other photon upconversion mechanisms and that require further attention in order to properly understand and model.

The typical differential equations that are used to model the energy kinetics of systems inherently assume homogeneous distributions of the energetic states involved. Many energy transfer processes are linear with respect to the excited state populations they draw from, and thus variations in local excited population will average out across the system in question. However, processes that rely nonlinearly on excited state populations will be dominated by spatial regions with anomalously high concentrations of excited states and so will not be accurately modeled by an averaged energy distribution model. Since CEP draws from two excited sensitizers simultaneously, this process meets the nonlinearity criterion.

This effect is compounded in systems with a heterogeneous distribution of excitations. If excitations are mobile with morphology-dependent diffusivities then there will arise preferential pathways for excitons migration. This will cause even an initially
homogeneous distribution of excitations to preferentially aggregate in specific regions, further affecting the any concentration-dependent nonlinear processes.

In [chapter 4] CEP was modeled by a kinetic differential equation model employing a term proportional to the square of the excited sensitizer population. While this model has shown good results for even nonlinear systems such as TTA [42], further experimentation has convinced us that this model was insufficient to accurately capture all the features of CEP and likely underestimating its potential yield. The main factors missing in this model are those that operate on a local scale. The first question that brings up is to determine what is a “local” scale, which naturally refers to the length scale at which CEP operates. While other upconversion processes rely on well-studied energy transfer processes such as Dexter and FRET whose length scales are known, the CEP energy transfer mechanism has not been as thoroughly investigated and clarification of its typical length scale would be beneficial. Secondly, exciton mobility plays an important role in determining the length scales at which excitons are expected to encounter each other. While knowledge of the excitation intensity is enough to model average distances between immobile excitons, investigation of exciton diffusion is necessary to understand whether initially-distant but mobile excitons might be able to diffuse into sufficient proximity to undergo CEP.

In this chapter we present calculations to determine the length scale at which CEP operates and derive a CEP radius with definition similar to the Förster radius in FRET. This CEP radius is then used as a parameter in a Monte Carlo simulation of CEP accounting for diffusing excitons. This simulation provides numerical estimates for the internal quantum yield of CEP for varying values of excitation intensity, exciton diffusivity, and CEP radius. These results are then analyzed to provide insights on pathways towards optimizing CEP systems.
5.2 Calculating the CEP radius

Since CEP is effectively a form of simultaneous energy transfer from two sensitizers to one acceptor it shares much in common with the FRET process. In FRET the rate of energy transfer is proportional to the distance between the sensitizer and acceptor to the sixth power and also proportional to the overlap between the emission spectrum of the sensitizer and the absorption spectrum of the acceptor. Similarly, CEP is proportional to the distance between the acceptor and each sensitizer to the sixth power (e.g. \( r_1^6 \times r_2^6 \)) and also proportional to the overlap between the emission spectrum of the sensitizer and the two-photon absorption spectrum of the acceptor \(^{15}\). As discussed in chapter 3, Theodor Förster was the first to use these properties to derive the distance at which there is a 50% probability of energy transfer occurring via FRET versus any other energy pathway (equation (3.3)). Here we follow a similar method to derive the distance at which CEP is 50% probable.

Since the goal of this calculation is to find a sensitizer-acceptor distance at which CEP is 50% probable, the result will inherently be dependent on all other energetic pathways available to an excited sensitizer state. These other pathways include radiative and non-radiative decay of the excited sensitizer state as well as any other form of non-CEP energy transfer, such as FRET or Dexter, if present in the system. Since the presence of the acceptor chromophore may introduce non-radiative decay pathways to the excited sensitizer state a measurement of the lifetime of the isolated sensitizer chromophore will not necessarily give an accurate value for the lifetime of the sensitizer in the CEP blend film. However, since CEP is nonlinearly dependent on excitation intensity at low intensities, a measurement of sensitizer lifetime in the blend film at very low excitation intensities should yield a lifetime for the sensitizer excited state with the CEP pathway effectively shut off. With this measurement, a CEP radius calculated based on the 50% transfer probability will be experimentally measurable.
5.2.1 Derivation of CEP radius

The following derivation was carried out in close collaboration with Michael LaCount based on discussions stemming from our joint publication LaCount et al. [15]. D.H. Weingarten initiated the idea of this derivation and laid out an initial outline. M.D. LaCount carried out the real work of putting the derivation on firm theoretical foundations and crafting the form presented here, with D.H. Weingarten providing feedback and adding the final conversion into experimentally measurable parameters.

To derive the CEP radius we begin with the rates of spontaneous emission, FRET, and CEP as derived from Fermi’s Golden Rule. These formulations are taken from Griffiths [49] (equation 9.56), Jenkins et al. [50] (equation 3.2), and Jenkins and Andrews [14] (equations 7, 8, and 9), respectively.

\[
\Gamma_{\text{rad}} = \frac{\omega^3 \mu^2_S}{3 \pi \epsilon_0 \hbar c^3} \tag{5.1}
\]

\[
\Gamma_{\text{FRET}} = \frac{2\pi}{\hbar} \left( \frac{\mu_S \mu_A k}{4 \pi \epsilon_0 R^3} \right)^2 \rho_A \tag{5.2}
\]

\[
\Gamma_{\text{CEP}} = \frac{2\pi}{\hbar} \left( \frac{\mu_{S_1}}{4 \pi \epsilon_0 r_{S_1 A}^3} \frac{k_{S_2 A}}{\alpha_A} \frac{k_{S_2}}{4 \pi \epsilon_0 r_{S_2 A}^3} \mu_{S_2} \right)^2 \rho_A \tag{5.3}
\]

where \(\Gamma_{\text{rad}}\) is the spontaneous emission rate of the sensitizer at frequency \(\omega\), \(\mu_S\) is the transition dipole moment of the sensitizer, \(\Gamma_{\text{FRET}}\) is the rate of FRET from a sensitizer to an acceptor, \(\mu_A\) is the transition dipole moment of the acceptor, \(k\) is a molecular orientation term, \(R\) is the distance between the sensitizer and the acceptor, and \(\rho_A\) is the density of final states in the acceptor. \(\Gamma_{\text{CEP}}\) is the rate of CEP energy transfer, \(\mu_{S_{1/2}}\) is the transition dipole moment of the 1\(^{\text{st}}/2\(^{\text{nd}}\) sensitizer, \(k_{S_{1/2} A}\) is the orientation term between the 1\(^{\text{st}}/2\(^{\text{nd}}\) sensitizer and the acceptor, \(r_{S_{1/2} A}\) is the distance between the 1\(^{\text{st}}/2\(^{\text{nd}}\) sensitizer and the acceptor, and \(\alpha_A\) is the two-photon absorption tensor of the acceptor.

We now relate the transition dipole moments to the one- and two-photon absorption cross-sections. We start with the typical relation between the absorption
rate and the absorption cross-section

\[ \Gamma_{\text{abs}} = \frac{I}{\hbar \omega} \sigma_1 \]  

(5.4)

where \( I \) is the excitation intensity and \( \sigma_1 \) is the one-photon absorption cross-section.

We can then relate this to the transition dipole using Fermi’s Golden Rule by following the lowest order term from equation 10 from Ford and Andrews [51] for the case of \( n = 1 \) and averaging over all polarizations according (following equation 24 from the same work):

\[ \Gamma_{\text{abs}} = \frac{\pi \rho_f}{\hbar} \left( \frac{l}{c \epsilon_0} \right) \left( \frac{n^2 + 2}{3n} \right) e_i \bar{e}_j \left[ \mu_i \bar{\mu}_j \right] \]

\[ = \frac{\pi \rho_f l}{\hbar c \epsilon_0} \left( \frac{1}{3} \right) \mu^2 \]

(5.5)

where \( e_i \) are the polarization vectors of the excitation beam and \( \rho_f \) is the density of final state in the absorber.

We then set equation (5.6) and equation (5.5) equal to each other to obtain the relation between the transition dipole and the one-photon absorption cross-section.

\[ \Gamma_{\text{abs}} = \frac{\pi \rho_f}{3h} \left( \frac{l}{c \epsilon_0} \right) \mu^2 = \frac{l}{\hbar \omega} \sigma_1 \]

\[ \mu^2 = \frac{3c \epsilon_0}{\pi \rho_f \omega} \sigma_1 \]

(5.6)

We follow a similar process to relate the two-photon absorption tensor to the two-photon absorption cross-section. We begin with the standard relation between the 2PA rate and the 2PA cross-section.

\[ \Gamma_{\text{2PA}} = \frac{l^2}{2\left(\hbar \omega\right)^2} \sigma_2 \]

(5.7)

where \( \sigma_2 \) is the 2PA cross-section, which is usually given in units of Goeppert-Meyer (GM) with units of \( 1 \text{ GM} = 10^{-50} \text{ cm}^4 \text{s photon}^{-1} \). We then find borrow a formulation for the 2PA rate, also from Ford and Andrews [51], and follow the lowest order term from
equation 14 with $n = 1$ and simplifying the orientation term using equation 30.

$$\Gamma_{2\text{PA}} = \frac{\pi \rho}{2\hbar} \left( \frac{l}{\epsilon_0} \right)^2 \left( \frac{n^2 + 2}{3n} \right)^4 e_i e_j \bar{e}_k \bar{e}_l \left[ \alpha_{ij} \bar{\alpha}_{kl} \right]$$

$$= \frac{\pi \rho}{2\hbar} \left( \frac{l}{\epsilon_0} \right)^2 \frac{1}{15} \alpha^2$$

(5.8)

We then set equation (5.7) and equation (5.8) equal to each other to obtain the relation between the 2PA tensor and the 2PA cross-section.

$$\Gamma_{2\text{PA}} = \frac{\pi \rho}{2\hbar} \left( \frac{l}{\epsilon_0} \right)^2 \frac{1}{15} \alpha^2 = \frac{\rho}{2 (\hbar \omega)^2} \sigma^2$$

$$\alpha^2 = \frac{15\epsilon_0^2 c^2}{\hbar \omega^2 \pi \rho \sigma^2}$$

(5.9)

We can now find the characteristic length scale by setting the rate in question equal to the emission rate. To ensure the validity of the method we will start by deriving the known equation for the Förster radius.

$$\Gamma_{\text{rad}} = \Gamma_{\text{FRET}}$$

$$\frac{\omega_0^3 \mu_S^2}{3 \pi \epsilon_0 \hbar c^3} = \frac{2\pi}{\hbar} \left( \frac{\mu_S \mu_A k}{4 \pi \epsilon_0 R^3} \right)^2 \rho_A$$

(5.10)

Using equation (5.6) for the acceptor transition dipole and averaging the orientation factors to the standard value of $k^2 = \frac{2}{3}$ to solve for $R^6$ we find

$$R^6 = \frac{3 c^4 \sigma_1}{4 \pi \omega^4}$$

(5.11)

$$= \frac{3 c^4 \sigma_1}{64 \pi^5 \omega^4}$$

(5.12)

which is equivalent to the Förster radius as presented on page 34 of Clegg [52].

With this validation of the derivation method we turn to finding the characteristic distance of CEP. In this case we are not interested in the distance at which CEP dominates over just spontaneous emission but over all competing energy pathways. As mentioned earlier, the lifetime of the sensitizer excited state at low excitation intensities can be assumed to be the inverse of the cumulative decay rate of the sensitizer excited
state in the absence of CEP. Making the assumption that both sensitizers have identical transition dipoles, using equations (5.1), (5.9), and (5.3), and again taking the orientation factors to identically be $\frac{2}{3}$ we have

\[
\frac{1}{\tau_S} = \Gamma_{\text{CEP}}
\]

\[
\frac{1}{\tau_S} = \frac{2\pi}{\hbar} \left[ \frac{\mu_{S1}}{4\pi \varepsilon_0 R_{S1A}^3} \alpha_A \frac{k_{S1A}}{4\pi \varepsilon_0 R_{S2A}^3} \mu_{S2} \right]^2 \rho_A
\]

\[
\frac{1}{\tau_S} = \frac{2\pi}{\hbar} \left[ \frac{\alpha^2}{3} \left( \frac{1}{4\pi \varepsilon_0 R^3} \right)^2 \rho_A \right]^2
\]

\[
\frac{1}{\tau_S} = \frac{2\pi}{\hbar} \left( \frac{3\pi \varepsilon_0 \hbar c^3 \Gamma_{\text{rad}}}{\omega^3} \right)^2 \frac{4}{2304 \pi^4 \varepsilon_0^4 R_{12}^2} \frac{15c^2 \varepsilon_0^2 \sigma_2}{\pi \rho_A \hbar \omega^2} \rho_A
\]

\[
R_{\text{CEP}}^{12} = \frac{15c^8 \varepsilon_0^2 \tau_S \Gamma_{\text{rad}}^2}{32 \pi^2 \omega^8}
\]

(5.13)

(5.14)

In this case we are left with a factor of $\tau_S$ since we did not make the assumption that spontaneous emission is the only competing energy pathway. However, from here we can use a few relations to simplify this equation to a form easily relatable to experimentally measurable quantities.

\[
\tau_S = \frac{1}{\Gamma_{\text{non-rad}} + \Gamma_{\text{rad}}}
\]

(5.15)

\[
\Phi = \frac{\Gamma_{\text{rad}}}{\Gamma_{\text{non-rad}} + \Gamma_{\text{rad}}}
\]

(5.16)

\[
\tau_S \Gamma_{\text{rad}}^2 = \frac{\Gamma_{\text{rad}}^2}{\Gamma_{\text{non-rad}} + \Gamma_{\text{rad}}}
\]

\[
= \Phi \Gamma_{\text{rad}}
\]

(5.17)

\[
= \frac{\Phi}{\Gamma_{\text{rad}}}
\]

where $\tau_S$ is the total decay lifetime of the sensitizer in the CEP system but without CEP energy transfer, $\Phi$ is the fluorescence quantum yield of the sensitizer, and $\Gamma_{\text{rad}}$ is the inherent radiative lifetime of the sensitizer.
Combining equation (5.17) with equation (5.14) and converting into units of wavelength we finally have

\[ R_{\text{CEP}}^{12} = \frac{15c^8 \sigma_2 \gamma_3 \Gamma^2}{32\pi^2 \omega^8} \]

\[ R_{\text{CEP}}^{12} = \frac{15c^8 \sigma_2 \frac{\Phi}{\tau_{\text{rad}}}}{32\pi^2 \left( \frac{2\pi c}{\lambda} \right)^8} \]

\[ R_{\text{CEP}}^{12} = \frac{15\sigma_2 \Phi \lambda^8}{2^{13} \pi^{10} \tau_{\text{rad}}} \]  

(5.18)

Incidentally, working through similar simplification procedures from the right hand side of equation (5.13), one arrives at an analogous and somewhat more useable form for the rate of CEP:

\[ \Gamma_{\text{CEP}} = \frac{15}{2^{13} \pi^{10}} \cdot \frac{\sigma_2 \lambda^8 \Gamma^2}{\frac{\Phi}{\tau_{\text{rad}}}} \]  

(5.19)

5.2.2 Discussion

A brief analysis of the form of the CEP radius yields insight into the most effective ways to increase the length scale of CEP in a system. The first thing to notice is that the CEP radius is scaled to the twelfth power. This drastic power law implies that linear, and even factor-of-ten changes in the parameters involved will have relatively minor effects on the total CEP radius. Since \( R_{\text{CEP}}^{12} \) is linearly dependent on \( \sigma_2 \), \( \Phi \), and \( \frac{1}{\tau_{\text{rad}}} \) it will scale with these factors, but only by \( \sim 20\% \) for every factor of ten that these parameters are varied. The \( \lambda^8 \) parameter ends up dominating the calculation simply due to having a relatively similar power law to \( R_{\text{CEP}}^{12} \). See table 5.1 for examples of how the calculated CEP radius scales with sensitizer parameters.

From this we find, somewhat un-intuitively, that lowering the energy of the excitation photons is the dominant factor in extending the range of CEP. Since the main goal of most applications of photon upconversion is improved use of low-energy light, the fact that the CEP radius – and CEP efficiency as well, as we shall see in the
next section – improves as the excitation photon energy is lowered is entirely synergistic with these goals. Photovoltaics typically waste low-energy photons, but the improved upconversion yields from CEP at precisely the low-energy regime could help boost overall energy conversion efficiency.

It is worth noting, however, that the wavelength-dependence of the radius and rate of CEP is (potentially) not quite as strong as it might appear at first glance. This is because the fluorescence rate $\Gamma_{\text{rad}}$ is itself related to the wavelength of emission according to $\Gamma_{\text{rad}} \propto \lambda^{-2}$, as derived by Strickler and Berg [53]. When propagated through equations 5.18 and 5.19 we are left with a $\lambda^4$ dependence for the CEP rate and a $\lambda^6$ dependence for the CEP radius, along with some additional factors related to absorptivity, degeneracy of initial and final states, and the index of refraction of the material. This interdependence between the emission rate and the emission wavelength is not entirely robust, however. Strickler and Berg’s derivation makes clear that this

### Table 5.1 | Select CEP parameters and calculated CEP radius and lifetime.

<table>
<thead>
<tr>
<th>$\sigma_2^*$</th>
<th>$\Phi^*$</th>
<th>$\tau_{\text{rad}}^*$</th>
<th>$\lambda^*$</th>
<th>$R_{\text{CEP}}^$</th>
<th>$\Gamma_{\text{CEP}}(2\text{ nm})^\♭$</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>0.1</td>
<td>1</td>
<td>700</td>
<td>1.80</td>
<td>0.275</td>
</tr>
<tr>
<td>100</td>
<td>1</td>
<td>1</td>
<td>700</td>
<td>2.18</td>
<td>0.275</td>
</tr>
<tr>
<td>10,000</td>
<td>0.5</td>
<td>1</td>
<td>700</td>
<td>3.01</td>
<td>27.5</td>
</tr>
<tr>
<td>10,000</td>
<td>0.5</td>
<td>1</td>
<td>1,000</td>
<td>3.82</td>
<td>477</td>
</tr>
<tr>
<td>10,000</td>
<td>0.5</td>
<td>0.1</td>
<td>700</td>
<td>3.65</td>
<td>2,752</td>
</tr>
<tr>
<td>10,000</td>
<td>0.05</td>
<td>3</td>
<td>677</td>
<td>2.22</td>
<td>2.33</td>
</tr>
<tr>
<td>10,000</td>
<td>0.5</td>
<td>0.1</td>
<td>1,100</td>
<td>4.94</td>
<td>$1.02 \times 10^5$</td>
</tr>
</tbody>
</table>

Rows one through five highlight the effects of each of the parameters on the overall CEP radius. Row six of the table represents a rough estimate of the experimental conditions in the ZnPC/ADS128 polymer-based CEP system from chapter 4. Row seven presents a optimized set of experimentally reasonable parameters that yield long-scale CEP.

* Two-photon absorption cross-section in units of GM.
† Fluorescence quantum yield of the sensitizer.
‡ Radiative lifetime of the sensitizer in units of ns.
§ Wavelength of sensitizer emission in units of nm.
♭ CEP radius in units of nm.

The interdependence between the emission rate and the emission wavelength is not entirely robust, however. Strickler and Berg’s derivation makes clear that this...
relationship only holds true if the electronic transition moment of the sensitizer can be accurately reduced to the zeroth-order term in a power series expansion about the coordinates of the molecule. This assumption is stated to be valid when the absorption band is strong and when the transition to the excited state does not alter the molecular configuration significantly. The sensitizer chromophores in a CEP system are generally chosen to be strong absorbers with high allowed transitions, making the first assumption generally valid. The second assumption is harder to prove, and the tendency of many sensitizer chromophores to form aggregates somewhat complicates the matter. However, to the extent that the Stickler-Berg relationship holds for the sensitizer chromophore within the CEP blend film, the CEP rate and radius can be assumed to have wavelength dependence with a power law less than $\lambda^8$.

A final point worth noting is that the final formulation of equation (5.18) is wavelength dependent. While this makes it useful for calculating rates of energy transfer at particular energies, it does not apply nearly as well to experimental conditions where emission spectra and 2PA cross-sections span wide ranges of the spectrum with varying strengths as a function of wavelength. Additionally, the equations derived above are not well-suited for calculating the overall rate of CEP (or CEP radius) between a particular set of sensitizer and acceptor chromophores because they do not take into account the full overlap of the emission and 2PA spectra. For both experimental and theoretical reasons it is desirable to derive the CEP rate and radius in proportionality to an overlap integral, analogous to the result derived by Förster for the rate of FRET [24]. Doing this would require a reformulation of the sensitizer radiative lifetime $\tau_S$ into the normalized emission spectrum of the sensitizer to be integrated over all wavelengths along with the acceptor 2PA cross-section $\sigma_2$ and all wavelength-dependent factors (e.g. $\lambda$). This derivation was attempted but no satisfactory results were achieved, leaving this result for future work.
5.3 Simulating exciton diffusion

The diffusivity of the singlet excitons can have large impacts on the highly nonlinear process of CEP by allowing for transient, localized increases in exciton concentration that can greatly increase the rate of CEP. In most other forms of upconversion the sensitizer excited states are not highly mobile and thus do not require modeling of their diffusivities in order to accurately model the upconversion process as a whole. However, singlet excitons - the primary donor state in CEP - have been found with diffusion lengths of up to 4 µm in organic systems [46], allowing for interactions between excitons that simple kinetic rate models would not account for.

To better account for the diffusion of excitons and their stochastic effect on CEP energy transfer we employed a numerical modeling package called Smoldyn. Smoldyn is a stochastic, particle-based reaction simulation software package that aims to achieve identical results to the Smoluchowski diffusion equation (i.e. Smoluchowski dynamics, which gave rise to the portmanteau “Smoldyn”) via Monte Carlo type computational simulation [54, 45]. This package is open-source and free code that allows a use to create a reaction space, various particle types, diffusion rates corresponding to particle types, and chemical reactions (up to second order) that may occur between the various particles.

5.3.1 Spatial stochastic simulation with Smoldyn

Using this software package we created a model system in which sensitizer excitons could be created (i.e. excitation), disappear (i.e. decay via non-CEP channels), diffuse (via Dexter and FRET between sensitizers), and interact (i.e. CEP). Each of these different reactions was assigned a reaction rate and simulated in a 60 nm³ lattice with periodic boundary conditions. After simulating for 100 ns with 1 ps time steps the total number of CEP upconversion events was summed and divided by the total number
of excitation events to output and IQY value for the given set of input parameters. By iterating this process over varying excitation intensity, diffusivity, and CEP radius parameters this series of simulations builds a volumetric data set allowing the extraction of the CEP efficiency as a function of the three key system parameters.

The temporal and spatial dimensions of the simulation were chosen via an iterative process. Larger dimension for the simulation space were explored and resulted in no change in overall CEP yield, so the dimensions were kept at 60 nm for the sake of computational efficiency. Similarly, a variety of time steps were investigated, with 1 ps steps appearing to yield overall accurate and repeatable results. While simulations using 100 fs time steps are slightly more accurate and tended to yield 1-3% larger CEP yields, these simulations took a long time to compute and since the simulation-to-simulation variation in CEP QY was of a similar magnitude to the difference found by reducing the time step from 1 ps to 100 fs the longer time step was used for computational efficiency. The simulation duration of 100 ns was chosen to be significantly longer than the sub-nanosecond duration of the CEP process so that the reduced yield during the first ~nanosecond of the simulation as sensitizer concentration is building towards steady-state levels comprises only a negligible fraction of the total simulation time.

This Smoldyn model of CEP is intended to perform a similar function as the kinetic model proposed in chapter 4. As discussed above, the kinetic model makes homogeneity assumptions that are likely to miss much of the key details of an actual CEP system. Similarly, the kinetic model does not have a clear way of incorporating morphology factors such as exciton diffusivity and CEP radius into its calculation. The rate of CEP is treated as a single input variable in the kinetic model which does allow for any variations in this rate due to molecular orientation, morphology, or channeling in the system. While the Smoldyn model employed in this work does not incorporate variable CEP rates either, it is built in a way to allow this functionality. One appealing design motif for CEP systems is directed diffusion via antenna assemblies that channel excitons to a
common reaction core, similar to the design of natural photosynthetic systems. Kinetic models would be unable to incorporate this type of design while numerical models of the type used in this work lay the groundwork for investigating such concepts.

A few fundamental assumptions are made in this simulation in order to compute in reasonable amounts of time. First, the model assumes that there is a constant and homogeneous diffusivity in all of space. This implies that the entire film is composed of sensitizer chromophores with hopping rates that vary according to the diffusivity parameter. While this is not entirely accurate to the experimental system it does serve to give an approximation for how diffusion can affect a real system. While the introduction of non-sensitizer sites to the model would alter the results, it would effectively create an inhomogeneous distribution of hopping rates, which effectively decreases of overall diffusivity and increases the channeling of diffusing excitons to particular pathways – two effects which would have opposing impacts on overall CEP yield.

Secondly, the model assumes a step-function in the distance at which a CEP reaction will occur. A CEP radius parameter is input into the model and Smoldyn will then model a CEP reaction at the end of any time step in which two excitons are within the inputted CEP radius of each other. The documentation for Smoldyn states that “it is also possible to specify that these reactions should only happen with some probability, but this has very little benefit and so is not standard.” Furthermore, the CEP reaction is proportional to $r^{-12}$, implying that even slight variations in the sensitizer-acceptor distance have large effects on the CEP rate. To put some numbers to this, if two sensitizers approach an acceptor with a distance of 5% less than the CEP radius then CEP will occur with 65% probability, while an approach distance of 10% less than the CEP radius yields a 78% probability of CEP. While an $r^{-12}$ dependence is not a true step function, it is a steep enough rise in CEP probability as a function of separation distance that the step function reaction model is a reasonable assumption.
The third assumption is that CEP is only modeled as a function of two sensitizers without the inclusion of any acceptors. In practice, this is equivalent to assuming that there are sufficient acceptors in the actual film that one would be found halfway between any two sensitizers at any moment in time and that the molecular orientation of the two sensitizers to the acceptor is unimportant. In our experimentally investigated films the blend ratio of 1:40 is sufficient to validate the assumption of ubiquitous acceptors. While assuming an averaging of molecular orientation factors is a standard practice in the modeling of energy transfer [51] it has also been shown that there can be dramatic variation in CEP efficiency as a function of molecular orientation [15]. Future models may uncover improved results with the incorporation of orientation-dependent modeling, but for now this feature must be assumed to be homogenous for computational efficiency.

Finally, this simulation assumed no FRET from excited acceptors back to sensitizers. The presence of FRET downconversion would not technically reduce the upconversion IQY since a CEP upconversion event did occur, but it would reduce the number of emitted high-energy photons and thus be a factor in any fluorescence-based experimental measurements. Any acceptor-to-sensitizer FRET would result in the creation of an excited sensitizer state and therefore not be a total energy loss pathway but merely a 50% energy loss, therefore making low rates of FRET an even more minor impact on a CEP system.

5.3.2 Results

The results of the Smoldyn exciton diffusion simulation indicate that excitation intensity, sensitizer exciton diffusivity, and CEP radius all have strong impacts on the overall yield of CEP. Figure [5.1] shows the isosurfaces of IQY as a function of the three different system parameters. It is immediately noticeable that the isosurfaces
are not entirely identical. The lower QY surfaces have more of a “boxy” shape to them while the higher QY surfaces have a more spherical/ellipsoidal contour. This indicates that at lower QY one of a system parameters – the one normal to the flat portion of the isosurfaces – is acting as a bottleneck and preventing higher yields no matter the increases in the other parameters.

Figure 5.1 | Isosurface view of CEP simulation data. The blue, green, yellow, and red surfaces are isosurfaces indicating the parameters at which CEP has an IQY of 20%, 40%, 60% and 80%, respectively. The excitation intensity is in units of $\text{photons/}nm^2\cdot\text{ns}$, diffusion coefficient is in units of $nm^2/\text{ns}$, and the CEP radius is in units of nm.

While all three parameters exhibit this bottleneck behavior on some scale it is informative to look closely at the behavior near these bottlenecks. One can see that the isosurfaces are more closely gathered at low values of diffusion coefficient and excitation intensity than they are along the CEP radius dimension. This indicates that at low levels minor improvements to the diffusivity of sensitizer excitons and minor increases in excitation intensity will yield the largest gains in CEP efficiency.
Figures 5.2, 5.3, and 5.4 show the behavior of the model at these bottleneck points in more detail. Each of these figures displays a slice of the simulation data corresponding to the flat portion of the isosurfaces pertinent to each of the simulation parameters, respectively, with the z-coordinate of the figure chosen normal to the isosurface. One can immediately note the relatively linear behavior of the two transverse parameters (upper left and lower right traces) in each of these figures. The CEP radius trace (upper-left subfigures in figure 5.4 and figure 5.2) are clearly quite linear indicating minimal gain along that parameter, as would be expected for movement along a relatively flat isosurface. The exciton diffusivity trace in upper-left of figure 5.3 and lower-right of figure 5.4 as well as the excitation intensity trace in figure 5.2 show asymptotic behavior beginning with relatively steep gains and then flattening out to a linear section that corresponds to the range of the flat portion of the isosurface.

In order to more carefully analyze the behavior of these gains as a function of one dominant parameter one can look at these traces on a log-log scale to probe the power-law of IQY gains as a function of an isolated parameter. The upper-right trace in figure (c) shows the quadratic-to-linear behavior typically seen in a nonlinear upconversion process as a function of excitation intensity [42]. This behavior stays true at all values of exciton diffusivity and CEP radius, which helps explain why this behavior has always been observed in models and experiments that did not take diffusivity and interaction distance into account.

Exciton diffusivity and CEP radius exhibit very different behavior as the other parameters are changed. The log-log trace of exciton diffusivity vs IQY is much simpler. This trace maintains a constant log-log slope that changes as a function of excitation intensity and CEP radius. This implies that IQY versus exciton diffusivity follows a simple power law dependence where the power law is a function of the other two system parameters. While that exact function is not immediately obvious from the data thus far, it is clear that the behavior of exciton diffusivity is markedly different from that of
Figure 5.2 | CEP simulation - exciton diffusivity cross-section. The lower left figure is a 2D cross-section taken across one value of exciton diffusivity. This cross-sectional slice was taken at a diffusivity value of 5.1 nm$^2$/ns as noted in the center of the figure and marked by the vertical blue line in the upper right trace. The trace in the upper right of the figure is a log-log graph of the exciton diffusivity versus CEP IQY along the parameter coordinates indicated by the light blue cross-hairs in the lower-left figure. The slices and traces extending above and to the right of the lower-left figure present the 2D slices and 1D traces taken along their respective axes.
Figure 5.3 | CEP simulation - CEP radius cross-section. The lower left figure is a 2D cross-section taken across one value of CEP radius. This cross-sectional slice was taken at a $2 \times$ CEP radius value of 1.22 nm, as noted in the center of the figure and marked by the vertical blue line in the upper right trace. The trace in the upper right of the figure is a log-log graph of the CEP radius versus CEP IQY along the parameter coordinates indicated by the light blue cross-hairs in the lower-left figure. The slices and traces extending above and to the right of the lower-left figure present the 2D slices and 1D traces taken along their respective axes.
Figure 5.4 | CEP simulation - excitation intensity cross-section. The lower left figure is a 2D cross-section taken across one value of excitation intensity. This cross-sectional slice was taken at an excitation intensity value of $1.95 \times 10^{-5}$ photons·nm$^2$/ns as noted in the center of the figure and marked by the vertical blue line in the upper right trace. The trace in the upper right of the figure is a log-log graph of the excitation intensity versus CEP IQY along the parameter coordinates indicated by the light blue cross-hairs in the lower-left figure. The slices and traces extending above and to the right of the lower-left figure present the 2D slices and 1D traces taken along their respective axes.
excitation intensity and introduces novel fundamental dependencies to the overall behavior of CEP.

The log-log trace of CEP radius vs IQY exhibits a smooth decrease in log-log slope as the radius is increased regardless of the other parameters. However, as excitation intensity and diffusivity are changed the slopes change everywhere along the CEP radius trace. This indicates complex behavior along this parameter with a changing power law as a function of excitation intensity and exciton diffusivity and not simply a transition from quadratic to linear as exhibited by the excitation intensity trace. More careful modeling over a wider range of parameter values must be undertaken in order to more fully understand this behavior.

5.4 Discussion

The theoretical and numerical models presented here indicate that CEP functions in a unique manner that is not fully described as an extension of previously investigated processes. The calculation for the interaction distance of CEP provides a fertile starting ground for quantitative application of CEP. Just as the formulation of the Förster radius allowed FRET to be used as a quantitative tool for distance measurement in molecules, the calculation of the CEP radius should allow for more quantitative analysis of the results of CEP systems.

Similarly, the exact formulation of the CEP radius provides insight on the most effective ways to increase the range of CEP. The dependence on the 2PA cross-section of the acceptor and the fluorescent quantum yield of the sensitizer are somewhat intuitive. However, the insight that the length-scale of CEP is inversely proportional to the radiative lifetime of the sensitizer runs counter to much of the thinking that has driven other forms of upconversion. In upconversion systems such as TTA and ETU the lifetime of the sensitizer state is of crucial importance and any decrease in this lifetime
results in nonlinear decreases in upconversion efficacy. However, since CEP relies on a radiative energy transfer mechanism, the fluorescent decay pathway is turned from a loss mechanism to a gain pathway. The ability to lose energy through decay is still maintained and represented by the dependence on the fluorescence QY of the sensitizer. While processes such as TTA are optimized when both QY and excited-state lifetime are high, two goals which are often found to be contradictory, CEP is optimized with a high QY and a short fluorescence lifetime – two characteristics than tend to be complementary. Thus, improving the efficiency of CEP may simply be a matter of finding sensitizer chromophores the are highly luminescent in solid-state, a goal that has been extensively researched in the LED community, rather than hunting for chromophores with custom-tailored exotic properties.

It is also worth noting the strong $\lambda^8$ dependence of the CEP radius. This wavelength dependence dominates over all parameters in the CEP radius formulation and suggests an efficient path towards improving CEP acceptors. While it is natural to focus on the 2PA tensor of an acceptor as being its dominant characteristic in contributing to CEP, equation (5.18) indicates that this is merely a minor factor. The CEP radius gains from a two-order of magnitude increase in $\sigma_2$, achievable through careful design of appropriate polymers, can be entirely matched by red-shifting the 2PA spectrum of the acceptor by a factor of $\sim 1.8$.

Together, these results indicate that the design of acceptors with 2PA spectra in the NIR/IR range and highly emissive sensitizers with short radiative lifetimes will provide the most effective gains for CEP.

The results of the stochastic simulation of CEP present a similarly productive perspective for pursuing improved CEP. Achieving upconversion at low excitation intensities – ideally solar irradiance or less – has long been a goal of upconversion research [55] and much of TTA research has focused on improving triplet exciton diffusivity as a means to reach that goal [56, 57]. However, the range of the actual
energy transfer mechanism has received far less attention as a means of improving upconversion yields. While some studies have shown that triplet energy transfer can occur over extended range \cite{25} via intermediated FRET-like processes that involve spin-orbit coupling, there has been relatively little focus on methods of extending the direct energy transfer range for the upconversion processes of TTA or ETU. The work presented here demonstrates that not only is it possible to extend the direct coupling range of CEP beyond 5 nm but also that this extension of range provides a third means of improving total CEP yield beyond excitation intensity and exciton diffusivity.

Poulsen et al. \cite{58} carried out a study of three-dimensional energy transfer in an organic system found that exciton diffusivity played a key role in overall donor-acceptor energy transfer efficiency and that energy transfer was not accurately modeled by the usual FRET equations. They further found the spatial dynamics of excitons within the system was only accurately describable on an atomistic scale, as verified by corresponding results in both experimental and simulated systems. This study emphasizes the importance of simulations in capturing the true, molecular-scale kinetics of such complex energy-transfer systems and validates the findings presented in this work regarding the need for models that account for heterogeneity in both film morphology and energy distribution.

The simulation presented here demonstrates that rather than optimizing a single parameter, the most efficient gains in overall CEP efficiency come from improvements to all three parameters: excitation intensity, CEP radius, and exciton diffusivity. However, these results also imply that a deficiency in one parameter may be overcome, to some degree, by an increase in the other two parameters and indicating a pathway towards efficient CEP at low excitation intensities. Indeed, our results show that CEP yields of 80% may be achieved at 10× solar intensities with sufficient optimization of diffusivity and CEP radius. The data also indicates that the largest gains are found from overcoming “bottlenecks” in each of the parameters and that CEP is unlikely to
occur efficiently if any one of the three key parameters is below its threshold value. Considering that the CEP systems studied in chapter 4 and chapter 6 both have highly disperse, nearly isolated sensitizers and hence are likely to have minimal sensitizer exciton diffusivity, these results suggest that increasing the sensitizer concentration and allowing for higher diffusivity may yield dramatic improvements to CEP efficiency.

5.5 Conclusion

Cooperative energy pooling is a highly nonlinear energy transfer process and therefore is not accurately represented by the traditional kinetic models of systems of differential equations. The heterogeneity inherent within solid-state films of blended chromophores has strong impacts on the efficiency of CEP and more accurate models or numerical simulations are needed to fully capture this behavior. Deriving a formula for the CEP radius enables the rational design of chromophores with optimized optical properties and geometries for increasing the range of CEP. Calculating the range of CEP under reasonable experimental conditions reveals that it can occur at distances ranging approximately 1-10 nm, indicating that upconversion yields are affected by mesoscale morphologies and not just nearest neighbor chromophores. Simulating exciton diffusion in CEP systems yields an improved understanding of overall CEP functionality and reveals that excitation intensity, CEP radius, and sensitizer exciton diffusivity all play pivotal roles in determining the quantum yield of a system. Further optimizing and modeling of exciton diffusivity in CEP systems will enable the possibility of greater control over directed energy flow and potential non-linear improvements to upconversion efficiency.
Chapter 6

Polymer-based cooperative energy pooling

6.1 Introduction

Having experimentally observed cooperative energy pooling in organic systems in [chapter 4], the next step naturally turned towards designing a system with improved CEP efficiency and taking more complex measurements of its behavior. Since the two-photon absorption (2PA) strength of the acceptor plays a key role in enabling CEP and the stilbene-420 acceptor used in the previous study had a middling 2PA cross-section that peaked at a suboptimal wavelength, our first design goal for a second generation of CEP was to find a superior acceptor chromophore.

While there are a number of carefully designed molecules with 2PA cross-sections upwards of $10^4$ GM [59], these molecules may require complex synthesis processes to create and are not readily available in large quantities, making them undesirable for continued experimentation and scalability. However, dendrimers and polymers demonstrate cooperative effects that have been shown to scale 2PA cross-sections quadratically with the number of chromophores in the molecule [60, 61], making these design archetypes an appealing candidate for the acceptor in a CEP system.

Polymers have numerous advantageous physical properties. Simple processing techniques allow for the creation of polymer nanoparticles, granting unique properties and allowing for tuning of the phase-separation properties of the resulting material.
The mechanical and thin-film forming properties of many polymers make them amenable to various coating and processing techniques, allowing for economical industrial-scale processing. Many polymers are also available commercially and in scalable quantities, making polymers more economically accessible than many other large-2PA candidate molecules. Additionally, energy transfer along and between polymers can be quite high, with singlet exciton diffusion values reaching up to $7.9 \times 10^{-3} \text{ cm}^2/\text{s}$ [63]. As discussed in chapter 5, exciton diffusion plays a key role in CEP, further enhancing the appeal of polymers as a template for CEP system design.

In this chapter present the results of two distinct polymer-based CEP systems, both of which presented improved CEP yields over the previous Rhod6G/Stilb420 CEP system. After presenting a similar analysis of the CEP properties as introduced in chapter 4, we present preliminary measurements of the internal quantum yield of CEP within one of the CEP systems. Finally, we present femtosecond-scale transient absorption spectroscopy (TAS) data displaying the CEP energy transfer process with time-resolution to clearly observe the energy transfer from sensitizers to acceptor.

### 6.2 Results

#### 6.2.1 Absorption, emission, and two-photon absorption spectra

Since the 2PA spectrum of the acceptor determines the emission properties required of the sensitizer, the first step in designing a second generation of CEP system was to identify strong 2PA acceptors. The fluorene moiety has been shown to have good 2PA properties [64], and polymers incorporating fluorene derivatives have shown impressively large 2PA cross-sections [65, 66]. Four variations of fluorene polymers and co-polymers (displayed in figure 6.1) were selected as promising candidates both due to their potential for strong 2PA in the wavelength range of interest as well as for their commercial availability in >100 mg quantities. These polymers were purchased
from American Dye Source and used as received to make solutions in THF solvent. The 2PA cross-section of these molecules was measured using the two-photon excitation fluorescence method, as detailed in appendix C. The measured 2PA spectra are displayed in figure 6.2.

Figure 6.1 | Molecular structure of 2PA polymers and sensitizers. (a) ADS259BE, (b) ADS128GE, (c) ADS329BE, (d) ADS251BE, (e) zinc phthalocyanine, (f) HIDC iodide.

For most potential applications of CEP it is desirable that the upconverted wavelength be in the near-IR range. The strong 2PA cross-section and extension into the near-IR made the ADS128 and ADS259 polymers particularly appealing as acceptors for CEP. Combinatorial testing of these polymers in blend films with various NIR dyes revealed optimized CEP upconversion yields in pairings of ADS128 with zinc phthalocyanine (ZnPC) and ADS259 with 1,1,3,3,3,3-Hexamethyl-indodicarbocyanine iodide (HIDC). The structures of ZnPC and HIDC are displayed in figure 6.1.
Blend films were fabricated via blade coating onto glass substrates and were optimized for maximum film thickness in order to maximize the detectable CEP emission signal. The blade coating was carried out with a blade height of 75 µm above the substrate with the blade moving at 99 mm/s with the substrate at room temperature and a stock solution of ~30 g/L. Stylus profilometry measurements determined that the films were approximately 250-300 nm in thickness with 20-25 nm rms roughness. The sensitizer-acceptor blend ratio is another key factor in optimizing the CEP emission signal, as discussed in chapter 4. Films of various sensitizer/acceptor blend ratios were prepared, with a 1:40 sensitizer/acceptor ratio producing the largest upconverted signal. This is the same blend ratio that was found to be optimal in the first Rhod6G/Stilb420...
system [67], indicating that both ZnPC and HIDC exhibit strong aggregation-induced self-quenching and require low concentrations in order to maintain excited-state lifetimes long enough for effective CEP to occur. There is mention in the literature of strong aggregation-induced non-radiative decay in ZnPC [68], further validating this claim.

Figure 6.3 | Spectral properties of ZnPC/ADS128 CEP system. (a) Normalized absorption, emission, and upconverted emission spectra of ZnPC/ADS128 blend film. Upconverted emission was measured under excitation at 677 nm. The emission spectrum is cut off due to the use of a 500 nm shortpass filter to prevent scattered excitation light from contaminating the upconverted signal. Normal emission was measured using 330 nm excitation light. (b) Normalized absorption and emission spectra of ADS128 (acceptor) and ZnPC (sensitizer) in pristine solutions with THF solvent. Steady-state emission spectra were measured under excitation at 350 nm.

The absorption and emission spectra of the two CEP blend films, displayed in figures 6.3 and 6.4, exhibit all of the features of CEP previously identified in the Rhod6G/Stilb420 system. Excitation at a wavelength corresponding to sensitizer absorption results in upconverted emission with a spectrum corresponding to that of the acceptor chromophore. In both systems the 2PA spectrum of the acceptor overlap significantly with the emission spectrum of the sensitizer, corresponding to strong coupling between the sensitizer transition dipole and the acceptor 2PA tensor ($\mu^0_{a(S)}$).
Figure 6.4 | Spectral properties of HIDC/ADS259 CEP system. (a) Normalized absorption, emission, and upconverted emission spectra of HIDC/ADS259 blend film. Upconverted emission was measured under excitation at 664 nm. The emission spectrum is cut off due to the use of a 500 nm shortpass filter to prevent scattered excitation light from contaminating the upconverted signal. Normal emission was measured using 390 nm excitation light. Magnified red emission peak measured under excitation at 590 nm to target sensitizer absorption. (b) Normalized absorption and emission spectra of ADS259 (acceptor) and HIDC (sensor) in pristine solutions with THF solvent. Steady-state emission spectra were measured under excitation at 330 nm and 520 nm for ADS259 and HIDC, respectively.

and $\alpha^{b0(A)}$ in equation (3.8)) and hence a large CEP rate. Additionally, both of these polymer CEP systems exhibit minimal overlap between the acceptor emission spectrum and the sensitizer absorption spectrum, indicating that energy loss due to FRET from acceptor to sensitizer will play a minimal role. Excitation of the pristine acceptor at the same wavelengths as that used for CEP film excitation resulted in minimal upconverted emission, less than one tenth the emission of the corresponding CEP blend films when excited at the same wavelength, indicating that the CEP process is responsible for the vast majority of the observed upconversion.
6.2.2 Excitation dependence and quantum yield

The excitation dependence of upconverted emission can be a strong indicator of the efficiency of the upconversion process. The turnover point in an excitation dependence graph, namely where the excitation dependence transitions from being quadratically dependent on excitation intensity to linearly dependent, is an indicator of what excitation intensities are needed for the upconversion process to run most efficiently. A quadratic dependence on excitation intensity indicates that energy pathways other than upconversion are dominant, and hence that much of the absorbed energy is being lost to other energetic pathways before being upconverted. Conversely, linear upconversion dependence on excitation intensity indicates both an improved efficiency of upconversion as well as a constant internal quantum yield of upconversion [69].

Both CEP systems measured show clear transitions from (near-)quadratic excitation dependence towards linear dependence over the two orders of magnitude range in excitation intensity measured. However, the onset and gradient of these transitions is noticeably different. The HIDC/ADS259 system exhibits a relatively small change in power law dependence and the gradient of the power law dependence as a function of excitation intensity is relatively shallow. On the other hand, the ZnPC/ADS128 system exhibits a clearer transition in power law dependence, appears to begin the transition at a lower excitation intensity, and has a steeper gradient in this transition that allows the system to reach near-linear excitation dependence at lower total excitation intensities. Both of the CEP films measured in this work exhibit excitation intensity dependencies that show improved CEP upconversion over that of the Rhod6G/Stilb420 system, indicating progress on the path towards more efficient CEP.

The quantum yield (QY) of a process is generally a useful parameter in characterizing the overall efficiency of that process relative to competing processes within a system.
Quantum yield is defined as the number of times a particular process occurs in a system per incident photon. In the case of external quantum yield (EQY), this refers to the total number of photons in the excitation pulse and hence provides an indicator of both the process efficiency and the absorption of the system. Internal quantum yield (IQY) refers to the total number of absorbed photons, and hence specifically indicates what percentage of the total energy in the system proceeds through the mechanism in question. A measurement of the IQY of CEP in these polymer systems would be helpful towards determining the effectiveness of the particular chromophore blend and the polymer approach in general.
Figure 6.6 | Excitation dependence of HIDC/ADS259 blend films. The green squares indicate the measured upconverted emission at 436 nm from HIDC/ADS259 blend films as a function of 664 nm excitation intensity plotted on a log-log scale. The colored lines are quadratic (blue) and linear (red) fits to the first and last three data points, respectively. The black circles represent the instantaneous power-law dependence of the measured excitation dependence as determined by the slope of a linear fit to a sliding boxcar window of eight points on the log-log plot of the excitation dependence data.

Unfortunately, there are a few complications that make QY measurements of these systems challenging. First, it must be stated that quantum yield values in general are of limited value in a system with non-linear dependence on excitation. Linear processes, such as stimulated emission and FRET, have a constant QY value that is independent of excitation conditions until secondary non-linear effects (such as exciton recombination) begin to play a role. In a non-linear system like CEP, however, the QY is expected to be vary with excitation intensity until the excitation is well into the linear dependence regime. Since the system measured in this work began to demonstrate burn effects at the high end of the accessible excitation intensities, we were unable to excite the system
fully in the linear regime and thus the QY values measured are only be relevant to the excitation intensity at which they were measured.

Due to the scattering properties and thickness inhomogeneity of the CEP films, it is quite challenging to take a reliable measurement of the quantum yield of CEP using a reference methodology. For solutions one can measure the emission from a known concentration of a standard whose fluorescence quantum yield is well-documented and use that measurement to calibrate the results of an emission measurement from another sample. However, thin films may scatter light inhomogeneously and with intensities that vary from point to point on a film, making it challenging to produce reliable measurements of a known standard under exactly repeatable conditions. Similarly, if the thin films in question have any variations in thickness then the overall intensity of emission may vary as a function of the location of the excitation beam spot, resulting in emission data that convolves the film thickness with the efficiency of the process being measured. This problem affects both the reference standard as well as the sample in question, further increasing the sources of error.

In order to accurately measure the quantum yield of a process occurring in a thin film it is preferable to use a measurement technique that does not rely on a reference standard and that can account for varying thickness in the film. An integrating sphere allows for QY measurements that meet these requirements. By exciting a sample in the center of a diffusely reflective sphere one can (ostensibly) collect all of the emitted light as well as all of the unabsorbed excitation light. de Mello et al. [70] presented a method whereby three different measurements taken in an integrating sphere allow for the calculation of the IQY of an emission process without the need to rely on external measurements of absorbance. This is accomplished by measuring the full light spectrum of the film when excited inside the sphere – including both scattered/transmitted excitation light as well as the stimulated emission signal – and calibrating this measurement via measurements of the film when indirectly excited (i.e.
excitation beam is directed onto wall of the sphere) and without a film in the sphere. These calibration measurements account for the full initial flux of the excitation beam as well as for the unabsorbed excitation light, which accounts for the exact absorption of the sample at the spot being measured. This process also accounts for the film’s secondary absorption of the scattered excitation light in the sphere and hence preventing under-counting the absorptivity.

The drawback to this measurement process, however, is that the measured upconversion signal must be collected simultaneously with the non-absorbed excitation light, and only after diffuse reflection from the sphere walls. This means that even for a highly reflective sphere (average reflection > 98% across the wavelengths of interest for the integrating sphere used in this work) the emission signal will be somewhat attenuated after multiple reflections. This makes accurate measurements of weak signals especially challenging, which precluded the measurement of QY of the Rhod6G/Stilb420 system. However, the improved CEP emission of the ZnPC/ADS128 system allowed for IQY measurements just barely above the noise floor.

Using the method of de Mello et al we measured an IQY of 0.0001% for CEP in the ZnPC/ADS128 system. This value is significantly less than the value predicted for the IQY of the Rhod6G/Stilb420 system by the kinetic model proposed in chapter 4.

There are a number of potential explanations for this deviation. First, the model used to fit the Rhod6G/Stilb420 data included a $\gamma$ term to model energy transfer among sensitizers. This term only effectively models radiative energy transfer between sensitizer (see equation (3.1)) and more recent work (see chapter 5) has shown that non-radiative energy transfer (FRET and Dexter) likely plays a more dominant role in the behavior of sensitizer excitons. The $\gamma$ term used in equation (4.1) does not accurately describe the contributions of non-radiative energy transfer, making the use of the $\gamma$ term likely to reduce the accuracy of the model’s results. Additionally, due to experimental restrictions the shortpass filter used in collecting the upconverted emission signal had
to be placed directly in front of the light fiber output port and inside the sphere. The shortpass filter used has a cutoff frequency halfway across the upconverted emission band of the CEP film, and despite efforts to reconstruct the full emission spectrum using Gaussian fitting methods, there was likely some error introduced in this process. Additionally, the shortpass filter is composed of a dielectric stack, which is sensitive to the angle of incidence of incoming light. Thus, there is the distinct possibility that the acceptance cone of light that could be successfully coupled into the output fiber was reduced by the shortpass filter, potentially substantially reducing the intensity of the detected signal and altering the detection properties from those accounted for in the spectral correction\(^1\). The ADS128 polymer is also susceptible to burning at the high excitation intensities used in the IQY measurement, with a noticeable drop in upconverted emission occurring within 2-5 minutes of excitation exposure. While efforts were taken to measure for limited times to reduce the potential for film burning, it is nonetheless possible that the final IQY measurements reflected reduced upconversion due to burn effects and therefore should be taken as lower-bound values for the true IQY.

In summary, we have measured an IQY lower-bound of 0.0001% for the ZnPC/ADS128 CEP system. There are a number of reasons why the measurement of IQY in this work is lower than the prediction of the kinetic model for the less efficient Rhod6G/Stilb420 CEP system. However, the sources of these errors indicate that the measured IQY value can be taken as a minimum and that the true IQY could potentially be larger.

\(^1\) While spectral corrections were taken to correct for the effects of the integrating sphere, light fiber, and detection apparatus these corrections were taken under conditions that may have been suboptimal. The spectral correction was carried with a known light source and a baffle between the excitation source and the output fiber, as is typical. However, there was no baffle between the beam spot of the excitation light on the sphere wall and the output port, causing the detected signal to potentially be dominated by the first-bounce light rather than the nth-bounce light that would better resemble the beam path of the measured upconversion signal and have spectral deviations from the sphere coating.
6.2.3 Time-resolved transient absorption measurements

Transient Absorption Spectroscopy (TAS) is a powerful tool capable of measuring the unique “fingerprint” of a material by detecting changes in the excited- and ground-state-absorption spectra of the material as a function of time after an excitation pulse. This change in optical density, or $\Delta OD$, is the transient absorption (TA) signal that allows for the identification of distinct excited species within a sample based both on their spectral properties as well as their decay lifetimes as described in detail by Berera et al. [71]. In the case of CEP, TAS provides an opportunity to directly observe the excitation of the sensitizer chromophore and follow the energy transfer to the acceptor over time after the initial excitation pulse. This type of measurement provides not only direct evidence for CEP energy transfer upconversion but also indicates the time-scales on which CEP operates.

To identify the characteristic spectra of the sensitizer and acceptor chromophores, measurements were taken of pristine films of ZnPC and ADS128. As is visible in figure 6.7, ADS128 has uniquely identifiable features centered at 469 nm and 515 nm, with a slight shoulder feature at 555 nm, all of which have $-\Delta OD$ signals. The shape of the spectra changes over time, as noticeable in the absence of the 515 nm and 555 nm features after ~100 ps, indicating that each of the features in the transient signal of the acceptor have distinct decay rates. While a more thorough analysis of these features might yield assignments to the various electronic and vibrational modes of the acceptor molecule, this type of analysis would reveal more about the behavior and characteristics of the ADS128 molecule itself than it would about the CEP process and hence is extraneous to this study. In this work we are primarily concerned with identifying the process of CEP energy transfer from the sensitizer (ZnPC) to the acceptor (ADS128), and since the ADS128 acceptor has distinctive transient features in its TA spectrum we can proceed with an analysis that is essentially binary: if the blend film exhibits transient
features matching those of the ADS128 spectrum then we conclude that there exists a population of acceptors in the excited state and vice versa.

Figure 6.7 | TA spectra of pristine ADS128 thin film. When excited at 400 nm the ADS128 polymer displays two noticeable features at 469 nm and 515 nm with a slight should feature at 555 nm, all with $-\Delta\text{OD}$ peaks. The 515 nm peak and the shoulder feature are nearly absent after 150 ps, indicating that the different features each have distinct lifetimes. The inset figure shows the kinetics of the 469 nm feature of the same film when excited at 677 nm. This peak is the only detectable signal when excited at two-photon absorption wavelengths and displays a noticeably short lifetime, with a FHWM of 100 fs.

When excited at the 2PA wavelength of 677 nm the ADS128 does exhibits only a signal at 469 nm, as displayed in the inset of figure 6.7 but this signal decays at an incredibly rapid rate and is entirely absent after $< 100$ fs. This timescale is shorter than the $\sim 150$ fs instrument response time, indicating that this signal may potentially be significantly shorter than the measured 100 fs and thus can not be accurately analyzed for its kinetics. However, this short timescale does allow for the exclusion of various processes that can not be responsible for the signal and a few suggestions as to what may be causing this signal.
Since single photon and two-photon absorption processes should nominally result in identical excited states in the ADS128 polymer, the dramatic difference in decay rates suggests that the signal observed in the acceptor under 677 nm excitation is not a typical excited state. While the local environment of a chromophore can affect the linear absorption spectrum to a small degree, the nearby electrostatic environment of a chromophore can have large affects on its 2PA cross-section [47], potentially indicating that the two-photon excited chromophores have selectively reduced lifetimes with rapid non-radiative decay. However, this explanation seems insufficient to explain such a dramatic change in excited state lifetime. Alternatively, 2PA is quadratically dependent on excitation intensity and is therefore most likely to occur at the precise locations where the film is most likely to burn. The TA data presented here was taken with femtosecond-scale excitation laser pulses that were observed to burn the film rapidly. While all measurements were taken at short timescales\(^2\) to minimize film burning, it is nonetheless possible that the chromophores that underwent 2PA were also subjected to the most intense laser excitation and thus were degraded during the \(~100\) fs excitation pulse, potentially explaining the short duration of the excited state.

The short-lived peak can not be due to stimulated emission from the pump pulse since the resulting signal would be independent of probe timing and hence would be a background signal across all delay times. Similarly, it can not be a Raman signal since it does not scale with excitation wavelength. The remaining potential explanations for this peak are cross-phase modulation (XPM) and the optical Stark effect (OSE). XPM is the result of overlap of the pump and probe pulses within a non-absorbing medium with a Kerr nonlinearity. Since the acceptor has essentially no absorption of the 677 nm excitation pulse, any nonlinear index of refraction in the material could allow the

\(^2\) Signal decay due to film burning was measured to be approximately 10% after 2 minutes, so all TA spectral scans were taken in under two minutes and the order of the time points was randomized. To compensate for the increased noise level of such rapid scans all scans were taken at ten different locations on the film and all spectra averaged together.
two beams to interact, potentially shifting the phase and, indirectly, the wavelength
of the probe pulse. XPM has been observed to produce short-lived artifacts in TA
measurements [72] and may be responsible for the signal observed in this work.
Alternatively, OSE may occur whereby the excitation pulse may interact with the
electronic states of the acceptor chromophore to alter the available energy states,
resulting in a temporary shift of absorption bands for the duration of the pump pulse. This
OSE may cause increased absorption at particular wavelengths for very short intervals
of time, as observed in TA data by Yang et al. [73], potentially explaining the signal
observed here.

Due to the limited temporal resolution of this experiment we are unable to probe
this rapid signal more thoroughly, and accordingly we are unable to confidently identify
the cause of this peak. We do note, however, that the signal is entirely absent after ~100
fs and hence will not have any affect on the overall kinetics of CEP film signal.

The TA spectrum of ZnPC (figure 6.8) has a broad plateau extending from ~430-
600 nm with a $+\Delta\text{OD}$ signal that is composed to sub-features at 485 nm, 530 nm,
and 596 nm, each with distinct decay rates and matching similar data in the literature
[74]. The feature at 596 nm has a noticeably faster rise and decay time than the other
features, further complicating any lifetime analysis.

While the acceptor and sensitizer chromophores have distinct and uniquely
identifiable features, the fact that the main features of ADS128 and ZnPC overlap in
wavelength, have opposite $\Delta\text{OD}$ signals, and have distinct lifetimes indicates that the
signal from the CEP blend film will be a complex superposition of the two signals as a
function of time. As expected, the TA signal from the CEP blend film (figure 6.9) does
appear to contain components from both sensitizer and acceptor TA spectra. The CEP
blend film exhibits a clear plateau extending from 485-590 nm that corresponds to a
similar feature in the sensitizer spectrum, as well as a dip centering around 469 nm that
corresponds to the acceptor signal peak.
Figure 6.8 | TA spectra of pristine ZnPC thin film. When excited at 677 nm the ZnPC sensitizer displays a main $+\Delta OD$ plateau feature stretching between ~430-600 nm, with slight sub-features at 485 nm, 530 nm, and 596 nm. Since the shape of the spectrum changes over time the different features must have slightly different lifetimes, but the data was too noisy for accurate fitting of the distinct decay lifetimes. The overall lifetime of the ZnPC excited state is noticeably longer than the ADS128 excited state lifetimes.

Analyzing the TA signal of the CEP blend film is somewhat complex due to the myriad energetic processes occurring within and among each of the chromophore types. As discussed above, the goal of this analysis is to characterize the process of CEP energy transfer from sensitizer to acceptor. Keeping this in mind, we will dispense with analysis of TA signals that are relevant primarily to the internal processes within a chromophore (i.e. the various peaks and associated lifetimes in the sensitizer or acceptor spectra) as well as signals related to processes that occur after the CEP process (i.e. any evolution of the signal components corresponding to the acceptor after its initial excitation). What remains is the evolution of the sensitizer signal after excitation and its subsequent energy loss processes (both CEP and various internal decay processes) as well as the growth of the acceptor signal due to CEP energy transfer from the sensitizer.
Figure 6.9 | TA spectra of ADS128/ZnPC CEP film. (a) TA spectra for the ADS128/ZnPC thin film under excitation at 677 nm. The main plateau feature of the ZnPC sensitizer and the $-\Delta OD$ peak at 469 nm of the ADS128 acceptor are both present, with the ADS128 feature rising at a later time than the ZnPC feature. This delayed rise indicates energy transfer from ZnPC to ADS128 and hence CEP, as discussed in detail in the text. The other sub-features of both chromophores are absent. Note that the overall signal is much lower in intensity than the previous TA spectra, largely due to the superposition of two signals with opposite $\Delta OD$. The data was binomially smoothed in five passes in order to reduce some of the noise inherent in such a low-strength signal. (b) Kinetic traces corresponding at the wavelengths of the component chromophore features are displayed on a normalized $\Delta OD$ axis to facilitate comparison of rise-times and decay times. The previously distinct features above 485 nm all appear with similar decay times. However, the kinetics at 469 nm show a fast rise in $-\Delta OD$ corresponding to the fast anomalous ultrafast signal in ADS128 at this excitation wavelength, followed by a rise to $+\Delta OD$ corresponding to the ZnPC excited state, and finally a decay to $-\Delta OD$ corresponding to a delayed rise of the ADS128 excited state and indicating CEP.

Crucial to this analysis is the ability to accurately identify the various features present in the TA data so that they may be properly assigned to their sources. This
is made somewhat easier by the fact that in the range of interest (~440-600 nm) the acceptor signal is entirely −ΔOD while the sensitizer signal is entirely +ΔOD. However, since there is an initial negative signal at 469 nm due to the anomalous ultrafast feature as well as subsequent decay of the positive sensitizer signal, both of which contribute features with −ΔOD weight, we must be careful to ensure that any signal attributed to CEP-induced acceptor excitation is not due to these other factors.

While the features at 485 nm, 515 nm, and 596 nm have distinct lifetimes in the pristine films, they appear in the blend film (figure 6.9b) with nearly identical decay lifetimes. The sensitizer TA spectrum exhibits roughly similar behavior at each of these wavelengths, suggesting that these wavelengths (as well as the entirety of the plateau of the signal) correspond to the sensitizer excited state.

The 469 nm feature’s kinetic trace has a delayed rise compared to the others, likely due to the aforementioned ultrafast anomalous acceptor signal, with a subsequent small rise to +ΔOD values. Since the kinetic trace of the acceptor at 469 nm never exhibits a +ΔOD signal we attribute this rise to excitation in the sensitizer. Since the anomalous ultrafast signal in ADS128 is entirely absent after 200 fs and the ZnPC signal is entirely +ΔOD, all −ΔOD signal at 469 nm after ~1 ps can be attributed to the main TA feature of the acceptor, and hence to acceptor states excited by the CEP process. After 1 ps, this 469 nm feature proceeds to decrease at a much faster rate than the other features and after a few 10s of picoseconds exhibits a −ΔOD signal.

The negative value of this 469 nm feature is significant because it allows us to positively identify this feature as corresponding to the excited acceptor. The ZnPC TA signal maintains a relatively uniform +ΔOD value throughout its entire decay lifetime, which suggests that any deviation from this flat, positive signal is due to excited acceptor. However, deviation from a flat signal would not be conclusive proof of excited acceptor states. A hypothetical +ΔOD signal at 469 nm that had reduced OD compared to the rest of the plateau signal at longer wavelengths could potentially be
caused by a change of shape of the sensitizer signal when in a blend film. Evolution of this hypothetical feature towards reduced, but still positive, OD could potentially indicate either increased acceptor excitation or simple decay of sensitizer excitation without the possibility of distinguishing between the two.

However, the feature at 469 nm is negative and since the sensitizer signal has no $-\Delta$OD components at any point in time it would be impossible for the TA signal to exhibit $-\Delta$OD without the presence of excited acceptor chromophores. The $-\Delta$OD may be either due solely to excited acceptors or due to a superposition of positive signal from excited sensitizers and a stronger negative signal from excited acceptor states, but either interpretation indicates that the acceptor has successfully been excited and hence CEP must have occurred\(^3\).

Simultaneous excitation of the acceptor and sensitizer could yield an increasingly $-\Delta$OD only if the $+\Delta$OD component of the signal (sensitizer) decayed more rapidly than the $-\Delta$OD component (acceptor), leaving an overall $-\Delta$OD signal after sensitizer decay. However, the TA spectra of the pristine samples indicates that the acceptor has a distinctly longer lifetime than the sensitizer, indicating that the growing $-\Delta$OD feature must be due to the acceptor becoming increasingly excited at delayed times. Since CEP requires excitation of the sensitizers followed by subsequent energy transfer to the acceptor, this delayed excitation evident in the data is further evidence for CEP.

Analyzing the actual kinetics of CEP in this system is somewhat complex due to the superposition of the sensitizer signal decay with both the prompt and delayed rise and subsequent decay of the acceptor signal at the same wavelength. Thus, while we can conclusively state that the delayed rise of a $-\Delta$OD peak could only occur in the

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\(^3\) While the actual TA spectrum in the 450-480 nm range appears to be quite noisy, it must be noted that the signals in that wavelength range in both the component chromophore spectra are quite clear, indicating that the noisy, near-zero signal is not due to a lack of signal but rather due to a super-position of positive and negative $\Delta$OD signals. While the absolute magnitude of the $-\Delta$OD signal is quite small, this signal was averaged over ten distinct measurements at different locations on the film and is also consistently negative with no signs of decay out to 1 ns, and thus is not an artifact of noise in the data.
presence CEP, we can not deconvolve the actual rate of CEP from the other overlapping processes occurring simultaneously and hence can not fit the data to extract a CEP rate.

Subtracting the signal at 469 nm from the average signal of the plateau region (490-590 nm) would yield a signal weighted by the numbers of excited sensitizers versus acceptors. Without the ability to accurately correct for that weighting the rate of change of the 469 nm feature would be a convolution of the sensitizer decay and the CEP rate, once again preventing the extraction of an actual rate of the CEP process.

After excluding all the methods of extracting rates of the CEP process, the remaining pathway forward is a general estimate of the timescale on which CEP occurs. Since the feature at 469 nm begins its negative slope in the 1-10 ps timescale and flattens out by ~500 ps, we can confidently estimate that the timescale of CEP in this system is in the range of tens-to-hundreds of picoseconds.

6.3 Discussion

Despite the lack of detailed lifetime analysis of the TA data, we observe that the acceptor signal rises to full $-\Delta \text{OD}$ strength within ~400 ps and then sustains with minimal decay beyond 1 ns.

Considering that the pristine acceptor signal decayed by a factor of two within ~150 ps, the endurance of the $-\Delta \text{OD}$ signal at 469 nm past 1 ns in the blend film is notable and potentially indicates excited acceptor states with lifetimes longer than hundreds of picoseconds. Similarly to the brief lifetimes of the anomalous ultrafast signal in the pristine acceptor, it is possible that the anomalously long lifetimes of the CEP-excited state is due to morphological selectivity of the CEP process. For instance, CEP is more likely to occur when there is a minimal separation distance between the sensitizers and the acceptor, and hence CEP energy transfer is likely to preferentially occur to acceptor chromophores whose nearest neighbors are sensitizers rather than other
acceptors. This isolation from other acceptors then potentially extends the lifetime of the CEP-excited state towards its inherent radiative lifetime by reducing pathways for non-radiative decay via self-quenching. Thus, heterogeneity of the CEP film morphology may play an important role in the CEP rates and excited state lifetimes. While it is possible that the persistence of the excited acceptor signal may indicate the transfer of energy to a longer-lived state in the acceptor, such as a triplet state, it is unlikely that such a state would exhibit a TA feature at an identical wavelength to that of the first excited singlet state. Further investigation into the excited state lifetimes of the particular chromophores that are the most likely to undergo CEP may yield insight into the role of local morphology on CEP rates.

Even without exact values for the rate of CEP in this system one can still use the approximate CEP rate to insert into equation (5.19) to find an approximate sensitizer-acceptor chromophore separation distance in the ADS128/ZnPC system. Using literature values for ZnPC [75] of $\tau_{\text{rad}} = 4.1$ ns and $\Phi = 0.28$ and combining these with the peak emission wavelength of ZnPC of $\lambda = 677$ nm and the approximate 2PA strength of the acceptor $\sigma_2 \approx 4 \times 10^5$ GM (approximating 2PA cross-section values using an analogous polymer acceptor from Wu et al. [76]), we find that the sensitizer-acceptor separation distance in this system is estimated to be between 2.3-3.2 nm. This is an entirely reasonable range of chromophore separation in a thin film, especially when considering that while the ZnPC chromophores are only 1-2 nm in width and much thinner in cross-section, one would expect to find them at somewhat greater (average) distances from the acceptor chromophores due to the low concentration of sensitizer chromophores in the CEP blend film. Further adjustments to film morphology could potentially reduce this separation distance and increase the overall rate and yield of CEP upconversion.

The overall results of this work indicate a step forward in the development of CEP systems. While the improved upconversion rates compared to the previous
Stilb420/Rhod6G system allowed for more advanced measurements techniques such as IQY and TA, there is still plenty of room for improvement. The low upconversion rates left yielded very small signals with high levels of noise, which increased the uncertainty in the data and reduced the extent of the analysis we were able to carry out. Higher signal-to-noise ratios would allow for improved measurements of IQY and better lifetime fits to the TA spectra.

While the polymer-based CEP systems presented in this work exhibit improved CEP over the previous generation CEP system, we are not able to isolate the exact mechanisms that have improved. This is because the systems in this work have larger acceptor 2PA cross-sections, 2PA that extends to longer wavelengths, improved spectral overlap between acceptor and sensitizer, and reduced FRET energy loss pathways, all of which are factors that are expected to improve CEP rates. The experiments carried out in this work are insufficient to isolate the dependence of CEP on each of these separate mechanisms and hence can not verify the CEP equations presented in chapter 5.

One aspect of the CEP system that was notably not improved in these polymer films was the self-quenching behavior of the sensitizer. As discussed in chapter 4, the 1:40 blend ratio is approaching the limit at which the average sensitizer chromophores is isolated from all other sensitizers. The fact that this blend ratio exhibited the highest CEP emission indicates that sensitizer self-quenching remains a dominant energy loss mechanism in these polymer CEP systems. The use of sensitizers with high QY even when aggregated would directly increase both the CEP rate but also the CEP radius, as shown in equation (5.3) and equation (5.18). The isolation of sensitizer chromophores in these systems also drastically reduces the diffusivity of sensitizer exciton. As shown in chapter 5 an overly small diffusivity will result in minimal CEP yields.

High self-quenching the sensitizer chromophore leads to reduced CEP radius, reduced overall absorbance of the blend film, and reduced exciton diffusivity, all of which
non-linearly reduce overall CEP yields. Therefore, the fact that we observe any CEP upconversion with such lossy sensitizers indicates that with even slightly improved sensitizers potentially dramatic improvements to CEP efficiency may result.

6.4 Conclusion

In this work we have presented two new CEP systems, both based on polymeric acceptors. These systems exhibited excitation intensity dependencies that show a clear transition from quadratic to linear, with the AD128/ZnPC system nearly approaching the linear regime. Internal quantum yield measurements on the ADS128/ZnPC system indicated minimum efficiency value of 0.0001%, but a number of factors indicate that the true efficiency may be higher than this. Transient absorption measurements on this same system revealed delayed excitation of the acceptor when excited at sensitizer absorption wavelengths, and displayed CEP occurring on a timescale of tens to hundreds of picoseconds. Further improvements to the CEP system, particularly the sensitizer chromophore, are expected to yield improved results and allow for more in-depth investigation utilizing advanced spectroscopies.

6.5 Methods

6.5.1 CEP film-making procedures

All acceptor polymers were purchased from American Dye Source. HIDC was purchased from Exciton and ZnPC was purchased from Alfa Aesar. All materials were used as received. To fabricate thin films acceptor and polymer chromophores were separately mixed into \(~30\text{ g/L}\) solutions in THF solvent. These solutions were blended together in a ratio of 40 parts acceptor to one part sensitizer. This blend solution was then coated onto a glass substrate using a Zehntner ZAA 2300 blade applicator with
the platen at room temperature, a blade height of 75 \( \mu \text{m} \) and a blade speed of 99 \( \text{mm/s} \) to produce films \( \sim 250-300 \) nm thick with 20-25 nm rms roughness. Glass substrates were cleaned via sonication in acetone and methanol for 5 minutes each and subsequent UV-ozone treatment for 2 minutes before film deposition.

### 6.5.2 Spectroscopy methods

All absorption data was taken on a VWR UV-1600PC Scanning Spectrophotometer. All emission spectra were taken on a LaserStrobe spectrometer from Photon Technology International using a GL-3300 nitrogen laser and GL-302 dye laser attachment, also from Photon Technology International. Upconverted emission spectra were measured with the emission filtered by a 500 nm short-pass filter from Thorlabs, model FES0500, to prevent reflected excitation light from interfering with the measured emission signal. Laser power was measured with a 919P-003-10 thermopile sensor from Newport. Quantum yield measurements were taken in a 4P-GPS-053-SL spectralon integrating sphere from Labsphere with some homebuilt ports and sample holders coated in a diffuse reflective coating mixed according to Knighton and Bugbee [77]. All spectra were corrected for the spectral responsivities of the systems used for data collection.

Transient absorption measurements were on the system described in Tseng et al. [78]. The fundamental excitation pulse was generated using an amplified Ti:sapphire laser from Spectra-Physics (Solstice, 800 nm, 1 kHz, \( \sim 150 \) fs pulse FWHM, 3.5 mJ/pulse max) which excited a TOPAS-C optical parametric amplifier from Light Conversion to generate the variable-wavelength (400 or 677 nm) pump pulse used in the experiment. The white light probe light was generated via a portion of the Ti:sapphire beam impinging upon a sapphire plate, the output of which was split into a probe and a reference beam. The pump pulses were passed through a depolarizer and chopped by a synchronized chopper to 500 Hz before reaching the sample. The pump and probe
beams were focused to overlap on the sample. The transmitted probe and reference beams were coupled into optical fibers and sent to multichannel spectrometers with CMOS sensors with 1 kHz detection rates where the reference signal was used to correct the probe signal for pulse-to-pulse fluctuations in the white-light continuum. The time delay between the pump and probe pulses was controlled by a motorized delay stage. All experiments were conducted at room temperature. The change in absorbance signal (ΔOD) was calculated from the intensities of sequential probe pulses with and without the pump pulse excitation. All data was measured at using randomized time points, meaning that the data was not taken in sequential time steps in order to avoid any artifacts resulting from beam damage to the sample over time. Each spectrum was taken in less than two minutes of time in order to minimize sample burning from beam exposure, and every spectrum was measured at 10 different locations on the film and averaged together afterwards to improve signal-to-noise. ZnPC spectra were taken at 0.1 mJ/pulse excitation intensity while ADS128 and CEP film spectra were taken with at 25 µJ excitation intensity, all with a beam spot of ~200 µm diameter. All data was corrected for chirp in the excitation pulse and any variance of T0 between measurements.
This work presented the first experimental investigation of cooperative energy pooling. Beginning with an expansion of the perturbative coupling between electronic states and applying Fermi’s Golden Rule allowed for the derivation of a unique form of energy transfer involving two sensitizers and a single acceptor. Connecting this initial intermolecular electronic coupling to the well-known processes of Förster resonance energy transfer and two-photon absorption allows for this energy transfer process to be understood in the simpler terms of a three-body resonant coupling between the emission states of two sensitizers and the two-photon absorption tensor of an acceptor.

That understanding allowed us to design and fabricate what we believe to be the first instance of an intentionally-designed CEP system. This blend of Stilbene-420 and Rhodamine 6G exhibited CEP photon upconversion with an improvement of a factor of 160 over the pristine acceptor (i.e. 2PA upconversion). Further analysis of this process facilitated the creation of a system of differential equations to model the energy kinetics of the CEP system. While this model did accurately fit the data from our experimental CEP system, it inherently made various assumptions of exciton homogeneity within the system that appeared to be insufficient in accurately modeling the true behavior of CEP.

Comparison with other energy transfer processes highlighted the non-linearity of CEP and indicated that the process was not accurately represented by the traditional kinetic models of systems of differential equations. The first step towards an improved
model for CEP was an understanding of the distance scales over which the process could occur. Since CEP is in many ways analogous to FRET, we used the template of Förster’s derivation of the radius of FRET to derive a CEP radius. Calculating the range of CEP under reasonable experimental conditions revealed that CEP can occur at distances ranging approximately 1-10 nm, indicating that upconversion yields are affected by mesoscale morphologies and not just nearest neighbor chromophores. In order to more accurately capture the behavior of CEP in a heterogeneous distribution of diffusing excitons that can interact at a distance, a computational simulation was carried with varying parameters of excitation intensity, CEP radius, and sensitizer exciton diffusivity. The results of this simulation revealed that while all three parameters strongly impact overall CEP efficiency, they each have threshold values that must be surpassed in order to achieve appreciable upconversion yields. However, the results also suggested that high CEP quantum efficiencies are still possible with low values of one parameter provided that the other two are sufficiently optimized, suggesting a design pathway for CEP at low excitation intensities.

Based on the results of this work a second generation of CEP system was designed with polymeric acceptors. The chromophores were selected to provide improved film morphology and larger 2PA cross-sections in order to extend the CEP radius. These systems exhibited markedly improved CEP upconversion with excitation intensity dependencies that showed a clear transition from quadratic to linear, with the AD128/ZnPc system nearly approaching the linear regime. Internal quantum yield measurements on the ADS128/ZnPc system indicated minimum efficiency value of 0.0001%, but a number of factors indicated that the true efficiency may be larger. Transient absorption measurements on this same system revealed delayed excitation of the acceptor when excited at sensitizer absorption wavelengths, and displayed CEP occurring on a timescale of tens to hundreds of picoseconds. Further improvements to
the CEP system, particularly the sensitizer chromophore, are expected to yield improved results and allow for more in-depth investigation utilizing advanced spectroscopies.
Chapter 8

Future directions

While the work presented above demonstrates measurable CEP upconversion, it is clear that the main effort ahead remains in further improving the overall CEP yield. While the 2PA gains from harnessing a polymer acceptor were impactful on the experiment presented in chapter 6, many of the benefits of polymeric chromophores would be even more relevant to the sensitizer. Further work exploiting the high fluorescent quantum yields and high exciton diffusivities of polymeric chromophores [79] could be expected to yield non-linear improvements in overall CEP efficiency. With the use of polymers, novel morphology states such as nanodots may be employed to further improve CEP behavior. Conjugated polymer dots have been shown to exhibit increased emission and 2PA properties over their standard morphologies [76, 80], indicating that future studies of dot-based CEP systems may yield promising results.

The design goals of the OLED community and the ideal CEP chromophore sensitizer are strikingly similar. Ideal materials for OLEDs and for CEP sensitization should have high exciton mobilities, short radiative lifetimes, high fluorescence quantum yields, and good film-forming properties. Investigating CEP with notable materials from OLED studies such as Yao et al. [81] and Tuong Ly et al. [82] may yield excellent results without the need for the development of novel chromophores. Additionally, while some of the OLED materials may not be polymers capable of forming nanodots themselves, there have been successful attempts to form polymer nanodots around them to
create sensitizer-acceptor pairs locked into close proximity and exhibiting efficient TTA upconversion \[83\]. Presumably these results could be successfully duplicated for CEP upconversion.

Investigation of the effects of external environments on the efficacy of CEP may be another promising avenue of research. Nanostructures such as nanogratings and nanocavities are known to have strong effects on the optical properties of materials in close proximity to them and these effects may be harnessed to improve CEP. Experiments on nanogratings have been show to greatly enhance the electrical field in localized regions and this technique has been successfully applied to enhanced upconversion in ETU systems \[84\]. Similar studies with CEP materials may yield similar gains. More interestingly, substrate effects may be used to enhance beneficial couplings and suppress loss pathways. Experimental work has shown that photonic crystals are capable of suppressing emission modes of chromophores \[85, 86\], reducing spontaneous emission by up to a factor of five. If a photonic crystal were tuned to suppress spontaneous emission of the sensitizer the resulting extended lifetime could have drastic impacts on CEP yields. Longer lived sensitizers would result in increased diffusion lengths and decreases in energy loss, both of which could greatly aid CEP.

Theoretical explorations of this concept and its applications to CEP in nanocavities have been carried out by LaCount and Lusk \[87\], revealing the potential for improvements in CEP yield by potentially a factor of \(10^4\). Experimental verification of this enhancement is yet another promising avenue towards enhanced CEP.

Further time-resolved measurements of CEP upconversion would help shed light on the CEP process itself and allow for verification or improvement of the theory underlying CEP. Further TAS studies with improved signal resolution and improved fitting models could yield measured rates for the CEP process that may be compared to theoretical predications. Detailed analysis of TAS data may allow for identification of the particular molecular states in the acceptor that are excited by the CEP process, allowing
for further investigation into the coupling modes between sensitizer and acceptor. Time-resolved photoemission spectroscopy (TR-PES) is another promising avenue for improved CEP data. TR-PES can provide high-energy-resolution data showing the change in state occupation over time, potentially directly revealing which energy states in the sensitizers are coupled to which energy states in the acceptor and on what timescales this energy transfer occurs. Since this form of spectroscopy directly measures excited electrons rather than their secondary effects on optical properties of the material, TR-PES could allow for investigating of the isolated properties of the CEP process without convolution with secondary absorption and emission signals.

There remain many potentially fruitful avenues of research to explore regarding theoretical and simulation-based investigations of CEP. As mentioned in [5], the formulation of the CEP rate in [5.3 on page 64] is only applicable to a single coupling wavelength between sensitizers and acceptor. In actuality the full CEP coupling is proportional to the entire emission and 2PA cross-section of the sensitizer and acceptor chromophores, respectively, and this must be taken into account in order to accurately calculate CEP rates and radii. Ongoing work in our group has begun to address this goal. As was also mentioned in [5], the current formulation of the CEP rate is only valid for two sensitizers and one acceptor. Since the radius of CEP can extend for multiple nanometers and encompass a large number of neighboring chromophores, the likelihood of coupling between multiple (>2) sensitizers and a single acceptor is high in a solid-state CEP system, rendering equation [5.3] incomplete, at best. Further work to accurately model multi-sensitizer scenarios could improve the accuracy of CEP theory.

Finally, the simulation presented in this work included a number of assumptions that may limit the effectiveness of its results. While the assumption of a uniform diffusivity for sensitizers excitons is not expected to result in false outcomes, it is likely to underestimate the effects that heterogeneous diffusivity rates would have on the concentration and funneling of excitons. Any slight spatial variation of sensitizer
exciton diffusivity within a CEP film is likely to create preferential direction for diffusion, resulting in areas of concentrated excitons which would non-linearly increase CEP rates. CEP simulations that could model spatially varying exciton diffusivities may find channeling effects similar to those found by [58] and resultant higher rates of CEP. Further extension of these models to include spatial lattices modeled after the morphological properties of actual acceptor and sensitizer chromophores in varying blend ratios could yield additional improvements to these simulations.
Citations


[77] Nick Knighton and Bruce Bugbee. A Mixture of Barium Sulfate and White Paint is a Low-Cost Substitute Reflectance Standard for Spectralon ® % Paint. *North, (Figure 1)*:4–6, 1981.


Appendix A

List of abbreviations

CEP - Cooperative energy pooling
FRET - Förster resonance energy transfer
TTA - Triplet-triplet annihilation
2PA - Two-photon absorption
ETU - Energy transfer upconversion
(I/E)QY - (Internal/external) Quantum Yield
Rhod6G - Rhodamine 6G
Stilb420 - Stilbene-420
ZnPC - Zinc phthalocyanine
HIDC - (1,1',3,3,3',3'-hexamethyl-2,2'-indodicarbocyanineiodide)
ADS128 - Poly[(9,9-dioctyl-2,7-divinylenefluorenylene)-alt-co-(1,4-phenylene)]
ADS259 - TFB or Poly[(9,9-dioctylfluorenyl-2,7-diyl)-co-(4,4'-(N-(p-butylphenyl))diphenylamine)]
TAS - Transient absorption spectroscopy
OD - Optical density
Appendix B

Film properties and sources of experimental error

B.1 Mechanical properties of CEP films

All CEP films made in this work (chapters 4 and 6) were optimized for maximum film homogeneity. Various parameters of the film fabrication process (substrate temperature, blade speed, stock solution concentration, blade height, and solvent) were optimized to yield films with the maximum achievable homogeneity as observed visually using a 300x microscope. The films were also observed to have uniform emission, rather than emissive clusters within the overall films, further indicating overall homogeneity in the films. Together, these analyses indicate homogeneity on the ~ 500 µm scale. However, there is likely molecular scale heterogeneity that was not detectable using the methods available in this experiment. Meso-scale structure could likely be detected via SNOM, STED, or STM techniques but these methods not employed in the work above.

Thickness measurements of the resulting films were measured using a Dektak XT stylus profilometer. Films were generally found to have 20-25 nm RMS roughness with variation of up to ~ 50 µm in thickness across the one inch width of the film. Both Rhod6G/Stilb420 and ZnPC/ADS128 films exhibited reasonably strong adhesion to the glass substrate, with the polymer films displaying a plasticity strong enough to allow for physical delamination from the substrate when peeled off.
B.2 Degradation and sources of measurement error

Organic molecules tend to exhibit degradation under high-intensity excitation and the materials in this study exhibited this tendency. Under maximum intensity excitation of the PTI LaserStrobe system (the system used for all normal emission and upconverted emission measurements) the emission signal would exhibit a decrease of ~ 10% typically within 1 - 2.5 minutes under continuous exposure to (pulsed) excitation (though no visible change in the film). To avoid signal error, all measurements were taken in less than one minute. Intensity dependence measurements were taken sequentially from low to high excitation and a data point at a middle point of the excitation range was taken afterwards to verify that extensive damage had no occurred to the sample at any point. Intensity dependence data sets were only kept if the final, duplicate data point exhibited < 15% deviation from the original measurement.

The femtosecond excitation pulses of the transient absorption experiment caused significant damage to the film, with ~ 20% changes in measured signal occurring within two minutes of continuous excitation accompanied by visible destruction of the film itself. To avoid film degradation contributing to data error all measurements were taken with a randomized sequence of pulse delay intervals and repeated at ten different spots on the film, with data from all ten points being averaged together for the final data set. Using these precautions we were unable to observe contributions from film degradation in the final data.

Intensity dependence measurements are highly dependent on the accuracy of measurements of the excitation power. Power measurements were taken with an EO12-3S-H2 thermopile power meter from Edmund Optics averaging over a six second window and yielding a precision of approximately $\pm 1 \mu W$ at the lowest intensities. This results in intensity dependence data with larger error contributions at lower excitation intensities than at the higher intensity points.
Appendix C

Methodology for measuring two-photon absorption cross-sections

This document derives a mathematical formula for the two-photon action cross-section (a.k.a. two-photon brightness) and presents it in a form directly calculable with data taken on the PTI LaserStrobe system (or any time-resolved spectroscopy system). We intentionally derive 2PA brightness – the product of the 2PA cross-section and the quantum yield $\sigma_2 \cdot \Phi$ – as opposed to the 2PA cross-section since the former is the experimentally relevant parameter that affects the material’s ability to actually emit measurable upconverted photons.

While measuring the 2PA brightness of a sample relative to a reference standard is straightforward, measuring the absolute 2PA brightness of a sample is relatively complex given the constraints of our measurement system. Consequently, this derivation will derive the measurable 2PA brightness up to an overall constant related to the detection parameters of the system which can later be determined in order to achieve absolute values.

The two-photon absorption process can be expressed for light propagating through a material in the z-direction as

$$\frac{dJ}{dz} = -\sigma_2(\lambda)CJ^2$$

where $J$ is the photon flux intensity (in $\text{photons/cm}^2\cdot\text{s}$), $\sigma_2(\lambda)$ is the 2PA cross-section (units of $\text{cm}^4\cdot\text{s/photon}$) at excitation wavelength $\lambda$, and $C$ is the concentration of the sample. We would like to relate this quantity to the more relevant quantities of number of excitation
photons and excitation intensity as a function of $$(x, y, t)$$, giving us

$$dJ = \frac{dN}{dtdxdy} = -\sigma_2(\lambda) C \left( \frac{l(x, y, t)}{\frac{hc}{\lambda}} \right)^2 dz$$

where $N$ is the number of photons in the excitation flux, $l(x, y, t)$ is the excitation intensity (in $W/cm^2$) at $(x, y, t)$ and $\frac{hc}{\lambda}$ is the energy per photon in the excitation pulse.

We assume that the number of photons absorbed in the 2PA process by the sample is small enough that there is no significant $z$ dependence in $l$ and thus $dz$ integrates out to $d$, the path length of the sample. In that case, the number of molecules excited during one excitation pulse $$(M_2)$$ at excitation wavelength $\lambda_x$ is one half the integral of the change in number of photons in the excitation pulse as it passes through the sample

$$M_2(\lambda_x) = -\frac{1}{2} \int dN = \frac{1}{2} \frac{\sigma_2(\lambda_x) dC}{\left( \frac{hc}{\lambda_x} \right)^2} \int l^2(x, y, t) dxdydt$$  \hspace{1cm} (C.1)

Using this, we can calculate the emission power of two-photon excited fluorescence at wavelength $\lambda_x$ under excitation at $\lambda_{pl}$ as

$$F_2(\lambda_x, \lambda_{pl}) = M_2(\lambda_x) \frac{hc}{\lambda_{pl}} \phi(\lambda_{pl})$$ \hspace{1cm} (C.2)

where $\phi(\lambda_{pl})$ is the differential quantum yield at emission wavelength $\lambda_{pl}$. Combining this with equation [C.1] gives us

$$F_2(\lambda_x, \lambda_{pl}) = \frac{1}{2} \frac{\sigma_2(\lambda_x) dC}{\left( \frac{hc}{\lambda_x} \right)^2} \frac{hc}{\lambda_{pl}} \phi(\lambda_{pl}) \cdot \int l^2(x, y, t) dxdydt$$ \hspace{1cm} (C.3)

Solving for the 2PA cross-section finally gives us the 2PA cross-section

$$\sigma_2(\lambda_x) = \frac{2hc\lambda_{pl}}{dC\lambda^2_x} \cdot \frac{F_2(\lambda_x, \lambda_{pl})}{\phi(\lambda_{pl}) \cdot \int l^2(x, y, t) dxdydt}$$ \hspace{1cm} (C.4)
Relating theory to measurable quantities

Our detector (PTI LaserStrobe) can measure emission as a function of time at a fixed wavelength or the emission spectrum at a fixed time. In order to relate our measurements to the 2PA cross-section above we must derive a relation between the excitation and 2PA emission powers \( I \) and \( F_2 \), respectively) and the measurable signals as a function of time or wavelength \( F_t \) and \( F_s \), respectively).

We begin by relating the total (actual) emission spectrum to the measured spectrum via

\[
F_2(\lambda_x, \lambda_{pl}) = F_m(\lambda_x, \lambda_{pl}) \times g(\lambda_{pl}, w_{slit})
\]

where \( F_m \) is the measured emission spectrum, \( g \) is a spectral correction function that is dependent on the detection wavelength \( \lambda_{pl} \) and the width of the entrance slit of the detector \( w_{slit} \). We can separate this \( g \) function into

\[
g(\lambda_{pl}, w_{slit}) = B(\lambda_{pl}) \times C(w_{slit}) \times \eta
\]

where \( B(\lambda_{pl}) \) is the spectral correction function for the monochromator/PMT system, \( C(w_{slit}) \) is the slit correction factor which was measured to be equal to \( \frac{1}{w_{slit}^2} \), and \( \eta \) is an overall proportion factor related to the collection efficiency of the detector system. \( \eta \) may be found via a reference sample of known quantum yield and concentration, but this was not carried out for this experiment.

The LaserStrobe system only allows us to measure either the emission spectrum at a particular delay time or the decay at a particular wavelength, forcing us to choose which measurement will best provide us with \( F_m \). Since we are already taking the differential quantum yield into account then a measurement of emission at one particular wavelength is sufficient to allow us to reconstruct the strength of the full emission spectrum. Therefore, we can measure \( F_m \) as a function of time, then integrate that signal over time in order to recover a signal proportional to the total number of photons emitted.
In our case we decided to integrate the temporal signal between the 2% boundaries in order to avoid additional error from noise in the tails of the signal.

\[ F_m(\lambda_x, \lambda_{pl}) = \int f_t(\lambda_x, \lambda_{pl}) \, dt \]

where \( f_t \) is the time-resolved emission decay at excitation wavelength \( \lambda_x \) and detection wavelength \( \lambda_{pl} \). The bounds of the integral are found by finding the times at which \( f_t(t) = 0.02 \cdot f_t[\text{max}] \) for \( f_t[\text{max}] \) as the maximum value of the measured emission decay.

The second component to measure is the excitation pulse intensity \( I(x, y, t) \). In order to accurately model the excitation pulse we can decompose it into its temporal and spatial components:

\[ I(x, y, t) = I_0 \times I_t(t) \times X(x) \times Y(y) \quad (C.5) \]

where \( I_0 \) is the peak intensity, \( I_t \) is the temporal component of the pulse, and \( X \) and \( Y \) are the spatial components. For simplicity, we will assume that all spatial parameters stay constant over all excitation wavelengths and condense them into a factor \( \beta \). To normalize the measured time profile of the beam we multiply by the measured pulse energy, \( E \), divided by the integral of the temporal profile to get

\[ I(x, y, t) = \frac{E \ast I_t(t)}{\beta \int I_t(t) \, dt} \quad (C.6) \]

Finally, we must relate the differential quantum yield \( \phi \) to the emission spectrum:

\[ \phi(\lambda_{pl}) = \frac{f(\lambda_{pl})\lambda_{pl}}{hc} \cdot \frac{hc}{\int f(\lambda) \, d\lambda} \ast \Phi = \frac{f(\lambda_{pl})\lambda_{pl}}{\int f(\lambda) \, d\lambda} \cdot \Phi \quad (C.7) \]

where \( f(\lambda_{pl}) \) is the emission spectrum of the sample and \( \Phi \) is the fluorescence quantum yield of the material.

\[ \sigma_2(\lambda_x) = \frac{2hc\lambda_{pl}}{dC\lambda_x^2} \cdot \frac{F_2(\lambda_x, \lambda_{pl})}{\phi(\lambda_{pl}) \cdot \int I^2(x, y, t) dx dy dt} \]

\[ \sigma_2(\lambda_x) = \frac{2hc\lambda_{pl}}{dC\lambda_x^2} \cdot \int f(\lambda) d\lambda \cdot \frac{\eta}{w_{slit}^2} \cdot B(\lambda_{pl}) \cdot \frac{\beta \cdot (\int l_i(t) dt)^2}{E^2 \cdot \int l_i^2(t) dt} \tag{C.8} \]

\[ \sigma_2(\lambda_x) \cdot \Phi = \frac{\gamma}{dC \cdot E^2 \cdot w_{slit}^2 \cdot \lambda_x^2} \cdot \int f(\lambda) d\lambda \cdot B(\lambda_{pl}) \cdot f(\lambda_{pl}) \cdot \frac{\beta \cdot (\int l_i(t) dt)^2}{E^2 \cdot \int l_i^2(t) dt} \tag{C.9} \]

where \( \lambda_{pl} \) is the measured emission wavelength, \( d \) is the path length through the sample, \( C \) is the molecular concentration of the material, \( E \) is the pulse energy of the excitation light, \( w_{slit} \) is the width of the detection/monochromator slit (assumed to be the same value), \( \lambda_x \) is the excitation wavelength, \( \gamma \) is a proportionality coefficient containing the \( 2hc \) coefficients, the detection efficiency \( \eta \) and the spatial variation factor \( X(x) \cdot Y(y) \) of the excitation beam. Since all the components of \( \gamma \) are related to the detection system they can safely be assumed to stay constant between measurements. \( f \) is the spectrally corrected emission spectrum of the material (at the same concentration as used the 2PA measurement), and \( B(\lambda_{pl}) \) is the detector’s spectral correction function at wavelength \( \lambda_{pl} \). \( F_m(\lambda_x, \lambda_{pl}) \) is the measured upconverted emission at wavelength \( \lambda_{pl} \) under excitation at wavelength \( \lambda_x \) and \( l_i(t) \) is the measured time decay of the excitation pulse.

The result of this measurement is a repeatable method to relate experimental parameters and measured data to the 2PA brightness of a material. A secondary measurement of the quantum yield \( \Phi \) will enable a final value for the 2PA cross-section. A calibration of the detection system using a known reference standard will allow for the measurement of \( \gamma \) and enable a final quantitative calculation of \( \sigma_2 \) in units of GM, but this was not necessary for the purposes of this experiment and hence was not carried out.
Appendix D

Smoldyn exciton diffusion simulation code

The Smoldyn simulation was carried out via a general Smoldyn script that ran the simulation and Python shell script that ran successive simulations with varying input parameter values. The Smoldyn script contains the overall parameters for the simulation space – simulation time of 100 ns with 1 ps time steps, simulation space of 60 nm$^3$, sensitizer exciton lifetimes of 2 ns – and lists the chemical reactions that the various particles (excitons) in the system can undergo.

The Python script contains manually inputted lists of values for CEP radius, excitation intensity, and sensitizer exciton diffusivity. The script then iteratively calls the Smoldyn simulation script with every possible variation of the input parameters – i.e. if there are five values for each parameter then the script is run $5 \times 5 \times 5 = 125$ times. The results of each simulation run are then analyzed by the Python script to determine the total number of CEP upconversion events that occurred and the total number of absorbed excitation photons, with the quotient of the two being the final CEP efficiency output at that configuration of input parameters.

This whole process was run twice for the same parameter list with the results averaged together to yield the results analyzed in chapter 5.

**Listing D.1** | Smoldyn exciton diffusion simulation code.

```plaintext
# Smoldyn Cooperative Energy Pooling Simulation

# UNITS:
```
# Time = ns
# Space = nm

# MODEL PARAMETERS
# Set model params if not defined in Python script call.
if undefine DIFFCOEF
    define DIFFCOEF 100
    # Diffusion coefficients (nm^2/ns=1e−5 cm^2/s). 10e−4 cm^2/s is an avg value for
diffusion coefficient in OPV polymers from Mikhnenko thesis (p. 52).

define K_EXC 3e−5
    # Excitation rate. Calculated as reaction likelihood per time step per unit
    # volume.
    # Solar flux is approx 3e21 s^−1 m^−2 for 2 eV photons at 961 W/m^2, which is
    # approx 3e−6 photons per nm pr ns.

define BINDRAD 0    # Units of nm.

define TEXTOUTPUT stdout
    # This line determines what file the output is printed to (or use stdout to print
    # the results in the terminal windows. Comment this line out to have no output

define OUTPUTFOLDER outputfilesNEW/
    # Define subfolder to dump output files into
#define LIFEOUTPUT Lifetimes.txt
    # Define default name for output file of exciton lifetimes.

#define MSDOUTPUT MSD.txt
    # Define default name for output file of exciton mean square diffusion distances.

#define REACTOUTPUT Reactions.txt
    # Define default name for output file of reaction log.

define UPCONVOUTPUT Upconv.txt
    # Define default name for output file of reaction log.

define EXCOUTPUT Exc.txt
    # Define default name for output file of reaction log.
endif

define TEXTOUTPUT stdout
define K_DECAY 0.5

    # Exciton decay rate. 0.1 yields approx 10 ns lifetime and 0.2 yields approx 5 ns
    # lifetime (in absence of CEP reaction).

display_def
dim 3 # 3D system
boundaries x 0 60 p # System boundaries on x axis (nm)
boundaries y 0 60 p # System boundaries on y axis (nm)
boundaries z 0 60 p # System boundaries on z axis (nm)
time_start 0 # Simulation starting time (ns)
time_stop 100 # Simulation stopping time (ns)
time_step 0.001 # Simulation time step (ns)

# GRAPHICAL OUTPUT
graphics opengl_good # Level of graphics quality (none, opengl, opengl_good, opengl_better)
frame_thickness 2 # Thickness of grid boundaries.
boxsize 50 # Determines size of boxes within frame.
grid_thickness 0.5 # Shows a grid in boundaries.
grid_color brown # Grid color. (must be something so that grid is not white and invisible)

# MOLECULAR SPECIES AND THEIR PROPERTIES
species E UC # species: E=exciton, UC=Upconverted Exciton, D=Decayed Exciton
diff E DIFFCOEF
color E(all) red # colors for graphical output
color UC(all) blue
display_size E 2 # display sizes for graphical output
display_size UC 6

# CHEMICAL REACTIONS
reaction Upconv E + E → UC # CEP upconversion reaction. Rate is missing since binding radius is used instead.
  binding_radius Upconv BINDRAD # Binding radius for CEP reaction.
reaction Decay E → 0 K_DECAY # Exciton decay (unimolecular reaction).
reaction Exc 0 → E K_EXC # Excitation rate.
reaction UCdecay UC → 0 3 # Makes UC molecules disappear to make simulation run faster.

# Output and other run-time commands
text_display time UC E # displays species counts to graphics
output_root OUTPUTFOLDER # Puts output files into this subfolder.
output_files UPCONVOUTPUT EXCOUTPUT
# file name for Reaction text output
reaction_log UPCONVOUTPUT Upconv all
    # Logs all the Upconv reactions that happen. For some reason this will only work if
    # Upconv creates a UC molecule, rather than just decaying to 0.
reaction_log EXCOUTPUT Exc all
    # Logs all the excitation reactions (absorbed photons) that happen.
# cmd B molcountheader TEXTOUTPUT
    # Header for time and molecule counts output at beginning
# cmd N 10 molcount TEXTOUTPUT
    # Time and molecule counts output every 10 time steps
# output_files LIFEOUTPUT MSDOUTPUT
#     # file names for text output
# cmd E residencetime E a r 1 10000 30000 LIFEOUTPUT
#     # Records lifetimes of molecules from creation to reaction.
# cmd E meansqrdisp2 E all a r 30000 2 MSDOUTPUT
#     # Records average total displacement of molecules over their lifetimes. The second moment
#     (last number) is the important one, being the mean square displacement.

del_file
    # end of this file
Listing D.2 | Python code for running Smoldyn simulation

# A python3 script for running the CEPsimulation.txt with varying parameters.
# Format for this script taken from Smoldyn template pyscript.py in S2 examples folder.

# We want to cycle diffusion coefficient and binding radius parameters. Excitation intensity might also be worth varying?

# Function of this code:
# - Create a new subfolder for all of the output data.
# - Ensure that all output data is named with appropriate parameters that can be read for later analysis.
# -

# NOTE!: Pressing CTRL + Z while the script is running will stop it cold. Good for bailing out of long run times :-(

import os

# Variables to define:
# DIFFCOEF — diffusion coefficient of excitons (default = 100)
# K_EXC — excitation intensity (default = 3e-5)
# BINDRAD — action radius of CEP (default = 3)
# OUTPUTFOLDER — Define name of folder for data output files.
# LIFEOUTPUT — Name of file for output of exciton lifetimes.
# MSDOUTPUT — Name of file for output of exciton mean-square-displacements.
# REACTOUTPUT — Name of file for output of all CEP reactions.

# TO DO LIST:

# 1. Set up iteration over all three parameters (BindRad, DiffCoeff, and ExcInt).
# a. Output files with 3 dimensions so that Igor ends up with a 3D array of values.
# 2. Figure out if longer times or larger simulation volumes affect the outcomes.
# 3. Get the simulation to run multiple times and output each result in order to allow for averaging of multiple runs.

BindRads = [0.02, 0.42, 0.82, 1.22, 1.62, 2.02, 2.42, 2.82, 3.22, 3.62, 4.02, 4.42, 4.82, 5.22, 5.62, 6.02, 6.42, 6.82, 7.22, 7.62, 8.02, 8.42, 8.82, 9.22, 9.62, 10.02]
Diffcoeffs $= [0.1, 5.1, 10.1, 15.1, 20.1, 25.1, 30.1, 35.1, 40.1, 45.1, 50.1, 55.1, 60.1, 65.1, 70.1, 75.1, 80.1, 85.1, 90.1, 95.1, 100.1, 105.1, 110.1, 115.1, 120.1, 125.1, 130.1, 135.1, 140.1, 145.1, 150.1, 155.1, 160.1, 165.1, 170.1, 175.1, 180.1, 185.1, 190.1, 195.1]$

ExcInts $= [3e-6, 0.000011, 0.000019, 0.000027, 0.000035, 0.000043, 0.000051, 0.000059, 0.000067, 0.000075, 0.000083, 0.000091, 0.000099, 0.000107, 0.000115, 0.000123, 0.000131, 0.000139, 0.000147, 0.000155, 0.000163, 0.000171, 0.000179, 0.000187, 0.000195]$

UpconvFileName = "Upconv.txt"

ExcFileName = "Exc.txt"

DataFolderName = "LongSim"

# Choose whether to iterate over all variables [2], Diffcoeffs (and Exc) [1], or BindRads (and Exc) [0]:

Case = 2

if not os.path.exists(DataFolderName):
    os.makedirs(DataFolderName)

os.chdir(DataFolderName)

if Case==2:
    for E in ExcInts:
        for D in Diffcoeffs:
            for B in BindRads:

                FileName = "B" + str(B) + "D" + str(D) + "E" + str(E)

                string = "smoldyn\"C:\\Users\\ShaheenGroup\\Desktop\\Daniel\\Smoldyn\\CEP_Exciton_Modeling\\NewVersions\\CEP_SmolPy.txt\"\n
                string += "−wt−−define\_DIFFCOEF={0}−−define\_K\_EXC={1}−−define\_BINDRAD={2}−−define\_UPCONVOUTPUT={3}−−define\_EXCOUTPUT={4}−−define\_OUTPUTFOLDER={5}\".format(str(D), str(E), str(B), UpconvFileName, ExcFileName, DataFolderName+ '/')

                os.system(string)

                UPCONvnum = sum(1 for line in open('Upconv.txt'))

                EXCnum = sum(1 for line in open('Exc.txt'))

                CEPeffFileName = FileName + '.txt'

                CEPeff = open(CEPeffFileName, 'w')

                CEPeffNum = UPCONvnum/EXCnum

                CEPeff.write(str(B)+'
')

                CEPeff.write(str(D)+'
')

                #CEPeff.close()

                #CEPeff = open(CEPeffFileName, 'a')

                CEPeff.write(str(E)+'
')

                CEPeff.write(str(CEPeffNum)+'
')

                CEPeff.close()
# print('EXC = ', str(EXCnum), ' and UPCONV = ', str(UPCONVnum), '
which yields CEP efficiency of: ', str(CEPeffNum))

os.remove(ExcFileName)
os.remove(UpconvFileName)

e11f Case==1:

for D in Diffcoeffs:
    for E in ExcInts:
        FileName = "D" + str(D) + "E" + str(E)
        BindRadVal = 3
        string = "smoldyn\Users\Daniel\Dropbox\Research\Stuff\Analysis\CEP/Modeling/Exciton\Diffusion\Smoldyn/CEP_SmolPy.txt-\wt-\define\DIFFCOEF={0}-\define\K_EXC={1}-\define\BINDRAD={2}-\define\UPCONVOUTPUT={3}-\define\EXCOUTPUT={4}-\define\OUTPUTFOLDER={5}'.
        format(str(D), str(E), BindRadVal, UpconvFileName, ExcFileName, DataFolderName+ '/')
        os.system(string)
        UPCONVnum = sum(1 for line in open('Upconv.txt'))
        EXCnum = sum(1 for line in open('Exc.txt'))
        CEPeffFileName = FileName + '.txt'
        CEPeff = open(CEPeffFileName, 'w')
        CEPeffNum = UPCONVnum/EXCnum
        CEPeff = open(CEPeffFileName, 'a')
        CEPeff.write(str(D)+"n")
        CEPeff.close()
        CEPeff = open(CEPeffFileName, 'a')
        CEPeff.write(str(E)+"n")
        CEPeff.write(str(CEPeffNum)+"n")
        CEPeff.close()

# print('EXC = ', str(EXCnum), ' and UPCONV = ', str(UPCONVnum), '
which yields CEP efficiency of: ', str(CEPeffNum))

os.remove(ExcFileName)
os.remove(UpconvFileName)

else:

for B in BindRads:
    for E in ExcInts:
        FileName = "B" + str(B) + "E" + str(E)
        DiffCoeff = 100
        string = "smoldyn\Users\Daniel\Dropbox\Research\Stuff\Analysis\CEP/Modeling/Exciton\Diffusion\Smoldyn/CEP_SmolPy.txt-\wt-\define\DIFFCOEF={0}-\define\K_EXC={1}-\define\BINDRAD={2}-\define\UPCONVOUTPUT={3}-\define\EXCOUTPUT={4}-\define\OUTPUTFOLDER={5}'.

        format(str(B), str(E), BindRadVal, UpconvFileName, ExcFileName, DataFolderName+ '/')
        os.system(string)
        UPCONVnum = sum(1 for line in open('Upconv.txt'))
        EXCnum = sum(1 for line in open('Exc.txt'))
        CEPeffFileName = FileName + '.txt'
        CEPeff = open(CEPeffFileName, 'w')
        CEPeffNum = UPCONVnum/EXCnum
        CEPeff = open(CEPeffFileName, 'a')
        CEPeff.write(str(D)+"n")
        CEPeff.close()
        CEPeff = open(CEPeffFileName, 'a')
        CEPeff.write(str(E)+"n")
        CEPeff.write(str(CEPeffNum)+"n")
        CEPeff.close()

# print('EXC = ', str(EXCnum), ' and UPCONV = ', str(UPCONVnum), '
which yields CEP efficiency of: ', str(CEPeffNum))

os.remove(ExcFileName)
os.remove(UpconvFileName)
format(DiffCoeff, str(E), str(B), UpconvFileName, ExcFileName, DataFolderName+:'/'),

os.system(string)

UPCONVnum = sum(1 for line in open('Upconv.txt'))

EXCnum = sum(1 for line in open('Exc.txt'))

CEPeffFileName = FileName + '.txt'

CEPeff = open(CEPeffFileName, 'w')

CEPeffNum = UPCONVnum/EXCnum

CEPeff.write(str(B)+'
')

CEPeff.close()

CEPeff = open(CEPeffFileName, 'a')

CEPeff.write(str(E)+'
')

CEPeff.write(str(CEPeffNum)+'
')

CEPeff.close()

# print('EXC = ' + str(EXCnum) + ' and UPCONV = ' + str(UPCONVnum) + ' which yields CEP efficiency of: ' + str(CEPeffNum))

os.remove(ExcFileName)

os.remove(UpconvFileName)

# Fun replacement strings:
# FILEROOT – always automatically replaces with the name of the filename (without extension) of the Smoldyn script containing the command.
# Any text defined in a define statement – automatically replaces itself even when in the middle of a word/phrase.