Title
Engineering the Inorganic Nanocrystal-Organic Molecule Interface by Surface Ligand Design for Functional Nanomaterials

Permalink
https://escholarship.org/uc/item/390558w5

Author
Li, Xin

Publication Date
2017

Peer reviewed|Thesis/dissertation
UNIVERSITY OF CALIFORNIA
RIVERSIDE

Engineering the Inorganic Nanocrystal-Organic Molecule Interface by Surface Ligand Design for Functional Nanomaterials

A Dissertation submitted in partial satisfaction of the requirements for the degree of

Doctor of Philosophy

in

Chemistry

by

Xin Li

September 2017

Dissertation Committee:
  Dr. Ming Lee Tang, Chairperson
  Dr. Christopher Bardeen
  Dr. Chia-en Chang
The Dissertation of Xin Li is approved:

Committee Chairperson

University of California, Riverside
Acknowledgements

It has been an unforgettable experience to be a graduate student in the Department of Chemistry at University of California, Riverside. The past five years has been the most important and fruitful period in my life. It a long journey that is full of tears and joys, frustration and success. It not only gets me ready to be an intellectually adequate scientist but also, more importantly, a mentally mature human being. I would like to take this opportunity to express my appreciation to many people who have made these years memorable.

First of all, I would like to thank my advisor, Professor Ming Lee Tang, for her invaluable guidance on my research. Throughout my whole time as a graduate student, I have always been impressed by her keen insight to find interesting scientific problems and the passion to solve those problems. She not only trained me on experimental techniques but also guide me through critical thinking, which is the most valuable and essential quality of being a competent scientist.

I would like to thank my defense committee members, Dr. Christopher Bardeen and Dr. Chia-en Chang. They gave me valuable suggestions in my research. I also want to thank the committee members of my qualifying exam, Dr. Hill Harman and Dr. Ruoxue Yan. Thanks for their useful comments and good questions during the exam.

I want to thank all my lab mates who provided me a lot of help in my research. They are Zhiyuan Huang, Melika Mahboub, Pan Xia, Emily Moses, Daryl Hawks, Carter Gerk, Narek Meherdich, Beverly Ru, and Helen Thayer, and all the alumni who have helped me both in lab and daily life. It’s so great working with them.
I would like to thank all my collaborators. They are Dr. Valentine Vullev, Dr. Dimtry Fishman, Dr. Valerie Nichols, Alex Fast. Thanks for teaching me the knowledge in the field that I was not familiar with, and showing me the experimental techniques with patience.

Finally, I want to show my appreciation to my families. I want to thank my parents and my husband, for their unconditional support and being so proud of me. I can never thank them enough for all the strength and comfort they brought me whenever I feel lost, hopeless and frustrated.
ABSTRACT OF THE DISSERTATION

Engineering the Inorganic Nanocrystal-Organic Molecule Interface by Surface Ligand Design for Functional Nanomaterials

by

Xin Li

Doctor of Philosophy, Graduate Program in Chemistry
University of California, Riverside, September 2017
Dr. Ming Lee Tang, Chairperson

Colloidal semiconductor nanocrystals (NCs) are a novel set of materials with unique properties. Due to their intrinsic high surface area to volume ratio, surfaces play a dominant role in many physical and chemical processes. Surface ligands — molecules that bind to the surface — is the essential component of nano-material synthesis, processing and application. My dissertation here is mainly focusing on two parts: (a) the characterization of surface ligand binding using fluorescence-based techniques and (b) the rational design and engineering of surface ligands for our targeted application: photon upconversion.

We start from developing a FRET based model sensing the initial few ligand binding events on the oleic-acid capped CdS NCs. The binding behavior can be described as an interaction between a ligand with single binding group and a substrate with multiple, identical binding sites. A modified Langmuir isotherm can be applied to obtain the average number of newly introduced ligand and its binding constant. With this model, we also demonstrate that inorganic NCs have distinct binding sites for different chemical species. This is evidenced by the results that only resonance energy
transfer (RET) is observed for the carboxylic acid ligand, while both RET and charge transfer are observed for the amine ligand.

Then, the length and binding geometries of surface ligand are prudently selected to promote triplet energy transfer, which is the key step in the photon upconversion process. First, a series of anthracene transmitter ligands with variable-length aromatic oligo-$p$-phenylene and aliphatic linkage were employed. The triplet sensitization of anthracene transmitter molecules by CdSe NCs shows a strong distance dependence. Anthracene transmitter bound closest to the NC surface gave the highest quantum yield of 14.3% for the conversion of green to violet light, the current record for a hybrid platform. Later, a series of bidentate bis-pyridine anthracene isomers that differ in binding geometries were designed to find the best complementary fit to the NC surface. Among them, only the ligand with an intramolecular $N-N$ distance of 8.2 Å had the best match to the surface of CdSe NCs, yielding a upconversion QY as high as 12.1±1.3%.

This work lays the foundation of incorporating the hybrid complexes as active materials in optoelectronic devices, such as solar cell, transistors and photodetectors, and also relate the performance of those devices to the structure at their atomic level.
# Table of Contents

Chapter 1  
Introduction .................................................................................................................. 1

1.1 Characterization of surface ligands ........................................................................... 1

1.2 Engineer surface ligand for functional nanomaterials. ........................................... 2

1.2.1 Triplet energy transfer on hetero inorganic-organic interface. ............................ 3

1.2.2 Dexter transport describes triplet energy transfer ................................................. 4

1.2.3 Visualizing and quantifying triplet exciton diffusion in thin film ...................... 7

1.2.4 Hierarchical order in harvesting triplet excitons ................................................. 13

1.3 Conclusions ............................................................................................................. 27

1.4 References ............................................................................................................. 29

Chapter 2  
Quantifying newly introduced ligands on the surface of CdS nanocrystals ..... 38

2.1 Introduction ............................................................................................................. 38

2.2 Derivation of FRET based model .......................................................................... 39

2.3 Result and Discussion ............................................................................................ 41

2.4 Experimental Section ............................................................................................. 47

2.4.1 Sample preparation for steady-state and time-resolved photoluminescence ...... 47

2.4.2 Synthesis of BODIPY ligands ............................................................................. 47

2.5 Conclusion ............................................................................................................. 49

2.6 References ............................................................................................................. 51

Chapter 3  
Distinct sites on nanocrystals affects energy and charge transfer ......................... 52

3.1 Introduction ............................................................................................................. 52

3.2 Result and Discussion ............................................................................................ 54
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.3</td>
<td>Experimental section .....................................................................</td>
<td>59</td>
</tr>
<tr>
<td>3.3.1</td>
<td>Steady-state photoluminescence measurements ..................................</td>
<td>59</td>
</tr>
<tr>
<td>3.3.2</td>
<td>Time-resolved photoluminescence measurements ..................................</td>
<td>59</td>
</tr>
<tr>
<td>3.3.3</td>
<td>Fitting using classic FRET model for both ligand ..............................</td>
<td>60</td>
</tr>
<tr>
<td>3.3.4</td>
<td>Fitting using combination of FRET and static quenching model ..............</td>
<td>60</td>
</tr>
<tr>
<td>3.4</td>
<td>Conclusion ....................................................................................</td>
<td>62</td>
</tr>
<tr>
<td>3.5</td>
<td>References ...................................................................................</td>
<td>63</td>
</tr>
<tr>
<td>Chapter 4</td>
<td>Length Dependence of Triplet Energy Transfer ..................................</td>
<td>65</td>
</tr>
<tr>
<td>4.1</td>
<td>Introduction ...................................................................................</td>
<td>65</td>
</tr>
<tr>
<td>4.2</td>
<td>Result and discussion ....................................................................</td>
<td>67</td>
</tr>
<tr>
<td>4.3</td>
<td>Experimental Section .......................................................................</td>
<td>74</td>
</tr>
<tr>
<td>4.3.1</td>
<td>Ligand exchange and sample preparation ..........................................</td>
<td>74</td>
</tr>
<tr>
<td>4.3.2</td>
<td>Determining average numbers of bound anthracene ligands ....................</td>
<td>75</td>
</tr>
<tr>
<td>4.3.3</td>
<td>Logarithmic relationship between $k_{et}$ and phenylene bridge length ....</td>
<td>76</td>
</tr>
<tr>
<td>4.3.4</td>
<td>Synthesis of anthracene ligands ....................................................</td>
<td>78</td>
</tr>
<tr>
<td>4.4</td>
<td>Conclusion ....................................................................................</td>
<td>84</td>
</tr>
<tr>
<td>4.5</td>
<td>References ...................................................................................</td>
<td>85</td>
</tr>
<tr>
<td>Chapter 5</td>
<td>Complementary Lock and Key Ligand Binding ..................................</td>
<td>89</td>
</tr>
<tr>
<td>5.1</td>
<td>Introduction ...................................................................................</td>
<td>89</td>
</tr>
<tr>
<td>5.2</td>
<td>Result and discussion ....................................................................</td>
<td>90</td>
</tr>
<tr>
<td>5.3</td>
<td>Experimental section .......................................................................</td>
<td>99</td>
</tr>
<tr>
<td>5.3.1</td>
<td>Ligand exchanged with pyridine ligands and sample preparation ............</td>
<td>99</td>
</tr>
</tbody>
</table>
Chapter 5

5.3 Measurement of bound ligands

5.3.2 Measurement and calculation of average bound ligands .................................. 100

5.3.3 Ultrafast Transient Absorption Spectroscopy ................................................. 101

5.3.4 Calculation of efficiency of triplet energy transfer ........................................... 102

5.3.5 Synthesis of bidentate pyridine ligands ......................................................... 103

5.4 Conclusion .............................................................................................................. 107

5.5 References ............................................................................................................ 108

Chapter 6 Supporting information .............................................................................. 111

6.1 Instrument ............................................................................................................. 111

6.2 Chemicals ............................................................................................................. 112

6.3 Synthesis of nanocrystal ...................................................................................... 113

6.4 References ............................................................................................................. 115
List of Figures

Figure 1.1. Triplet energy transfer (TET) can be considered as the correlated transfer of two electrons. ......................................................................................................................................................... 4

Figure 1.2. Representation of four possible electronic configurations of the donor and acceptor molecules, A and B in their excited states A* and B* respectively. Φ₁ and Φ₄ represent locally excited configurations of molecules A (A*B) and B (AB*), respectively. Φ₂ and Φ₃ define the ionic configuration (A⁺B⁻) and (A⁻B⁺), which are to be mixed with the locally excited configurations. ........................................................................................................................................ 7

Figure 1.3. Illustrations of the experimental geometry used to determine triplet diffusion lengths using (a) phosphorescent quenching and (b) remote phosphorescent sensing. ........................................ 8

Figure 1.4. Imaging tetracene exciton transport in time and space. (a) Schematic of the experimental setup showing the initial exciton distribution spreading in the plane of the crystal. (b) Schematic of the optical apparatus. The time-resolved photodetector (an avalanche photodiode) is scanned across the sample to obtain a map of emission intensity as a function of position and time. (c) Map of the emission intensity as it evolves in space and time. The distribution at a particular time has been normalized to emphasize changes in the distribution width. (d) Cross-sections of the emission intensity map at four time points showing spatial broadening of the intensity distribution. σ is the standard deviation of the Gaussian distribution. Adopted with permission from ref 81. Copyright 2014 Nature Publishing Group. ......................................................................................... 11

Figure 1.5. The kinetics controlling singlet and triplet populations revealed by ultra-fast transient absorption measurements on tetracene films. The unprecedented spatial and temporal resolution revealed a new mechanism of singlet-mediated triplet energy transfer. Adopted with permission from ref 83. Copyright 2016 Wiley-VCH. ......................................................................................... 12
Figure 1.6. Chemical structures of branched alkyl chain functionalized 9,10-diphenylandtracene (DPA) 1 emitter and Pt(II) porphyrin sensitizer 2 used in nonvolatile solution-based photon upconversion mediated by triplet fusion. ................................. 17

Figure 1.7. Schematic representation of triplet energy migration in ionic liquids. The purple block is the sensitizer, Pt(II) octaethylporphyrin (PtOEP). Upon excitation, the triplet exciton generated in the sensitizer can transfer to 9,10-diphenylanthracene (DPA) derivatives IL1 (shown as red blocks, green wavy line indicates its counter ion) through triplet-TET (TTET). Instead of diffusion, the triplet excitons migrate along the ionic liquid matrix defined by IL1. Once two triplet excitons encounter each other, upconverted light is emitted through triplet-triplet annihilation (TTA). Adopted with permission from ref 106. Copyright 2015 Wiley-VCH. ................................. 18

Figure 1.8. Schematic illustration of the self-assembled membrane structure. Emitter molecule 3 and sensitizer molecule PtOET spontaneously self-assembles in solution. Upon photoexcitation of donor molecules (PtOET) by green light, donor-to-acceptor triplet-TET (TTET) is followed by triplet energy migration among the acceptor networks. It leads to efficient TTA between acceptor triplets and subsequent emission of the upconverted violet light. Adopted with permission from ref 107. Copyright 2015 Nature Publishing Group. ................................. 19

Figure 1.9. Structure of the Ru based MOF (a) within a bilayer and (b) at the bilayer-bilayer interface (dotted red line). In this MOF structure, the carboxylic acid group functionalized bispyridine ligand for Ru is linked through a tetrahedral Zn node. Therefore, each Ru center is covalently linked through a Zn-carboxylate bridge to 12 other Ru centers within the bilayer. The minimum distance between Ru atoms within the Zn–Ru₄ subunit is 11 Å. At the bilayer–bilayer interface (dotted red line), the minimum Ru–Ru distances are 8 Å (solid black lines), and there are no covalent links between the Ru centers belonging to different bilayers. Therefore, the shortest separation between Ru-Ru centers leading to the strongest electronic coupling are at the bilayer-
bilayer interface, denoted as the b axis here. (c) TET in this MOF is shown to be one-dimesional along the b axis in the lattice where the electronic coupling between two Ru centers is strongest. Each blue dot corresponds to a metal-polypyridyl centered triplet excited state. Adopted with permission from ref 109. Copyright 2013 American Chemical Society.

Figure 1.10. (a) An anthracene-based MOF for photon upconversion that has its outer surface decorated with highly fluorescent material as an energy sink. Triplet excitons can diffuse through the anthracene network within the MOF structure towards this outer layer that emits light. This spatially defined energy cascade enhances the upconversion quantum yield. (b) Energy diagram of the DPA based MOF photon upconverting system involving a highly fluorescent dye (Coumarin 343) as energy collector. Adopted with permission from ref 115. Copyright 2016 American Chemical Society.

Figure 2.1. The CdS NCs and ligand functionalized dye molecules form a good fluorescence resonance energy transfer (FRET) donor-acceptor pair. This can be seen by the normalized absorption (dotted lines) and photoluminescence (PL)/emission (solid lines) spectra of CdS (red), Dye 1 (blue), Dye 2 (green) where good overlap of CdS PL and dye absorption occurs.

Figure 2.2 (a-c) Evolution of CdS NC photoluminescence spectra with (a) carboxylic acid containing Dye 1; (b) methyl ester group terminated Dye 2; and (c) acetic acid as a control. FRET is only observed between CdS and Dye 1, as Dye 1 is a FRET acceptor bound to the NC surface. Samples were dissolved in dry and degassed toluene, excited at 405 nm at RT.

Figure 2.3. TRPL decay curves of CdS at different CdS-Dye 1 molar ratios. Solid curve show fits to experimental data (scatter plot) at molar ratios of CdS: Dye 1 = 1:0 (cyan), 1:10 (green), 1:20 (orange), 1:60 (red) and 1:120 (blue). The fitting parameters, $N_D$, $k_i$, and $k_q$ are given in Table 2.2.
Figure 2.4. (a) Experimental values for the SSPL quenching of CdS from Figure 2.2(a) are plotted against the concentration of Dye 1 (black line, hollow circle). It compares well with predicted SSPL (red solid square) using parameters NDi, ki, kq and m from the fit to the TRPL data. As the concentration of Dye 1 increases, CdS is strongly quenched by the bound dye molecules. (b) Average number of labeled ligands, m, that interact with a CdS NC vs. its concentration. Solid line is the fit to a model with multiple, equivalent binding sites on CdS NCs, squares are experimental data points.

Figure 3.1 Schematic of energy transfer from CdS nanocrystals to molecular acceptors with acid and amine binding groups (Aacid and Aamine). (a) Energy transfer to Aacid involves FRET to ligands bound to multiple, identical sites, while Aamine induces both FRET and static quenching in the CdS donor, indicating selective binding to distinct sites. kq and κ represent the FRET and static quenching constants respectively. (b) Normalized absorption (dotted lines) and photoluminescence / emission (solid lines) spectra of CdS with diameters of (i) 3.4 nm (black), (ii) 4.0 nm (red), (iii) 5.0 nm (blue) and (iv) Aacid (yellow), (v) Aamine (green). The spectra were measured at RT in toluene with a small amount of dichloromethane.

Figure 3.2 Monitoring energy transfer in steady-state photoluminescence (SSPL) and time-resolved photoluminescence (TRPL). (a) Evolution of 4.0 nm CdS nanocrystal steady SSPL spectra with Aacid. Samples were prepared in dry and degassed toluene, excited at 375nm at RT. Corresponding TRPL spectra for the 4.0 nm CdS nanocrystals with the molecular acceptors in (b) 1 ns window and (c) 100ns window. (d) Evolution of 4.0 nm CdS nanocrystal SSPL spectra with Aamine. Corresponding time-resolved photoluminescence (TRPL) spectra for the 4.0 nm CdS nanocrystals with the molecular acceptors in (e) 1 ns window and (f) 100ns window. Samples (b), (c), (d), (f) were excited at 400 nm with a laser power of 15 μW. All spectra were collected at RT.
Figure 3.3 Energy transfer for A\textsubscript{acid} and A\textsubscript{amine}. (a) For A\textsubscript{acid}, FRET from CdS entirely explains donor quenching. Parameters extracted from the TRPL data (dashed line) can be used to fit the normalized SSPL data well, two independent experiments (see Supplementary Information). (b) For A\textsubscript{amine}, a combination of static quenching (SQ) and FRET (dotted line) is used to reconcile the quenching of the CdS PL. The FRET only model (dashed line) is shown for comparison. Introducing the SQ component significantly improves the fitting quality. (see Supplementary Information). CdS PL was normalized with CdS emission in the absence of acceptor. Experimental data for 3.4 nm (filled black triangle), 4.0 nm (filled red circle) and 5.0 nm (filled blue square) are shown.

Figure 3.4 Bathochromic shift of the acceptor’s emission maxima in SSPL experiments. A bathochromic shift of the acceptor’s emission maxima occurs as its’ concentration increased. This red shift is especially pronounced for A\textsubscript{acid} compared to A\textsubscript{amine}.

Figure 3.5 (a)-(d) SSPL spectra for the 3.4nm and 5.0nm CdS with A\textsubscript{acid} and A\textsubscript{amine}; (e)-(h) Normalized donor PL and acceptor emission as a function of increasing acceptor concentration.

Figure 3.6 Time-resolved photoluminescence measurement. TRPL decay kinetics for 3.4 nm CdS in the presence of A\textsubscript{acid} ligand at (a) 1 ns and (e) 100 ns window and with A\textsubscript{amine} ligand at (c) 1 ns and (g) 100 ns window. Experiments of 5.0 nm CdS with A\textsubscript{acid} ligand at (b) 1ns and (f) 100ns window and A\textsubscript{amine} ligand at (d) 1ns and (h) 100ns window. Samples were excited at 400 nm with laser power of 15 mW. All spectra were collected at room temperature.

Figure 3.7 Average number of bound ligands, m, for the (a) amine and (b) carboxylic ligands on three different sizes of CdS (3.4 nm, cross center; 4.0 nm, dotted center, 5.0 nm, half filled). Assuming FRET from CdS to acceptor ligands bound in a Poissonian manner, m is extracted from global fits to the TRPL data with a common Förster quenching constant (k\textsubscript{q}). The 100 ns window TRPL data was used in fitting both A\textsubscript{amine} and A\textsubscript{acid}.
Figure 4.1 (a) Schematic of the energy transfer in this hybrid photon upconversion platform. The energy diagram depicts the triplet excitonic states of the CdSe NC, the p-phenylene (ph) bridges when n=1 and 2, and the anthracene transmitter. (b) Absorption, fluorescence spectra for 9ACA, CPA, CPPA, CP4A, CP9A ligands and 2.6 nm CdSe NCs. The spectra were taken at room temperature in hexane, the same solvent as the upconversion experiments. The green arrow indicates the 532 nm excitation wavelength.

Figure 4.2 The relationship between upconversion quantum yield versus the concentration of each anthracene transmitter during ligand exchange: rigid transmitters (solid square) 9ACA (red), CPA (orange), CPPA (dark yellow); flexible transmitters (hollow circle) CP4A (green) and CP9A (navy). Upconversion samples were prepared in a strictly air free manner and were excited with a 12.7 W/cm² 532 nm laser at RT.

Figure 4.3. Time resolved photoluminescence measurements of CdSe NCs (black scatter plot) on (a) 1ns, (b) 1000ns time scale. The solid red curve shows the both sets of experimental data can be fit with a biexponential decay. The fitting parameters, A_i, k_i and τ_i, are given in the inset, where i = 1 and 2, corresponding to the first and second time constants.

Figure 4.4 The rate of triplet energy transfer (k_{et}, red squares) and maximum upconversion QY (blue triangles) are shown versus the phenylene bridge length of covalently bound transmitter anthracene ligands on CdSe nanocrystals. The logarithmic relation of k_{et} is consistent with Dexter energy transfer and a damping coefficient, β, of 0.43±0.07 Å⁻¹.

Figure 4.5. The efficiency of triplet energy transfer can be calculated from equation (4.3) in the main text (left, Φ_{ET in red}), or from equation (4.6) below (right, Φ_{ET(NC)} in blue).

Figure 4.7 The absorption spectra of bound anthracene transmitter ligands (a) 9ACA, (b) CPA, (c) CPPA, (d) CP4A, (e) CP9A, added at different ratios relative to the CdSe NCs during ligand exchange. These spectra were used to calculate n, the number of bound ligands per NC. The free
anthracene ligands have been removed (see text for details). The absorption spectra of the pure anthracene ligands are shown in magenta for comparison................................................................. 76

Figure 4.8 The logarithmic relation of $k_{et}$ versus phenylene bridge length is consistent with Dexter energy transfer. A data point for the original ODPA-capped CdSe NCs is included. The Dexter damping coefficient, $\beta$, is $0.42\pm0.03 \text{ Å}^{-1}$................................................................. 76

Figure 4.9. The experiments in the main text were repeated on a different batch of 2.6 nm CdSe nanocrystals (NCs). (a) The optical properties of the CdSe NCs in the main text and this section.

(b) The upconversion quantum yield from these NCs using the optimized ligand exchange conditions shown in Figure 4.1 and Table 4.1. (c) The logarithmic relation of $k_{et}$ versus ligand length for the rigid ligands in this experiment. The Dexter damping coefficient, $\beta$, is $0.61 \pm 0.04 \text{ Å}^{-1}$................................................................. 77

Figure 5.1 (a) The N-N distance between two pyridine groups within the three isomers is drawn together with the \{0001\} facet of wurtzite CdSe nanocrystals (NCs). The neighboring cation distances are labeled. (b) Absorption and emission spectra of three bis-pyridine anthracene isomers and 2.4 nm diameter CdSe NCs. The spectra for both NC and three molecules are measured in hexane at room temperature. (c) Schematic of possible binding geometries and the energy transfer in this hybrid photon upconversion platform. The energy diagram depicts the triplet excitonic states of the CdSe NC, the anthracene transmitter and 9, 10-diphenylanthracene annihilator. ............... 90

Figure 5.2. Femtosecond transient absorption (TA) difference spectra in hexanes solution of (a) CdSe nanocrystals (NCs) only and (b) CdSe NCs with surface anchored 2,3-PyAn. CdSe NCs were selectively excited with a 505 nm 100 fs pulsed laser. Experimental delays span from 2.4 ps (orange) to 3 ns (purple). (c) Depletion of CdSe excited state absorption monitored by kinetic traces at 437 nm. The dots are the raw data from TA measurements for CdSe NCs only (red), CdSe NC/transmitter complexes with 3,3-PyAn (orange), 2,2-PyAn (bright green) and 2,3-PyAn (dirty
green) ligands. The black solid lines are the fits for each complex. (d) An energy diagram depicting the physical processes during TA measurements. The solid lines denote the pump and probe wavelengths, dashed lines denote the relaxation processes on CdSe NCs and wavy lines denote the possible quenching process induced by ligand, such as triplet energy transfer (TET).

Figure 5.3 The intensity in the difference spectra of the CdSe nanocrystal ground state bleaching (monitored at 463 nm) versus different excitation powers plotted in a log-log scale. Multi-photon annihilation was observed under higher power where the slope changes from 1 to 0.5. Our experiments were performed in the linear region with a pump power of 220 nJ.

Figure 5.4 Picosecond TA difference spectra of CdSe nanocrystals (NCs) that have surface anchored (a) 2,3-PyAn (b) 3,3-PyAn, (c) 2,2-PyAn ligands in a hexane solution. The CdSe NCs were selectively excited with a 505 nm pulsed laser. Experimental delays span from 2.4 ps (orange) to 3 ns (purple). The red line indicates background scattering from the pump source before time 0.

Figure 5.5. The efficiency of TET measured by transient absorption spectroscopy, $\Phi_{\text{TET(TA)}}$, (black circle) for each bis-pyridine anthracene transmitter correlates with the corresponding photon upconversion quantum yield (red square).

Figure 5.6. The absorption spectra of isolated CdSe-PyAn complex for 2,3-PyAn (black), 2,2-PyAn (red) and 3,3-PyAn (olive) respectively. All these three samples were used for TA measurement and spectra were taken after experiment. Comparing to CdSe only (blue), there is no peak shift in CdSe-PyAn, indicating that CdSe is stable and did not degrade during the whole process, including ligand exchange, sample cleaning and TA measurement.

Figure 5.7 (a) Kinetic traces at 445 nm mainly correspond to the excited state absorption of T1L $\rightarrow$ TnL transition of anthracene transmitter molecules in CdSe/PyAn complexes. The background signal from the ESA of CdSe NC only spectra (red) is subtracted from the decay traces of the CdSe/
PyAn complexes (black) to obtain the ESA of the triplet formed on PyAn (blue). The CdSe NC only spectrum (red) is normalized to have the same ΔA with the CdSe/ PyAn sample (black) at CdSe ground state bleaching peak (we choose 461 nm in this case) and the decay at 445 nm for CdSe NC only sample after scaling is regarded as background. (b) Fits for ESA of the PyAn triplet state are in solid lines for NC-ligands complexes with 3,3-PyAn (red), 2,3-PyAn (black) and 2,2-PyAn (blue). The fitting parameters for each CdSe-isomer complex are listed in the inset, where A1 is the amplitude, $t_{TET}$ is the time constant for the formation of the first triplet excited state on PyAn ligand and $y_0$ is the fitting offset. The $t_{TET}$ correlates well with CdSe NC quenching induced by PyAn ligands, $t_q$. 

Figure 5.8 Determination of threshold for excitation intensity.
List of Tables

Table 2.1 The maximal first exciton and emission wavelength for CdS, maximal absorbance and emission wavelengths for Dye 1 and Dye 2, extinction coefficients, and calculated Förster distances. .................................................................................................................................................................................. 42

Table 2.2 List of the fitting parameters for $N_{Dk}$, $k_{i}$, and $k_{q}$ for the decay curves ............ Error!

Table 3.1. Förster distances for all CdS QDs donor and organic acceptor pairs. ................. 54

Table 3.2 Fitting parameters for TRPL data for $A_{amine}$ and $A_{acid}$ experiment with classic FRET model. .................................................................................................................................................................................. 56

Table 4.1. The absorption and emission maxima for the anthracene ligands and CdSe nanocrystals (NCs) along with their extinction coefficients in hexanes at RT are listed. The average number of bound anthracene ligands (n) on a CdSe NC correspond to the value that results in the maximum upconversion quantum yield (QY). The average upconversion QY obtained by repeating the upconversion measurements under these optimized conditions is shown for comparison. ..... 69

Table 5.1. The quantum yield of photon upconversion ($\Phi_{UC}$), and the efficiency of triplet energy transfer (TET) (from both upconversion and transient absorption (TA) spectroscopy, $\Phi_{TET(UC)}$ and $\Phi_{TET(TA)}$ respectively), and the average number of bound ligands per CdSe (m) are listed. From TA data, analysis of the kinetics of the NC donor provides the decay time constants of surface trapping and quenching on the NC induced by PyAn ligands, $t_{trap}$ and $t_{q}$. Analysis of the kinetics of $T_{1L} \rightarrow T_{nl}$ on the PyAn transmitters gives the time constant and rate of TET ($t_{TET}$ and $k_{TET}$ respectively) from CdSe NCs. .................................................................................................................................................................................. 96

Table 5.2 Parameters obtained from fitting kinetic traces of excited state absorption at 437 nm using a multiexponential decay function. Data is from transient absorption kinetics of CdSe
nanocrystals with and without surfaced bound three bidentate pyridine ligands suspended in hexane 
($\lambda_{ex} = 505$ nm). ................................................................. 96

Table 5.3 extinction coefficients, absorption and emission maxima for all bis-pyridine anthracene ligands and two different batches of CdSe NCs. ................................................. 101
Chapter 1  Introduction

1.1  Characterization of surface ligands.

Colloidal semiconductor NCs are a novel set of materials with unique properties, such as size-tunable band gaps, spectrally narrow photoluminescence and high photoluminescence quantum yields (PLQY)\textsuperscript{1-3}. These factors, and the potential for low-cost, solution-based processing, make them prime candidates for biological reporters \textsuperscript{4-5}, or the active material in various optoelectronic devices, including light-emitting diodes\textsuperscript{6-7} and light harvesting elements in solar energy conversion systems\textsuperscript{8-9}. These applications require control of the photophysical properties of NCs, which are directly influenced by the surface states\textsuperscript{10-11}. It is well known, for example, that surface states introduce trap sites that may change the PLQY of a NC\textsuperscript{12-22}. A molecular understanding of the NC-ligand interface, and the way it affects the electronic properties, is still lacking.

The challenge in correlating the NC surface to its electronic properties lies in the difficulty in distinguishing between free and bound ligands on NCs. So far, Nuclear Magnetic Resonance (NMR) has proved to be the workhorse in the field, as ligands in solution and on the surface of the quantum dots are differentiated by changes in line width and chemical shift\textsuperscript{23-24}. However, one of the main drawbacks of using NMR is the relatively high concentration required to achieve adequate signal. This obscures detection of the first few binding events between NC and ligands. These initial binding events are interesting as they might correspond to the most reactive sites on the NC unique to a particular ligand. Insight into the initial binding sites may provide a handle for tuning the photophysical or chemical properties of NCs.

Previous photoluminescence (PL) based ligand exchange studies distinguish between free and bound ligands by assuming a linear relationship between NC PL and ligand binding. This assumption is not necessarily valid\textsuperscript{25}. Evidence for nonlinear relationships between ligand binding
and PLQY includes the observation that a single octanethiol molecule can quench the luminescence of CdSe NCs by at least 50% \(^26\). Most recently, Owen and co-workers found that PLQY of CdSe NCs has a strongly superlinear dependence on the surface coverage of cadmium-carboxylates, while below a threshold of 2 carboxylates/nm\(^2\), the PLQY was <1% \(^27\). Previous PL based studies of ligand binding with amines on CdS NCs have assumed a Langmuir adsorption model based on a linear relationship between surface coverage and PLQY. With this model, Peng et al. \(^28\) reported an equilibrium constant, K, in the range of 50-100 M\(^{-1}\) for their CdS-Octylamine NC-ligand complex. This is 2-3 orders of magnitude smaller than that reported by Bullen and Mulvaney for a CdS-amine system \(^29\), and about 3-4 orders of magnitude smaller than the value estimated by Munro et. al. for the binding equilibrium constant between CdS NCs and native amine ligands \(^15\). Considering that these reports concern the same equilibrium constant between CdS and amines, in the same solvent, chloroform, the distribution of ligand binding strengths reported questions the fundamental assumptions and validity of the model.

1.2 **Engineer surface ligand for functional nanomaterials.**

Our ultimate goal of investigating surface chemistry of nanocrystal is to exploit multiexciton process inherent in semiconductor nanocrystals. To do that we need to engineer the interface between the inorganic and organic material by designing molecules with well-defined distance, photophysics, energy offsets and optical profile which complements the surface of NC donor or acceptor. More specifically, in my dissertation, we want to optimize nanocrystal sensitized upconversion process through promoting efficient triplet energy transfer across NC and organic transmitter. In the following section, I will give a deep insight of mechanism and characterization for triplet energy transfer as well as its device fabrication. Those theories lay the foundation of the design of the following ligands, allowing us to relate the performance of those functional nanomaterial to the structure at the atomic level.
1.2.1 **Triplet energy transfer on hetero inorganic-organic interface.**

Triplet excitons are usually forsaken in favor of their singlet brethren, whether in nature or in optoelectronic devices. For example, in higher plants, photosystem II non-photochemically quenches potential triplets by rearranging the light harvesting proteins to minimize the production of singlet oxygen that is damaging to cells; in organic light emitting diodes (OLEDs), triplet excitons created by charge injection are converted to emissive singlet states by thermally activated delayed fluorescence (TADF) or through spin-orbit coupling in organometallic compounds. Despite being overlooked, triplet excitons play a key role in multi-excitonic processes like singlet fission and triplet-triplet annihilation (TTA), which are plausible ways to redistribute the energy contained in the solar spectrum. Through singlet fission, a photon of high energy is split into two triplet excitons of lower energy, thus allowing the energy lost in the thermalization of photons more energetic than the bandgap of a semiconductor-based solar cell to be captured. In a related process, near infrared (NIR) radiation currently transmitted through solar cells can be harnessed through photon upconversion mediated via triplet fusion. Either of these photon up- or down-conversion processes could potentially overcome the Shockley-Queisser limit and improve the power conversion efficiency (PCE) of solar cells by as much as 44% under one sun conditions.

These processes are efficient in certain organic semiconductors, which like colloidal semiconductor nanocrystals, are amenable to solution-based, roll to roll processing for potentially inexpensive, flexible optoelectronic devices. Quantum confined semiconductor NCs have dark excitonic states responsive to magnetic fields in thermal equilibrium with their dipole allowed bright states at room temperature. This tripet-like character stems from a non-zero exchange term resulting from the Wannier excitons in the bulk being confined at the nanoscale. Excitons are neutral excited states with Coulombically bound electron hole pairs. Excitons with a net spin of zero or one are termed singlet or triplet excitons respectively. Förster type dipole-dipole coupling
has traditionally been used to describe energy transfer between organic molecules and inorganic NCs, but recently, triplet energy transfer (TET) across this interface has been demonstrated.\textsuperscript{49,50} Efficient TET from NCs to acene emitters have resulted in state of the art photon upconversion quantum yields (QYs) under sub-solar excitation densities, even for NIR radiation.\textsuperscript{43} In fact, the large extinction coefficient and size dependent bandgaps of semiconductor NCs make them good sensitizers of molecular triplet states. However, an on-going challenge in this field is to translate these encouraging results from solution into commercially relevant thin-films, ideally made by low-cost printing methods.

1.2.2 Dexter transport describes triplet energy transfer

![Diagram of Dexter transport]

**Figure 1.1.** Triplet energy transfer (TET) can be considered as the correlated transfer of two electrons.

One particularly compelling reason to consider triplet excitons is the fact that there is no fundamental limit to their diffusion length. This is not the case with singlet excitons.\textsuperscript{51} As shown in Fig. 1.1, excitons are tightly bound electron hole pairs that typically occur in organics or artificial molecules like nanocrystals, where excited electronic states with the net spin of zero or one are labelled singlets or triplets, respectively. For singlet-excited states, increasing the dipole moment increases the Förster radius, thus enhancing resonance energy transfer. However, this also increases the radiative rate, decreasing the lifetime of the singlet exciton. This trade-off results in a maximal
diffusion length for singlets, calculated by Yost et al to be about ~ 100 nm for crystalline tetracene. There is no such limitation for triplet excitons, because the diffusion coefficient and lifetime are not directly related. Triplet excitons in free molecules typically have inherently long microsecond lifetimes, due to spin-forbidden recombination to the ground state.

The triplet diffusion coefficient is governed by wavefunction overlap between the donor and acceptor species, or Dexter energy transfer, i.e. the correlated exchange of two electrons between nearest neighbors. Therefore, the migration of triplet excitons can be described as a random walk. The diffusion length is defined as the root mean square displacement of a particle from its initial position during this diffusion process, as given below:

\[ L_D = \sqrt{\frac{\sum (dL_i)^2}{N}} = \sqrt{2ZD\tau} \]  

where \( dL_i \) is the displacement of an exciton \( i \) from its original position, \( N \) is total number of excitons, \( D \) is the diffusion constant, \( \tau \) is the life time of the triplet exciton and \( Z \) is equal to 1, 2 or 3 which corresponds to one-, two- or three-dimensional diffusion respectively. In fact, the factor of two is usually omitted in many scientific publications, leading to:

\[ L_D = \sqrt{2ZD\tau} \]  

The exciton diffusion constant, \( D \), in equation (2) can be estimated using the Smoluchowski–Einstein theory of random walks. In a simple cubic lattice model where a particle is surrounded by six neighbors with interparticle spacing \( a \), the diffusion is assumed to be isotropic and limited to interactions with these six nearest neighbors, leading to

\[ D = \frac{a^2}{6\tau_H} \]  

\( \tau_H \) is the hopping time constant, i.e. the time constant for Dexter energy transfer. Combining eqn (2) and (3), the Dexter-mediated diffusion length is:
However, $1/\tau_H$ in eqn (1.4), the rate of triplets hopping from site to site, or the rate of Dexter energy transfer, can be estimated using Marcus theory\textsuperscript{52, 55-58}:

$$L_D = \sqrt{\frac{Za^2\tau}{6\tau_H}}$$

(1.4)

where $h$ is Planck’s constant, $J_{DA}$ is the electronic coupling between donor and acceptor, $\lambda$ is the reorganization energy, $T$ is the temperature, $k_B$ is the Boltzmann constant and $\Delta G$ is the difference in Gibbs free energy between donor and acceptor. The exponential dependence of the triplet diffusion length on the distance between donor and acceptor means that shorter donor-acceptor distances can significantly improve hopping events between neighbours, thus increasing the diffusion length. Therefore, efforts promoting closer contact between donors and acceptors in various geometries, e.g. self-assembled structures, crystalline molecular and metal-containing frameworks etc. will be discussed in later.

Since Dexter-type triplet transfer can be considered a correlated exchange of two charges (Fig. 1.1), the same structure-property relationships governing charge transport in organic semiconductors apply to both TET and charge transfer from triplet excitons. It has been found that the rate of triplet transfer is proportional to the product of the diffusivity of the electron and hole in amorphous films, organic crystals, and in solution, provided molecular reorganization energy is taken into account.\textsuperscript{58-61} Closs, Scholes, and others have shown the rate of TET can be estimated from the product of the rate of electron transfer and hole transfer.\textsuperscript{60} As shown in Figure 1.2, Scholes et. al. showed that during TET, the excited configurations of the donor A and acceptor B, represented by $\Phi_1(A*B)$ and $\Phi_4(AB^*)$ respectively, are each allowed to mix with bridging ionic configurations, $\Phi_2(A^*B^-)$ and $\Phi_3(A*B^+)$ respectively, to form the new donor and acceptor wave
functions.$^{39}$ In this theory, the requisite short-range orbital overlap between donor and acceptor is described by a ‘through-configuration’ exciton resonance interaction term that replaces the Dexter exchange integral. These ionic, charged intermediates result in the same exponential dependence on donor and acceptor distance, described by the original ‘Dexter-type’ model.$^{62-64}$ In other words, TET across short bridges with high tunneling barriers involve either sequential or simultaneously transfer of ionic intermediates.$^{65}$ Formally, the matrix element for Dexter transfer is proportional to the square of the orbital overlap between the donor and acceptor, as shown in eqn. (1.5), but for charge transfer, it is proportional to orbital overlap only. In other words, the damping coefficient for Dexter energy transfer should be twice as large as that for charge transfer for a physical system with the same driving force and bridge between the donor and acceptor.

![Figure 1.2](image)

**Figure 1.2.** Representation of four possible electronic configurations of the donor and acceptor molecules, A and B in their excited states A* and B*, respectively. $\Phi_1$ and $\Phi_4$ represent locally excited configurations of molecules A (A*B) and B (AB*), respectively. $\Phi_2$ and $\Phi_3$ define the ionic configuration (A+B-) and (A-B+), which are to be mixed with the locally excited configurations.

### 1.2.3 Visualizing and quantifying triplet exciton diffusion in thin film

The reported triplet diffusion lengths in organic semiconductors span a relatively large range, from 10–20 nm up to a few micrometers.$^{66-70}$ Interfacial morphology is particularly important. For example, the long triplet diffusion lengths and lifetimes in crystalline acenes$^{39, 71-72}$ can be contrasted with the fast recombination of charges derived from triplet excitons in the polymeric solar cells reported by Lacquai et al.$^{73}$ Thin films of tetracene have triplet diffusion lifetimes on the
order of microseconds,\textsuperscript{72, 74–76} orders of magnitude larger than thin films of pentacene (15 ns).\textsuperscript{79} Moreover, different values have been published for same materials. For example, different triplet diffusion values in the range of 10–60 nm have been reported for 4,4’-bis(carbazol-9-yl)1,1’-biphenyl (CBP), a commonly used host material in the emissive zone of OLEDs.\textsuperscript{77–80} Such controversy sometimes originates from the use of different measurement methods. Here we summarize the commonly used methods for measuring triplet diffusion length and the associated problems. Unless otherwise specified, in the following section, the “sample” refers to the species whose triplet diffusion length needs to be determined, the “quenching layer” is the layer that quenches the phosphorescence signal and the heavy metal containing compounds used for reporting the presence of triplet states via their phosphorescence is termed the “detector” or “dopant” layer.

![Diagram](image.png)

**Figure 1.3.** Illustrations of the experimental geometry used to determine triplet diffusion lengths using (a) phosphorescent quenching and (b) remote phosphorescent sensing.

1. Phosphorescent quenching
For the materials with efficient radiative decay of triplet excitons (usually organometallic compounds containing heavy metals), phosphorescent quenching methods can be directly applied.\textsuperscript{66, 81-82} For example, triplet diffusion lengths of 18.0±0.6 nm and 5.7±0.5 nm have been measured for amorphous films of platinum(II) octaethylporphyrin (PtOEP) (phosphorescence QY= 0.45) and platinum(II) tetraphenyltetrazenoporphyrin (PtTPBP) (phosphorescence QY= 0.51) respectively.\textsuperscript{66} In this method, the strongly phosphorescent material is cast as a film and then a thin quenching layer (usually composed of fullerene or TiO\textsubscript{2}) is brought into contact with it (Fig. 1.3a). If the thickness of the sample layer is on the order of its triplet exciton diffusion length, then the majority of triplet excitons generated within the sample layer will diffuse to the quenching layer and phosphorescence will be quenched. Consequently, the degree of quenching can be measured from thickness dependent time-resolved photoluminescence (PL) or steady-state PL and compared to the isolated sample film. The steady-state or time-resolved quenching data as a function of the thickness of the sample film can then be fit using appropriate models (Monte Carlo simulations or the Stern–Volmer equation) to extract the diffusion length. We must note that that triplet excitons can be also transported via Förster energy transfer in some heavy metal-coordinated compounds, which may complicate the analysis.\textsuperscript{83}

(2) Remote phosphorescent sensing

When the phosphorescence QY of the sample is low, a remote phosphorescent sensing technique can come into play. By introducing a sensing layer that is heavily doped with a phosphorescent molecule, the triplet exciton can be detected (Figure 1. 3(b)).\textsuperscript{77, 84} To be more specific, the triplet exciton created in the sample layer diffuses into the doped layer, where energy transfer to the dopants is detected as phosphorescence. We should also note that, as the excitons diffuse, they undergo TTA that results in delayed fluorescence. Consequently, the fitting model has to involve four fitting parameters, including the exciton diffusion length, the rate of triplet–triplet annihilation,
the rate of energy transfer from sample to phosphorescent dopant and the initial triplet density. The large number of fitting parameters and the complex theoretical model limits the accuracy and the ease of using this model.

A more straightforward method was developed by introducing a triplet injection layer on top of the sample layer and the dopant detector layer. In this method, the injection and detector layer should be carefully selected such that the energy of the triplet exciton in the sample layer is in between these two layers. Thus optically excited triplet excitons can be transferred from the injection layer to the sample layer of known thickness, then diffuse to the detection layer and quantified by phosphorescence of the dopant. With the triplet injection layer, the initial triplet density is proportional to the intensity of the incident light and the TTA can be accurately accounted for. This method ameliorates the systemic error that can be significant when the TTA is not properly accounted for during the measurement. This may be the reason for the large spread of $L_D$ values reported on the same materials in the literature, in which TTA is usually neglected.

(3) Photocurrent in solar cells

The triplet exciton diffusion length can be also measured using the photocurrent modeling. Here, it is important to distinguish between the contributions of triplet and singlet excitons to photocurrent. The effect of triplet–triplet annihilation also leads to inaccuracies as discussed above.

(4) Measurement in organic light emitting diodes (OLEDs)

In OLEDs, triplet excitons are created in a charge recombination region spatially confined between electron and hole transporting layers. A phosphorescent dopant is added into one of the charge transporting layers at certain distance $L$ away from the charge recombination layer as a detector layer to optically report on the presence of triplet excitons. The dopant is selected such that TET from the sample is favorable in order for phosphorescence to be measured at the
detector layer. During the measurement, the relationship between the phosphorescence intensity of dopant molecules versus distance $L$ is recorded to extract the triplet exciton density. The distance dependent profile of triplet exciton density can be modeled to obtain the exciton diffusion length.

Figure 1.4. Imaging tetracene exciton transport in time and space. (a) Schematic of the experimental setup showing the initial exciton distribution spreading in the plane of the crystal. (b) Schematic of the optical apparatus. The time-resolved photodetector (an avalanche photodiode) is scanned across the sample to obtain a map of emission intensity as a function of position and time. (c) Map of the emission intensity as it evolves in space and time. The distribution at a particular time has been normalized to emphasize changes in the distribution width. (d) Cross-sections of the emission intensity map at four time points showing spatial broadening of the intensity distribution. $\sigma$ is the standard deviation of the Gaussian distribution. Adopted with permission from ref 94. Copyright 2014 Nature Publishing Group.

(5) Direct visualization of TET

Recently, a few groups have directly monitored the spatial and temporal profile of triplet diffusion in thin film.94-97 As shown in Figure (1.4), the spatial spread of the signal at each delay time can be fitted with a Gaussian function parameterized by variance $\sigma$. The exciton diffusion length $L$ at delay time $t$ is then related to the exciton density characterized by variance $\sigma$,

$$L = \sigma(t) - \sigma(0) = 2Dt$$  \hspace{1cm} (1.6)

enabling the diffusion constant, $D$, to be extracted. For the direct visualization of triplet diffusion, both time-resolved PL and transient absorption spectroscopy have been integrated with diffraction-limited resolution, as discussed in detail below:
a. Delayed luminescence

If time-resolved luminescence is monitored, the spatial spread of delayed fluorescence is measured as a function of time. Upon optical excitation, the triplet excitons generated by singlet fission or intersystem crossing can randomly hop to their nearest neighbors by Dexter energy transfer. When two diffusing triplets encounter each other, triplet fusion occurs to produce a singlet exciton, which then undergo radiative relaxation, known as delayed fluorescence. This fluorescence can be optically detected and used as a direct probe of the triplet exciton density. Using this method, Akselrod et al. measured the triplet diffusion length in tetracene crystals to be about 0.61 μm and a diffusion constant of 1.35±0.01 × 10\(^{-3}\) cm\(^2\).s\(^{-1}\).\(^{94}\) They also demonstrated that the mechanism of exciton transport depends strongly on the nanoscale morphology. Note that these measurements were performed at long-time scales, up to 7 μs with a temporal resolution of 100 ns. For the spatially resolved dynamics of triplet diffusion at early time scales, i.e. picoseconds and nanoseconds, ultra-fast transient absorption measurements were elegantly employed, as discussed below.

![Figure 1.5](image_url) The kinetics controlling singlet and triplet populations revealed by ultra-fast transient absorption measurements on tetracene films. The unprecedented spatial and temporal resolution revealed a new mechanism of singlet-mediated triplet energy transfer. Adopted with permission from ref 96. Copyright 2016 Wiley-VCH.

b. Ultra-fast transient absorption measurements

Transient absorption can be used to study the dynamics of excited states in organic semiconductors. Since the absorption spectrum of the triplet exciton usually differs from the singlet
exciton, monitoring the time evolution of their spectrally resolved optical profiles will enable extraction of triplet diffusion parameters. Using this approach, Wan et al. studied the triplet diffusion dynamics in tetracene crystals at the picosecond and nanosecond time scales. They selected 633 and 810 nm as the probe wavelengths to selectively monitor the singlet and triplet excitons respectively. They estimated the diffusion constant for triplets in tetracene crystals with 200 fs time resolution, providing significantly more detail than the previous PL based measurements. Data obtained at these early timescales provided evidence for a new singlet-mediated transport mechanism for triplets. In a tetracene thin film, both triplets and singlets are involved in exciton diffusion, with rapid interconversion between both species. As a result, the triplets travel much faster than expected considering they are typically limited by Dexter transport, because they can take advantage of the dipole-dipole coupling between singlets. This new mechanism (shown in Figure 1.5) increases the effective triplet exciton diffusion length to about 5.6 μm on short picosecond and nanosecond timescales.

1.2.4 Hierarchical order in harvesting triplet excitons

Ordered structures enabling efficient energy transfer along a certain direction are important for all kinds of optoelectronic devices, e.g. solar cells, LEDs, photodetectors, photocatalysts, etc. For example, it would be desirable to couple the light from a photon upconverting thin film efficiently to a solar cell or photocatalyst. Based on equation (5), it is essential to increase orbital overlap between neighboring molecules in order to efficiently harvest the energy contained in triplet excitons. Therefore, here we summarize recent work implementing ordered structures for the purpose of enhancing TET. Various self-assembly methods involving small molecule design, block copolymers and long range order enabled by frameworks like MOFs are discussed. These reports may give inspiration and shed light on future prototypes that can efficiently harvest the energy in triplet excitons.
(1) **Polymer scaffolds:**

**a. Conjugated polymers**

Since Dexter transfer is the correlated exchange of two charges and can be parameterized by ionic intermediates, the extensive research regarding charge transfer in the field of conjugated polymers applies to the design of thin films with optimized morphologies for TET. Early reports established that crystalline organic semiconductors displayed better charge transport than their amorphous analogues. As a result, many conjugated polymers designed to have good charge transport properties by increasing regioregularity, π stacking or crystallinity have been reported.\(^{96-101}\) However, it is also well known that polymer processing conditions greatly affect the interactions between the conjugated core. More significantly, highly disordered or even seemingly amorphous polymers have field effect mobilities as high as their crystalline counterparts.\(^{98, 102-103}\)

Noriega et al. proposed a general model describing charge carrier transport in conjugated polymer films. They brought together relevant data (such as mobility, degree of polymerization, etc.) from years of research on conjugated polymers in the literature and reexamined the relationship between charge mobility and the morphology.\(^{104}\) They proposed that in heterogeneous microstructures where both crystalline and amorphous areas coexist, the ordered regions are largely responsible for charge transport because there is an energy barrier for charges to move from ordered to amorphous regions across grain boundaries. In the meantime, the chain segments connecting ordered regions provide an efficient charge transport pathway between grains, allowing charges to shuttle between each isolated crystalline aggregates. Therefore, the effect of crystallinity on charge transport in semicrystalline polymers is subject to an intrinsic and general trade-off: low molecular weight short chain polymers improve the local crystallinity, but also suffer from poor electrical connectivity between ordered regions, thus reducing the overall mobility. Increasing polymer crystallinity can only improve the charge transport to a limited extent due to this intrinsic trade-off.
On the other hand, careful design of polymers that reduce the $\pi-\pi$ stacking distance or increase orbital overlap can greatly improve the charge transport efficiency by enhancing transport in the local ordered regions.

**b. Block copolymer templates**

Many attempts have been made to use polymers to control the nano or mesoscale separation in organic bulk heterojunctions since Friend and Heeger independently demonstrated that solvent assisted annealing improved exciton dissociation and charge transport in PV devices.$^{105-106}$ For example, conjugated donors and acceptors covalently attached to the polymer backbone, whether alternating in block-copolymer form or with one component pendent to a basic repeating unit were synthesized. The motivation behind this is that the self-assembly of flexible block-copolymers can be described in terms of the volume fraction, number of statistical segment lengths and the Flory-Huggins interaction parameter of each block.$^{107-110}$ However, the rigidity of conjugated block copolymers make it difficult to predict their morphology, especially at the donor-acceptor interface. Consequently, the performance of photovoltaic devices based on block copolymers or ‘cable polymers’ that have electronically active pendent groups is still low. For the latter, the low concentration of the fullerene results in a lack of control in the ratios of the donor and acceptor.

More significantly, there are charge transport problems from recombination or trapping in these polymeric thin films. Perhaps this is analogous to the short-lived triplet pairs produced from intramolecular singlet fission in dimers of tetracene and pentacene. Instead of the tens of microsecond lifetimes commonly observed in isolated molecules, these dimers have triplet lifetimes on the order of nanoseconds because of enhanced recombination.$^{111-113}$ On the other hand, monolithic blocks of conjugated polymers exclusively comprising of either donors or acceptors can have the degree of crystallinity, solubility, polydispersity etc. pre-designed by controlling the side chains and rigidity of the monomers. The best performing conjugated block copolymer consisting
of P3HT donor and benzothiadiazole acceptor blocks have a PCE of 3%,\textsuperscript{114} a factor of 4 lower than state of the art OPV materials. For further insight into this sub-field, please see a recent review by Lee and Gomez.\textsuperscript{115}

c. Rigid polymer hosts

As discussed earlier, a long triplet diffusion length can arise either from an extended exciton lifetime, or a larger diffusion coefficient, $D$. Monguzzi and co-workers increase the triplet exciton lifetime by embedding the molecular upconversion materials in a rigid polystyrene (PS) matrix that inhibits intramolecular relaxation.\textsuperscript{116} This rigid PS host simultaneously minimizes the decay of the triplets by first-order processes while introducing a barrier to oxygen. The efficiency of TET was 70\% of that in the diffusion-limited case in solution. Though the upconversion QY was 10x lower than the reference solution at 2.5\%, the threshold intensity was reported to be around 6 mW/cm\textsuperscript{2}, which is close to the solar flux for the green wavelengths used for excitation.

\textbf{(2) Molecular assemblies:}

TTA based photon upconversion is a process where two or more lower energy photons are converted to one high energy photon. Among reported upconversion methods, it is the only one that has demonstrated potential for harvesting incoherent photons from the sun without concentrators. Monguzzi et al. proposed a figure of merit for TTA based upconversion\textsuperscript{117}: the threshold excitation intensity, $I_{th}$, at which efficiency of TTA is 0.5. They showed that:

$$I_{th} = \alpha \phi_{ET} \frac{8}{\kappa T} D a_0 \left( \frac{1}{\tau_{T}} \right)^2$$

where $\alpha$ is the donor absorption coefficient at the excitation wavelength, $\phi_{ET}$ is the quantum efficiency of TET, $D$ is the diffusion constant of the annihilator/ emitter’s triplet excited state, $a_0$ is the minimum distance required for the annihilation of two triplets on the acceptors ($a_0 = 9$ Å for DPA), and $\tau_T$ is the life time of triplets. Below $I_{th}$, the dynamics of acceptor triplet states is dominated by spontaneous nonradiative decay where TTA is inefficient. Only when the incident
power is higher than $I_{th}$, the TTA process dominates and the upconversion QY can be maximized. Note that sunlight is $\sim$100 mWcm$^{-2}$ across the entire solar spectrum, thus only a few mWcm$^{-2}$ at the excitation wavelengths selected during experiments. Therefore, to use sunlight for photon upconversion, the TTA based upconversion system should be carefully designed such that the $I_{th}$ is well below solar irradiance. Based on eqn. (1.6), it is essential to improve TET to lower $I_{th}$. Inspired by biological photosynthetic systems, the self-assembly of functional molecules into ordered molecular assemblies for efficient energy migration has been reported. Here we summarize some self-assembled systems that aim to improve triplet diffusion for the application of TTA-based photon upconversion.

![Chemical structures of branched alkyl chain functionalized 9,10-diphenylanthracene (DPA) emitter and Pt(II) porphyrin sensitizer](image)

**Figure 1.6.** Chemical structures of branched alkyl chain functionalized 9,10-diphenylanthracene (DPA) emitter and Pt(II) porphyrin sensitizer used in nonvolatile solution-based photon upconversion mediated by triplet fusion.

a. **Self-assembly of small molecules**

So far, the most efficient molecular photon upconversion systems have been demonstrated in volatile organic solvents that conveniently eliminate triplet diffusion as the bottleneck for TET. However, practical applications require these liquid phases to be replaced, ideally with oxygen barriers. Recently, Duan et. al. developed a nonvolatile solution that can perform photon upconversion in air. Duan et al. functionalized the commonly used 9,10-diphenylanthracene (DPA) emitter and Pt(II) porphyrin sensitizer with a long branched alkyl chain, molecules 1 and 2 in Fig. 1.6. The functionalized DPA emitter 1 containing 0.01 mol % Pt(II) sensitizer 2 exhibited blue emission upon excitation with a 532 nm green laser even in air. This system demonstrated an
efficient upconversion QY of about 28%, comparable to the record 35% that was obtained from the unfunctionalized sensitizer and emitter pair in an organic solvent. The upconverted emission is still observed below the glass transition temperature, indicating triplet energy migration occurred in the glassy phase, along the electronically active \( \pi \)-conjugated core within the self-assembled molecules. However, the triplet diffusion constant \( D_T \) was low, on the order of \( 10^{-7} \) cm\(^2\) s\(^{-1}\) and the intensity threshold was relatively high at 50 mW cm\(^{-2}\). This was ascribed to the large interchromophore distance, about 2.1 nm, between the DPA emitters, imposed by the alkyl chain. This large separation impedes the efficient migration of triplet states among DPA emitter, thus lowering the diffusion constant of triplet states.

**Figure 1.7.** Schematic representation of triplet energy migration in ionic liquids. The purple block is the sensitizer, Pt(II) octaethylporphyrin (PtOEP). Upon excitation, the triplet exciton generated in the sensitizer can transfer to 9,10-diphenyl anthracene (DPA) derivatives IL1 (shown as red blocks, green wavy line indicates its counter ion) through triplet-TET (TTET). Instead of diffusion, the triplet excitons migrate along the ionic liquid matrix defined by IL1. Once two triplet excitons encounter each other, upconverted light is emitted through triplet-triplet annihilation (TTA). Adopted with permission from ref 119. Copyright 2015 Wiley-VCH.

**b. Ionic liquids**

In order to realize a much closer stacking of the emitter, Hisamitsu et. al. used ionic liquids (ILs) that contain closely packed charged chromophores.\(^{119}\) In their work, sulfonated DPA anion IL1 (Fig. 1.7) was used with an alkylated phosphonium counter cation, eliminating alkyl chains. Excitation
of the Pt (II) porphyrin sensitizer PtOEP that was dissolved in the DPA ionic liquid resulted in upconverted violet emission detected at around 450 nm. Here the inter-molecular distance between DPA emitters is much closer than those in the self-assembly system mentioned above. The excitation intensity threshold was successfully reduced to a low value of 3.0 mW.cm$^{-2}$, which was ascribed to long triplet diffusion length (0.63 μm) and relatively high diffusion constant $1.16 \times 10^{-6}$ cm$^2$ s$^{-1}$. Low temperature measurements showed that excitons diffuse predominantly by energy migration along the molecular assemblies rather than by molecular diffusion.

Figure 1.8. Schematic illustration of the self-assembled membrane structure. Emitter molecule 3 and sensitizer molecule PtOET spontaneously self-assembles in solution. Upon photoexcitation of donor molecules (PtOET) by green light, donor-to-acceptor triplet-TET (TTET) is followed by triplet energy migration among the acceptor networks. It leads to efficient TTA between acceptor triplets and subsequent emission of the upconverted violet light. Adopted with permission from ref 120. Copyright 2015 Nature Publishing Group.

c. Membranes

The self-assembly of chromophores for photon upconversion was promoted by amide group-enriched glutamate with the formation of hydrogen bond networks. Ogawa et al. used an amphiphilic DPA emitter, compound 3, functionalized with a lipophilic alkyl chains linked by lipophobic L-glutamate connectors. In this system, they observed a remarkable triplet diffusion constant of $D_T = 1.4 \times 10^{-5}$ cm$^2$ s$^{-1}$, which is comparable to the molecular diffusion constant of DPA in a low-viscosity solvent ($1.2 \times 10^{-5}$ cm$^2$ s$^{-1}$) or in an ordered anthracene crystal. With this structure, the intensity threshold was reduced to as low as 8.9 mW.cm$^{-2}$ and the upconversion QY
was about 30%. One problem associated with this measurement is the use of an oxygen sensitive sample (PtOEP and DPA in degassed THF) as a standard when reporting the photon upconversion quantum yield. Air-stable compounds with widely accepted fluorescence quantum yield values should be employed as standards instead.\textsuperscript{121} In addition, even though the self-assembled structure was characterized on thin film, there was no direct characterization of this self-assembly structure in solution.

They also claimed that this molecular assembly demonstrated excellent oxygen resistance: about 83% of the upconversion signal was maintained even in the presence of dissolved oxygen. The authors attributed this oxygen barrier to the presence of hydrogen bonding networks. However, another possible reason for the oxygen resistance is that oxygen may be depleted in the vicinity of the acceptors by reaction of the photo-excited molecules with singlet oxygen. Ogawa et al report that the upconverted emission for their self-assembly structures exhibited a gradual increase in the first 100 seconds. This suggests that the surrounding oxygen molecules have been consumed as reported elsewhere.\textsuperscript{122-123}

Self-assembly employing amphiphilic acceptors that can be used in aqueous media was also reported.\textsuperscript{124} This time, hydrophilic quaternary ammonium groups were functionalized at both ends of the DPA emitter through an amine bond. Hydrogen bond networks were observed in the hydrophobic interior. This compensates for the lower stacking ability intrinsic to the structure of DPA. The upconversion QY and diffusion constant ($D$) were measured to be \(\sim 6.5\%\) and \(\sim 1.4 \times 10^{-4} \text{ cm}^2 \text{s}^{-1}\) respectively.

We note that in these examples of self-assembled molecular systems, the diffusion coefficients are estimated using Equation 6, where the $\Phi_{\text{ET}}$ is assumed to be one and $\tau_T$, the lifetime of the triplet states is obtained by monitoring the photoluminescence decay of the upconverted emission. When measuring $\tau_T$, the relation $I_{UC}(t) \propto \exp(-t/\tau_{UC}) = \exp(-2t/\tau_T)$ was used, where $\tau_{UC}$ and $\tau_T$ are the
lifetimes of the emission from the acceptor’s singlet and triplet state, respectively. Since the diffusion coefficient is inversely related to the square of $\tau_T$, accurate measurements of $\tau_T$ are highly desirable for a reliable determination of the diffusion coefficient as well as the triplet diffusion length in the molecular assembly systems.”

(3) **Crystalline frameworks**

Metal organic frameworks (MOFs) or covalent organic frameworks (COFs) are crystalline, porous, covalently linked extended structures that may promote efficient energy transfer. The long-range order in these frameworks could potentially eliminate local variations such as traps and defects, leading to higher rates of energy transfer if orbital overlap between the donor and acceptor is enhanced.

a. **Metal organic frameworks (MOFs)**

![Figure 1.9](image_url)

**Figure 1.9.** Structure of the Ru based MOF (a) within a bilayer and (b) at the bilayer-bilayer interface (dotted red line). In this MOF structure, the carboxylic acid group functionalized bispyridine ligand for Ru is linked through a tetrahedral Zn node. Therefore, each Ru center is covalently linked through a Zn-carboxylate bridge to 12 other Ru centers within the bilayer. The minimum distance between Ru atoms within the Zn–Ru$_4$ subunit is 11 Å. At the bilayer–bilayer interface (dotted red line), the minimum Ru–Ru distances are 8 Å (solid black lines), and there are no covalent links between the Ru centers belonging to different bilayers. Therefore, the shortest separation between Ru-Ru centers leading to the strongest electronic coupling are at the bilayer-bilayer interface, denoted as the $b$ axis here. (c) TET in this MOF is shown to be one-dimensional along the $b$ axis in the lattice where the electronic coupling between two Ru centers is strongest. Each blue dot corresponds to a metal-polypyridyl centered triplet excited state. Adopted with permission from ref 122. Copyright 2013 American Chemical Society.
The group of Wenbin Lin explored the possibility of long range TET in MOFs by designing Ru(II) and Os(II) MOFs with bipyridyl ligands. By increasing the concentration of Os(II) complexes doped into Ru(II) MOFs, the triplet excited states of Ru(II) were readily quenched by energy migration to the Os trap sites. The energy migration was evidenced by the growth of Os(II) complex emission along with the decrease of the lifetime of Ru(II) complexes shown from time-resolved PL spectroscopy. Analysis showed that the Ru triplet state can travel about 15 - 55 nm over its lifetime before it is trapped on the Os (II) complexes center. Using the same Ru(II) and Os(II) complexes based MOFs, Kent et al. also showed these MOFs crystal can also be quenched oxidatively or reductively at the MOF-solution interface. This system demonstrates long-range TET over several hundred nanometers. In addition, quenching by methylene blue at the MOF-solution interface is amplified by 7000-fold relative to a model complex in solution. These results reveal that in these MOF systems, ‘outer-sphere’ electron transfer is favorable. As shown in Fig. 1.9, the hierarchical order within a MOF establishes certain pathways for exciton migration. Theoretical investigations showed that this incoherent hopping of triplet excitons occurs by a Dexter energy transfer. In contrast to FRET, Dexter energy transfer rates drop exponentially with distance and are strongly sensitive to the electronic coupling between the neighboring chromophores.

Does Förster or Dexter energy transfer dominate in these MOFs? Depending on the composition of the building blocks, both the Dexter and Förster processes occur. Experimentally, TET was observed when the Morris group impregnated Zr-based MOFs with ruthenium or osmium polypyridyl complexes, then characterized the loading and the changes in lifetimes when compared to the original isolated organometallic compound. Theoretically, Beratan et al predict negligible Förster energy transfer due to the relatively weak transition dipole strength of the lower metal to ligand charge transfer (MLCT) singlet states. In their calculations, they assume the lowest
Ru(bpy)$_3^{2+}$ excited state consists of 10% singlet character and 90% triplet character. Furthermore, they point out that the vibronically broadened energy levels of the triplet states preclude coherent coupling because it requires the coupling of energy levels to resonant a precision of 0.1 meV. Separately, Lin and Wang observed efficient energy transfer and exciton migration from truxene ligands in the Zn-framework to infiltrated coumarin dye molecules. They saw long distance, through space energy migration accounting for up to 33% of energy transfer in 3D truxene-tribenzoate based Zn MOFs that have no Ru, Ir or Re ions for spin-orbit coupling. The remainder 67% was attributed to nearest-neighbor hopping of singlet excitons. In these reports, the acceptors are irregularly dispersed throughout the framework such that it is difficult to draw definite conclusions because the distribution is unknown. In addition, the MOF-based environment might perturb the nature of the excited states.

In the past year, there have been two reported attempts to harness order in the MOF framework for photon upconversion. Oldenburg et al made a trilayer structure where the sensitizer ((Pd(II) 5,15-diphenyl-10,20-di(4-carboxyphenyl) porphyrin light absorber) was sandwiched by the DPA light emitter held together by Zn nodes. While they demonstrated relatively low threshold intensities for the linear regime in their upconversion measurements, overall upconversion QYs
were less than 0.1%, probably because the fluorescence QY of the annihilator layer was only 1.8% (vs 95% for the free DPA, indicating losses via non-radiative decay pathways), and TET from donor to acceptor was severely constrained, possibly due to the lattice mismatch between the 2 layers and roughness/ defects in the MOF lattice. In the meantime, Mahato et al. synthesized another DPA-containing MOF for photon upconversion, to take advantage of triplet exciton migration between DPA molecules that are closely assembled and aligned. While the enhanced orbital overlap significantly improves the efficiency of triplet migration, it decreased the fluorescence QY of DPA, like in the work of Oldenburg and co-workers. Mahato’s solution to this problem was the introduction of an energy sink for the triplet excitons, a light-harvesting layer composed of a highly fluorescent material, coumarin 343, on the surface of MOF (Fig. 1.10). With this directed energy transfer to the emitter on the surface of the MOF, their photon upconversion QY was boosted from 0.35% to 2.3% and the I_th was 6.5 mW.cm^-2 at 532 nm, close to the solar flux at 532 nm of 1.6 mW/cm^2. In terms of increasing photon upconversion QYs by maximizing the probability that triplet fusion will result in a singlet excited state, Monguzzi and Menaidi have employed perylene as the annihilator/ emitter. Perylene’s second excited triplet state, E(T_2) ~4.0 eV, which is much larger than double the value of the first excited triplet state, E(T_1) ~1.5eV. Hence the probability of forming a singlet-excited state with the fusion of two triplets is one with this acceptor.

b. **Covalent organic frameworks (COFs).**

COFs have also been used to harvest light, whether in the form of singlet or triplet excitons. Phthalocyanines when photoexcited decay to their triplet state within picoseconds, so COFs incorporating these building blocks demonstrate TET. The concept of using COFs to introduce an electronic heterojunction, e.g. between a donor and acceptor has been implemented two ways. Firstly, the donor can anchor the framework, while the acceptor (usually a C_{60} derivative)
can be used to infiltrate the pores. Chen and Jiang have used click chemistry to covalently bind C_{60} to the COF framework after infiltration. They showed that the photoinduced triplets on the ZnPc-COF framework are split into radical cations in the ZnPc columns, while the radical anions end up in the C_{60} molecules within the pores.\textsuperscript{134} Alternatively, both the donor and acceptor can be used to build the framework, for example in the case of phthalocyanine donor and arene diimide acceptors linked by boronate ester. Jiang and Irle argue that the photoinduced excited state on these COFs have a lifetime on the order of microseconds as indicated by the ground state bleach in TA spectroscopy. Further resolution of the photodynamics was inhibited by the poor solubility of the COFs.\textsuperscript{135} In other donor-acceptor COFs, e.g. triphenylene-napthalene diimide,\textsuperscript{136} shortened lifetimes given by time-resolved fluorescence spectroscopy of the donor, coupled with electron paramagnetic resonance spectroscopy, indicate enhanced photoinduced charge separation. Time-resolved microwave conductivity showed that the electron withdrawing benzothiadiazole units within the framework could induce electron transport in a Ni-phthalocyanine COF (mobility \sim 0.6 cm^{2}/Vs).\textsuperscript{137} TA of benzodithiophene-triphenylene COFs infiltrated with PCBM show polaron formation supporting charge-dissociation at the interface.\textsuperscript{138} Despite all this spectroscopic evidence of photoinduced charges created on the donor and acceptor components, it remains a challenge to extract the charges derived from these photoexcited states. In terms of photovoltaic devices, PCEs less than 1\% have been reported, e.g. a thieno[2,3-b]thiophene (TT)-based COF combined with PCBM has a PCE of 0.053\%,\textsuperscript{139} while a pyrene-based COF with C_{60} has a PCE of 0.9\%. The authors argue that the grain boundaries present between misaligned COF crystals in the active area inhibit charge transport, thus resulting in the low PCEs.\textsuperscript{140}

\textbf{(4) Triplet excitons in solar cells}

If photocurrent in a solar cell is derived from triplets (e.g. via singlet fission), there will be a magnetic field dependence. A decrease in photocurrent at high magnetic field points to charges
originating from triplet excitons, while the converse, an increase in photocurrent with large magnetic fields implies that triplet excitons are unable to dissociate into holes and electrons, perhaps due to triplet-polaron or triplet-charge annihilation.\textsuperscript{141-142} The 109 % EQE at 670 nm in pentacene solar cells indicates that triplets from acenes can be harvested in a photovoltaic device.\textsuperscript{40} Triplet excitons arising from singlet fission have been collected as charge in hybrid solar cells made of acenes and nanocrystals.\textsuperscript{41,143-144} Photovoltaic cells composed of bilayers of pentacene/ PbSe and TIPSpentacene/ PbX have reported PCEs of ~4.8 %.\textsuperscript{41,145}

Excitonic solar cells rely on efficient light absorption, exciton formation, charge transfer state creation, charge separation, charge diffusion and collection. The microscopic mechanism by which charge separation proceeds from the transient charge transfer states is still unknown. Zhu has shown that at the pentacene/ \textit{C}_60 interface, singlet fission into triplets occurs faster than charge dissociation.\textsuperscript{146} In 2013, Friend et al reported that if the energy level of the T\textsubscript{1} state is lower than the CT state with triplet character, \textit{3}CT, formed upon exciton dissociation, then triplet excitons become non-radiative recombination centers.\textsuperscript{147} They showed that this can be avoided when enhanced wavefunction delocalization in the electron acceptor lowers the energy level of both the singlet and triplet charge transfer states, \textit{1}CT and \textit{3}CT, such that the resultant energy cascade funnels the electrons into the acceptor.

Crystallinity within the active layer significantly affects the energy level of charge transfer states. Lin et. al. reported that the charge transfer state of a rubrene/ \textit{C}_{60} solar cell could be shifted by over 300 meV by simply crystallizing the as-deposited amorphous film. This made the dissociation of the triplet exciton more favorable compared to the amorphous film, thus increasing the photocurrent. A more crystalline film also has better charge transport properties due to the increased coupling between molecules.
1.3 Conclusions

Triplet excitons, with their long lifetimes, can potentially be harnessed to make next-generation photovoltaic cells that exceed the Shockley-Queisser limit. Triplet excited states are key intermediates in singlet fission and molecular or nanocrystal-based photon upconversion, multi-excitonic processes that can optimize the use of sunlight, in particular the energy contained in the green and NIR wavelengths respectively. As described in the first section, the parameters affecting TET closely mirror those affecting charge transport in organic semiconductors, especially if CT intermediates are involved. Over the recent 30 years, much progress has been made to understand the factors affecting charge mobility in optoelectronic devices based on these solution processable materials, including semiconductor nanocrystals, which like the organic materials, also have tightly bound Frenkel excitons. Therefore, it would be prudent to selectively apply the lessons learnt in optimizing the mobility in organic thin film transistors and the power conversion efficiency in organic photovoltaics to engineering thin films with long triplet diffusion lengths. In particular, the synthetic ease in tuning molecular or nanocrystal structure should in principle enhance wavefunction or orbital overlap between donors and acceptors, while maintaining control of the appropriate energy offsets, depending on whether exciton or charge transport is desired.

In terms of materials design and synthesis, the challenge is to maximize electronic coupling in the thin film over distances exceeding infinity in terms of molecular dimensions. This can be achieved by eliminating defects, whether at the grain boundaries in organic semiconductors, the mid-gap states in semiconductor nanocrystals, dislocations in MOFs or COFs and other unintentional impurities in the thin film. While oxygen must be eliminated to prevent quenching of triplet excitons, it may be possible to use oxygen barriers that are
already commercially available, e.g. polyisobutylene,\textsuperscript{148-149} or the barrier layers used in the commercial production of OPV cells.

Solutions to the challenges in transporting triplet excitons in thin film must bridge traditional disciplines. In terms of theory, Skourtis and Beratan have recently proposed an alternative mechanism to TET involving the simultaneous transfer of both the hole and electron comprising the triplet exciton, eschewing ionic intermediates.\textsuperscript{63} Their calculations suggest this alternative mechanism may be favored for long bridges energetically resonant between the donor and acceptor. Clearly, it will be up to spectroscopists and synthetic chemists to build and characterize systems that support this theoretical prediction. The development of new spectroscopic tools to visualize and quantify the contributions of singlet and triplet excitons to the transport in thin films is invaluable. Current investigations into the intermediates in singlet fission, e.g. bound triplet pair excimers\textsuperscript{113} or strongly interacting triplet pairs,\textsuperscript{150} etc. enabled by various monomer or dimer configurations\textsuperscript{111, 151-156} will shed light on the dielectric environment needed to stabilize triplet excitons. Such interdisciplinary approaches will reveal the fundamental structure-property relationships affecting triplet diffusion in thin film, and ultimately enable the engineering of optoelectronic devices making use of multi-excitonic processes.
1.4 References


138 (20), 6541-6549.


144. Ehrler, B.; Wilson, M. W. B.; Rao, A.; Friend, R. H.; Greenham, N. C., Nano Letters 2012,
12 (2), 1053-1057.


Chapter 2  Quantifying newly introduced ligands on the surface of CdS nanocrystals

2.1  Introduction

In this work, fluorescence resonance energy transfer (FRET)\(^1\) is used as a sensitive probe for the first few binding events of a ligand on cadmium sulfide (CdS) NCs. Here, the relationship between 5.0 nm CdS PLQY and ligation is well understood in terms of FRET from a CdS donor to a boron-dipyrromethene dye acceptor functionalized with a carboxylic acid binding group. By invoking Poissonian binding statistics, a model with multiple, identical but finite binding sites on a NC can explain two independent measurements, both our SSPL and TRPL data. A simpler approach based solely on FRET\(^2\) can describe the SSPL quenching, but would not be able to fit the TRPL data. TRPL experiments confirm that FRET based energy transfer occurs. This is first time the binding behavior of the carboxylic acid group with cadmium chalcogenide NCs is studied quantitatively at low, micromolar concentrations. Without this FRET based assay, such a study is precluded by the sensitivity of NMR and the spectroscopically silent nature of the carboxylic acid group, as the NC PL is unchanged by the exchange of a few new carboxylic acid groups. Indeed, our data shows that an average of 3.0 new carboxylic acid ligands exchange onto oleic-acid capped CdS NCs with a binding constant, \(K_a\), of \(3.4 \times 10^5\) M\(^{-1}\).
2.2 Derivation of FRET based model

![Figure 2.1](image)

**Figure 2.1.** The CdS NCs and ligand functionalized dye molecules form a good fluorescence resonance energy transfer (FRET) donor-acceptor pair. This can be seen by the normalized absorption (dotted lines) and photoluminescence (PL)/emission (solid lines) spectra of CdS (red), Dye 1 (blue), Dye 2 (green) where good overlap of CdS PL and dye absorption occurs.

The distribution of the number \(n\) of functionalized dye molecules attached to one NC follows a Poisson distribution\(^3\). This is due to the low concentrations of both donors and acceptors used in this work, where a fixed amount of CdS NCs at 0.17 nmol is allowed to equilibrate from 5 to 200 equivalents of Dye 1 or 2 (see **Figure 2.1**) in a volume of 2.1 mL. The probability of \(n\) ligands bound to a NC with \(m\), the mean number of ligands, \(L\), is:

\[
P(n \text{ bound}) = \left(\frac{m^n}{n!}\right) e^{-m}
\]

(2.1)

Energy transfer occurs in competition with the intrinsic PL decay processes in CdS NCs, represented by an intrinsic decay constant, \(k_0\):

\[
\begin{align*}
\text{CdS}^* &\overset{k_0}{\longrightarrow} \text{CdS} \\
\text{CdS}^* - L_n &\overset{n k}{\longrightarrow} \text{CdS} - L^* - L_{n-1} \longrightarrow \text{CdS} - L_n
\end{align*}
\]

(2.2)

where CdS* indicates an excited CdS NC which relaxes to the ground state CdS NC. In turn, an excited CdS NC, \(CdS^*\) can transfer its energy to one of the attached ligands non-radiatively, forming \([CdS - L^* - L_{n-1}]\), which represents a CdS NC with one of its dye ligands in its excited state. The excited dye ligand can then fluoresce, forming \([CdS - L_n]\), where both species have returned to
their ground-states. The CdS PL decay rate is accelerated by $k_\text{q}$ for each dye ligand attached. The rate constant for the excited state decay of the $[\text{CdS-*-L}_n]$ complex is then given by $k_0 + nk_\text{q}$ and the TRPL of the CdS is:

$$I(n, t) = I_0 \exp(-k_\text{o}t - nk_\text{q}t)$$ \hspace{1cm} (2.3)

where $I_0$ is the initial PL of the NCs before any decay processes occur. The corresponding ensemble averaged decay curve is given by$^{4-5}$,

$$I_{\text{os}}(t, m) = \sum_{n=0}^{\infty} P(n) I(n, t) = I_0 \exp\left[-k_0t - m\left(1 - e^{-k_\text{m}t}\right)\right]$$ \hspace{1cm} (2.4)

Equation (2.4) can be applied to our SSPL measurements by integrating over the entire time range:

$$\text{SSPL}(m) = \int_0^\infty I_{\text{os}}(t) \, dt = I_0 \sum_{n=0}^{\infty} \frac{m^n e^{-m t}}{n!} \frac{1}{k_0 + nk_\text{q}}$$ \hspace{1cm} (2.5)

If $m = 0$, in the absence of bound ligands, $\text{SSPL}_0 = I_0/k_0$. As a result,

$$\frac{\text{SSPL}(m)}{\text{SSPL}_0} = \sum_{n=0}^{\infty} \frac{m^n e^{-m t}}{n!} \frac{k_0}{k_0 + nk_\text{q}}$$ \hspace{1cm} (2.6)

where SSPL is the NC PL intensity and SSPL$_0$ corresponds to case where CdS is not bound to any dye labeled ligand. So far, this analysis has assumed that the energy donor has only a single lifetime $k_0$. However, PL decays of CdS NC we used exhibit 3 exponential components. In order to take this into account, we parameterize the intrinsic decay of CdS as a triexpontial, corresponding to three distinct emitting populations $N_{D_1}, N_{D_2}, N_{D_3}$ each with their own PL lifetimes ($k_1$, $k_2$ and $k_3$ respectively). The three different decay components can be taken into in a straightforward way, leading to the expressions of equation (2.7) and (2.8).

$$I_{\text{os}}(t, m) = \sum_{n=0}^{\infty} \frac{m^n e^{-m t}}{n!} \left[N_{D_1}^0 \exp(-k_1 t - nk_\text{q}t) + N_{D_2}^0 \exp(-k_2 t - nk_\text{q}t) + N_{D_3}^0 \exp(-k_3 t - nk_\text{q}t)\right]$$ \hspace{1cm} (2.7)
The six parameters \((N_{D_1}, N_{D_2}, N_{D_3} \text{ and} k_1, k_2, k_3)\) are obtained from fitting the decay curve of CdS NC only sample. Since for the SSPL equation (2.8), the sum converges quickly when \(n = 7\), we can compare the calculated SSPL/SSPL\(_0\) to the experimental. Note that Equations (2.7) and (2.8) provide a way for our model to describe two independent experimental observables. Measurement of I(t) and the SSPL/SSPL\(_0\) ratio provide a way to rigorously test whether the model is fully consistent with multiple types of data.

### 2.3 Result and discussion

CdS NCs in the diameter of 5.0 nm were employed as a photoluminescent donor, while two boron-dipyrrromethene dyes (Dye 1 and Dye 2) terminated with carboxylic acid and methyl ester groups respectively, were designed and synthesized as potential acceptors (see Figure 2.1). CdS NCs were synthesized and purified according to procedures by the Peng group\(^6\). All experiments were strictly air free, with samples made inside a glove box and kept in the dark, in air-tight fluorescence cuvettes during the entire experimental period. Experimental results were reproducible across different batches of NCs.

NC-ligand conjugates were prepared by adding 5 to 200 equivalents of ligand to a fixed 0.17 nmol of CdS NCs. The concentration of CdS was determined according to Yu et. al.’s calibration curve\(^7\). For the SSPL experiments, all samples were excited at 405 nm, which is near the first exciton of CdS NC and also at the minimum of the dye absorption spectrum. This was done to reduce interference from direct excitation of the acceptor. Any direct excitation of the dye by 405 nm light was accounted for by subtracting dye fluorescence recorded in the absence of CdS. To avoid inner filtering effects, all NC-conjugate solutions had optical densities below 0.05 at the excitation wavelength.
**Figure 2.2** (a-c) Evolution of CdS NC photoluminescence spectra with (a) carboxylic acid containing Dye 1; (b) methyl ester group terminated Dye 2; and (c) acetic acid as a control. FRET is only observed between CdS and Dye 1, as Dye 1 is a FRET acceptor bound to the NC surface. Samples were dissolved in dry and degassed toluene, excited at 405 nm at RT.

<table>
<thead>
<tr>
<th></th>
<th>$\lambda_{\text{abs}}$ (nm)</th>
<th>$\lambda_{\text{ems}}$ (nm)</th>
<th>$\varepsilon$ (M$^{-1}$cm$^{-1}$) $\times 10^5$</th>
<th>Förster Distance $R_0$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CdS</td>
<td>445</td>
<td>458</td>
<td>7.98</td>
<td>N/A</td>
</tr>
<tr>
<td>Dye1</td>
<td>503</td>
<td>514</td>
<td>1.11</td>
<td>32.4</td>
</tr>
<tr>
<td>Dye2</td>
<td>505</td>
<td>517</td>
<td>1.27</td>
<td>33.2</td>
</tr>
</tbody>
</table>

**Table 2.1** The maximal first exciton and emission wavelength for CdS, maximal absorbance and emission wavelengths for Dye 1 and Dye 2, extinction coefficients, and calculated Förster distances, $R_0$, for Dye1-CdS and Dye2-CdS pair. CdS, Dye 1 and Dye 2 were measured at RT in toluene, dichloromethane and a mixture of dichloromethane and methanol respectively.

Fluorescence resonance energy transfer occurs solely between CdS and Dye 1, the carboxylic acid containing dye, and not with Dye 2, the methyl terminated dye, even though both labeled ligands have an identical spectral profile (**Figure 2.1/ Table 2.1**). In **Figure 2.1(a)**, there is a clear enhancement in acceptor emission as a function of increasing concentration of Dye 1, accompanied by a progressive quenching of the CdS NC PL. The enhancement in dye fluorescence reaches a plateau when more than 60 equivalents of Dye 1 are added to CdS, then starts to drop. This decrease in dye fluorescence at high molar ratios of dye may be due to excimer stacking that can occur if the ligands bind at close proximity. A reproducible red shift in the dye emission is observed as the ratio of Dye 1 to CdS is increased from 10 to 200. This is ascribed to a change in the dielectric environment of the dye, as it is incorporated into the existing oleic acid ligand shell of the NC.

The CdS PL is unchanged in the presence of Dye 2 or acetic acid (**Figure 2.2(b), (c)**). Dye 2 is the methyl ester terminated dye, which does not have a functional group that can bind to the NC,
though it can function as a FRET acceptor from a CdS donor. No FRET-based acceptor emission can be seen in Figure 2.2(b). Conversely, though acetic acid can bind to CdS with its carboxylic acid moiety, it does not induce dramatic PL quenching. The extremely small decrease in CdS PL observed with acetic acid in Figure 2.2(c), which is within instrumental measurement error, indicates that the binding of acetic acid at these concentrations does not affect the photophysics of NC. These three experiments confirm that only bound ligands labeled with a suitable acceptor can induce energy transfer from CdS. The change in PL of CdS is thus directly correlated with the binding of the carboxylic acid functionalized ligands.

**Figure 2.3.** TRPL decay curves of CdS at different CdS-Dye 1 molar ratios. Solid curve show fits to experimental data (scatter plot) at molar ratios of CdS: Dye 1 = 1:0 (cyan), 1:10 (green), 1:20 (orange), 1:60 (red) and 1:120 (blue). The fitting parameters, \( N_Di, k_i \), and \( k_q \) are given in Table 2.2.

TRPL studies confirm that FRET does occur between CdS NCs and Dye 1. This can be seen by the shorter decay times when CdS forms bound complexes with Dye 1 (Figure 2.3). The same samples measured by SSPL were used for TRPL experiments. The decay curves were fit according to Equation (2.7), with fitting parameters \( N_Di, k_i, k_q \) and \( m \). \( N_Di \) and \( k_i \) were obtained from the CdS only sample. \( m \) was fixed to be the same for all 3 components of each decay and \( k_q \) is the same for all decay curves. As such, both \( k_q \) and \( m \) were obtained by fitting all decay curves simultaneously. The fits are robust. When both \( N_Di \) and \( k_i \) were allowed to vary one standard deviation\(^8\), and \( k_q \) and \( m \) are allowed to vary freely, these values come out closely to the original fits. The discrepancy in the fit at the highest ligand loading in Figure 2.3 may be due to a cooperative binding effect. \( N_Di \),

<table>
<thead>
<tr>
<th>( N_D1 )</th>
<th>( N_D2 )</th>
<th>( N_D3 )</th>
<th>( k_1 ) (ns(^{-1}))</th>
<th>( k_2 )</th>
<th>( k_3 )</th>
<th>( k_q ) (ns(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.136</td>
<td>0.283</td>
<td>0.608</td>
<td>0.022</td>
<td>0.128</td>
<td>1.39</td>
<td>0.228</td>
</tr>
</tbody>
</table>

Table 2.2 List of the fitting parameters for \( N_Di, k_i \), and \( k_q \) for the decay curves.
$k_i$ and $k_q$ are shown in Table 2.2 for varying mole ratios of Dye 1, while $m$ is plotted against the concentration of Dye 1 in Figure 2.4 (b).

Figure 2.4. (a) Experimental values for the SSPL quenching of CdS from Figure 2.2(a) are plotted against the concentration of Dye 1 (black line, hollow circle). It compares well with predicted SSPL (red solid square) using parameters $N_{Di}$, $k_i$, $k_q$ and $m$ from the fit to the TRPL data. As the concentration of Dye 1 increases, CdS is strongly quenched by the bound dye molecules. (b) Average number of labeled ligands, $m$, that interact with a CdS NC vs. its concentration. Solid line is the fit to a model with multiple, equivalent binding sites on CdS NCs, squares are experimental data points.

The fitting parameters to the CdS decay times, $N_{Di}$, $k_i$, $k_q$ and $m$, used to predict the SSPL quenching for the CdS donor (see equation 2.8 for the relationship) match the experimentally measured SSPL well. Figure 2.4(a) plots $SSPL/SSPL_o$ as a function of the corresponding ligand concentration. $SSPL/SSPL_o$ represents the SSPL from CdS after equilibration with Dye 1 (Figure 2.2(a)), normalized by SSPL from the same amount of CdS measured under the same conditions. Both $SSPL$ and $SSPL_o$ are directly proportional to the area under the PL peak. The excellent fit between the predicted and actual CdS SSPL values further confirms the validity of our model, where Poissonian binding of the ligand and subsequent FRET-based quenching relates CdS PL and ligand binding in a non-linear fashion. The small deviation at the largest two ligand concentrations may be due to the low signal to noise ratio in the TRPL experiments.

The average number of ligands that are bound to surface of each CdS NC, $m$, can be modeled with a modified Langmuir isotherm, as shown in Figure 2.4(b). In Figure 2.4(b), $m$, obtained by fitting the CdS decays at different ligand concentration, is plotted against ligand concentration. At the highest dye concentrations, $m$ plateaus at about 2.7. In other words, the surface of each oleic
acid capped CdS NC can have up to 3 carboxylic acid functionalized dye molecules adsorbed. In order to discuss the binding interactions, we simply denote the ligand as $L$ and the binding sites on the NC as $N$. If each NC has a single, specific binding site for a ligand with one functional group that can bind, the binding behavior can be modeled\textsuperscript{9},

$$[CdS - L] = \frac{K_a [CdS]_0 [L]}{1 + K_a [L]} \quad (2.9)$$

where $[CdS - L]$, $[L]$ are the total concentrations of the CdS NC and ligand complex, ligand respectively. $[CdS]_0$ is the initial CdS NC concentration and follows the mass conservation equation $[CdS] = [CdS] + [CdS - L]$, where $[CdS]$ is free CdS NC without ligand binding. $K_a$ is the association constant. In this case, the molarity of specific ligand binding sites is identical to the molarity of the NC. However, since there is more than one binding site on the surface of our NCs, this simple one-to-one binding model is inadequate. This naturally leads to a model with multiple binding sites on the CdS NC. In the simplest case of multisite binding, each distinguishable, non-interacting site behaves independently and identically with respect to ligand binding. That is, the affinity of each site for the ligand is the same as all other binding sites and the binding of ligand at one site does not influence the affinity of other binding sites on the surface of the NC. Equation (2.9) can still apply to this situation, but the number of binding sites available for the ligand needs to be increased by a factor of $N_0$ to $N_0 \times [NC]$, where $N_0$ is the number of binding sites per NC. If there are $n$ ligands on a specific CdS NC, modified Langmuir isotherm can be written as,

$$\sum_{n=0}^{N_0} n [CdS - L_n] = \frac{K_a N_0 [CdS] [L]}{1 + K_a [L]} \quad (2.10)$$

If we divide both sides by $[CdS]$, and denote the average number of bound ligands as $m$, equation (2.10) can be rearranged to,

$$m = \frac{K_a N_0 [L]}{1 + K_a [L]} \quad (2.11)$$
This resembles the Langmuir adsorption isotherm. The solid line in Figure 2.4(b) shows the fit using equation (2.11) to our experimentally derived data points, marked with filled squares. From this fit, the total number of binding sites on each NC, \( N_0 \), is 3.0 and the association binding constant, \( K_a \), is \( 3.4 \times 10^5 \) M\(^{-1}\).

We wanted to test whether the surface of the NC has more than one type of binding site, with each site type having a different binding association constant. In this case, the total binding isotherm can be shown to take the form of the sum of two or more individual binding isotherms. For example, if there are two types of binding sites on the surface of the NC totaling \( N_1 \) and \( N_2 \), with association constants \( K_{a_1} \) and \( K_{a_2} \), respectively, the overall binding isotherm is given by:\(^{10,11}\):

\[
m = \frac{K_{a_1} N_1[L]}{1 + K_{a_1}[L]} + \frac{K_{a_2} N_2[L]}{1 + K_{a_2}[L]} \tag{2.12}
\]

If the difference between \( K_{a_1} \) and \( K_{a_2} \) is more than a factor of 100, it should be possible to observe a deviation from the standard shape of a Langmuir isotherm\(^{45}\). This is not observed in the isotherm in Figure 2.4(b). Therefore, a model of nanoparticles with multiple, equivalent binding sites is suitable for the self-exchange of carboxylic acid ligands on oleic acid capped CdS NCs.

It is interesting to note that the self-exchange of labeled carboxylic acid ligands on oleic acid CdS NCs is limited to an average of three new ligands per NC. This observation matches well with a recent NMR based report on chalocogenide NCs where Anderson et. al. show that a relatively strong Lewis base is required to displace all native oleic acid ligands\(^{12}\). These three new ligands may replace existing oleic acid ligands, or they may bind to unpassivated sites on the NC surface. While it is not clear from our ensemble experiment if there is a sub-population of NCs averse to ligand exchange and another sub-population more responsive to self-exchange, it is clear that a majority of the original oleic acid ligands remain. Single molecule experiments are underway now to investigate this.
2.4 Experimental Section

2.4.1 Sample preparation for steady-state and time-resolved photoluminescence

All sample preparation was performed in a nitrogen glovebox. NC-dye conjugate complexes were prepared by adding appropriate amounts of dye molecules dissolved in dichloromethane into pure toluene in a 1 cm path length fluorescence cuvette. Then 0.17 nmol of CdS NC were injected into cuvettes with different dye concentrations. Molar ratios of dye to QD were discretely varied among samples from 0-100. The final volume of each solution was fixed at 2.1 mL. The spectra of each sample were taken immediately after the mixing of CdS and Dye and then after reaching equilibrium (at least 5 hours) using the SPEX Fluorolog fluorimeter. All samples were excited at 405 nm, which is near the first exciton of CdS NC and also at the minimum of the dye absorption spectrum in order to reduce interference from direct excitation of the acceptor.

Fluorescence lifetime data were taken using front face detection with a Hamamatsu C4334 streakscope picosecond streak camera with a time resolution of 15 ps. The 400 nm excitation pulse was generated by frequency doubling the 800 nm pulse from a 1 kHz Coherent Libra regenerative amplifier. Scattered pump light was removed by placing a 400 nm long wave pass filter and 420 nm color filter on the input lens before the streak camera. The fluorescence was detected at 54.7° relative to the pump to eliminate rotational diffusion effects. Measurements of the fluorescence decay at different laser intensities yielded similar decays, indicating that exciton-exciton annihilation did not influence the results.

2.4.2 Synthesis of BODIPY ligands

Scheme 1.1. Synthesis routine of Dye1
**Compound 1** Compound 1\textsuperscript{13} was synthesised and purified according to procedures published by Michel et. al.\textsuperscript{14}.

**Compound 2** Compound 1(4.1 mg, 0.012mmol), methyl succinyl chloride (1.75mg, 0.012mmol) and potassium carbonate (0.6 mg, 0.0042 mmol) in 1.0 mL dry DMSO was bubbled under argon for 15 min. Then the reaction was heated to 90\textdegree C under protection of argon atmosphere and stirred overnight to yield a clear brown solution, which was then allowed to cool down to room temperature. After adding distilled water, a turbid orange-brown solution was obtained. This was extracted with dichloromethane to give a bright orange solution. \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 400MHz): \(\delta_H\) 7.39(d, 2H, J=8Hz), 7.24(d, 2H, J=8Hz), 6.08(s, 1H), 5.97 (s, 2H), 4.55(d, 2H, J=6.0Hz), 3.70(s, 3H), 2.74(t, 2H, J=6.1Hz), 2.61(t, 2H), 2.52(s, 6H), 2.04(s, 3H), 1.36(0, 6H). HRMS (+ESI/ APCI) \textit{m/z}: 468.2270 (MH\textsuperscript{+}).

**Dye 1** Dye 1 was obtained by deprotecting compound 2 following a method published by Blum et. al\textsuperscript{15}. Compound 2 (6.08mg, 0.013mmol) was dissolved in tetrahydrofuran (0.2 mL) and methanol (0.8 mL) were mixed and degassed under argon for 15 min. Then lithium hydroxide (1.64mg, 0.034mmol) in distilled water was added dropwise into the reaction flask. This reaction was stirred at room temperature and all solvent evaporated after 2h. The product was purified by column chromatography with dichloromethane. \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 400MHz): \(\delta_H\) 7.37 (d, 2H, J=7.37Hz), 7.22(d, 2H, J=7.22Hz), 6.38(s, 1H), 5.96(s, 2H), 4.51(d, 2H, J=8Hz), 2.71(s, 2H), 2.53(s, 2H), 2.54(s, 6H), 1.35 (s, 6H) ppm. \textsuperscript{13}CNMR (600MHz, CDCl\textsubscript{3}) \(\delta_C\) 155.7, 143.2, 141.4, 139.2, 134.3, 131.5, 128.5, 128.3, 121.4, 43.4, 30.9, 29.8, 14.7, 14.2 ppm. HRMS (+ESI/ APCI) \textit{m/z}: 453.2053 (MH\textsuperscript{+}).
Dye 2 Dye 2 was synthesised by a method published by Chang et. al.\textsuperscript{14} 2,4-Dimethylpyrrole (0.288mg, 3.03mmol) and 4-(acetoxy)benzoyl chloride (0.285mg, 1.436mmol) in 8.5 mL dichloromethane was refluxed at 50°C with an oil bath for 1h 30min to yield a light orange solution. Then dichloromethane was removed under vaccum until only 2~3 mL was left. 19.5mL toluene was added followed by triethylamine (0.667g, 6.58mmol) and boron trifluoride diethyl etherate (1.16g, 8.20mmol) to give a bright yellow suspension, which was heated at 50°C for another 1h. The reaction was cooled down to room temperature and put on vaccum for 20 min to remove all toluene. Product was extracted with dichloromethane, washed with water for 3 times and then dried with MgSO$_4$. Silica gel chromatography (dicholoromethane as eluent) afforded a bright orange colored fraction that was collected (76.2 mg, 13.8%).$^1$H NMR (CDCl$_3$, 400MHz): $\delta$H 7.30-7.25(m, 2H), 7.23-7.19(m, 2H), 5.99(s, 2H), 2.55(s, 6H), 2.33(s, 3H), 1.42(s, 6H) ppm. $^{13}$C NMR (600MHz, CDCl$_3$): $\delta$C 169.0, 155.8, 143.2, 140.8, 132.5, 132.0, 131.6, 129.3, 122.6, 121.5, 21.3, 14.6, 14.9 ppm. HRMS (+ESI/ APCI) $m/z$: 382.1789 (MH$^+$)

2.5 Conclusion

The initial ligand binding events on CdS NCs were studied quantitatively by correlating the change in CdS PL with energy transfer to a bound ligand. The CdS donor was paired with a specially designed dye acceptor functionalized with a NC binding group to form a good FRET pair. A model invoking both FRET and Poissonian binding statistics can be used to fit the TRPL decays from the CdS donor, while the fitting parameters extracted from the decays predict the
experimentally measured steady-state photoluminescence spectra well. A modified Langmuir
isotherm involving a ligand with a single binding group to NCs with multiple, identical binding
sites was found to describe the self-exchange of carboxylic acid ligands with oleic acid capped CdS
NCs. Specifically, there is an average of up to 3 new carboxylic acid labeled ligands that bind to
the CdS NC surface with a binding constant, $K_a$ of $3.4 \times 10^5$ M$^{-1}$. This is the first time that
quantitative information about the initial ligand binding events is obtained for any NC-ligand
system. This FRET-based platform is general, and can be extended to study other functional groups
in combination with any semiconductor NC.
2.6 References


Chapter 3  Distinct sites on nanocrystals affects energy and charge transfer

3.1  Introduction

Energy transfer forms the basis for emerging photovoltaic technologies centered on hybrid thin films composed of semiconductor nanocrystals and conjugated organic compounds.\textsuperscript{1-4} Within the hybrid structure, one can combine the superior charge-transport properties of inorganic semiconductor components with the strong light-matter interactions in organic compounds.\textsuperscript{5-9} Charge or exciton transfer is a key factor affecting the performance of all hybrid optoelectronic devices.\textsuperscript{10-12} In general, wavefunction overlap, phonon activated hopping, tunneling, or a Dexter transfer process are invoked.\textsuperscript{13} Recent work has shown unexpectedly efficient RET between triplets generated in acenes to lead chalcogenide acceptor nanocrystals nominally more than 1 nm apart.\textsuperscript{14-15} There, the mechanism of RET is elusive due to the difficulty in characterizing the nanoparticle-ligand interface. Our work directly addresses RET at this ill-defined interface using molecular acceptors with distinct binding groups to nanoparticle donors. Here, we show that while Förster resonance energy transfer (FRET) from quantum dot (QD) donors to molecular acceptors may occur, other static charge transfer processes may be induced by the chemical bond at the organic-inorganic interface.
Figure 3.1 Schematic of energy transfer from CdS nanocrystals to molecular acceptors with acid and amine binding groups (A_{acid} and A_{amine}). (a) Energy transfer to A_{acid} involves FRET to ligands bound to multiple, identical sites, while A_{amine} induces both FRET and static quenching in the CdS donor, indicating selective binding to distinct sites. $k_q$ and $\kappa$ represent the FRET and static quenching constants respectively. (b) Normalized absorption (dotted lines) and photoluminescence / emission (solid lines) spectra of CdS with diameters of (i) 3.4 nm (black), (ii) 4.0 nm (red), (iii) 5.0 nm (blue) and (iv) A_{acid} (yellow), (v) A_{amine} (green). The spectra were measured at RT in toluene with a small amount of dichloromethane.

The proposed charge and RET is depicted schematically in Figure 3.1(a). CdS QDs are used as the donors while borondipyrromethene dye acceptors functionalized with amine (A_{amine}) or carboxylic acid (A_{acid}) groups serve as potential FRET acceptors. When the molecular acceptor binds to the QD with the carboxylic acid group, RET can be described in terms of Poissonian binding to multiple, identical binding sites, resulting in FRET from the QD donor to the dye. However, RET from the QD donor to the amine acceptor results in two acceptor populations: one dark, one bright. While FRET from the CdS donor to the amine and carboxylic acid acceptor occurs at about the same rate, for A_{amine}, static quenching results in a dark acceptor population. This equilibrium constant for this static process decreases from 94 M$^{-1}$ to 61 M$^{-1}$ and 24 M$^{-1}$ as the QD diameter increases from 3.4 nm to 4.0 nm and 5.0 nm. This work shows that ignoring the chemical nature of the NC binding group comes at the peril of overlooking the vastly dissimilar processes and rates of energy transfer that may arise.
3.2 Result and Discussion

**Figure 3.2** Monitoring energy transfer in steady-state photoluminescence (SSPL) and time-resolved photoluminescence (TRPL). (a) Evolution of 4.0 nm CdS nanocrystal steady SSPL spectra with $A_{\text{acid}}$. Samples were prepared in dry and degassed toluene, excited at 375 nm at RT. Corresponding TRPL spectra for the 4.0 nm CdS nanocrystals with the molecular acceptors in (b) 1 ns window and (c) 100 ns window. (d) Evolution of 4.0 nm CdS nanocrystal SSPL spectra with $A_{\text{amine}}$. Corresponding time-resolved photoluminescence (TRPL) spectra for the 4.0 nm CdS nanocrystals with the molecular acceptors in (e) 1 ns window and (f) 100 ns window. Samples (b), (c), (d), (f) were excited at 400 nm with a laser power of 15 $\mu$W. All spectra were collected at RT.

**Table 3.1.** Förster distances for all CdS QDs donor and organic acceptor pairs.

<table>
<thead>
<tr>
<th></th>
<th>$R_0(\text{Å})$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>3.4 nm</td>
</tr>
<tr>
<td>$A_{\text{acid}}$</td>
<td>22.4</td>
</tr>
<tr>
<td>$A_{\text{amine}}$</td>
<td>22.8</td>
</tr>
</tbody>
</table>

RET between the CdS QDs donors and the two molecular acceptors was examined using steady-state and time-resolved photoluminescence (SSPL and TRPL). Different aliquots of ligand, ranging from 5 to 150 equivalents with respect to the QD, were added to 0.081 $\mu$M of CdS NCs in dry and degassed toluene, as described in the Supplementary Information. As synthesized CdS NCs are passivated with oleic acid, and their optical properties, along with that of the two ligands are shown.
in **Figure 3.1**(b). Both the amine and carboxylic acid functionalized acceptors, \(A_{\text{amine}}\) and \(A_{\text{acid}}\) respectively, have similar Förster and donor-acceptor distances when paired with QD donors (see **Table 3.1**). Our dye acceptors are neutral to eliminate non-specific binding. Without the carboxylic acid or amine functional group, no binding and consequently, no FRET between the QD and ligand occurs.\(^{16}\) For the 4.0 nm QDs, the SSPL results are shown in **Figure 3.2**(a) & (d) and their corresponding TRPL measurements in 1ns and 100ns are shown in **Figure 3.2**(b), (c) & (e), (f) respectively. In all the SSPL figures, fluorescence due to direct excitation of the acceptor has been subtracted. The same trends are observed for the 3.4 nm and 5.0nm diameter QDs. The data for these QDs can be found in section 3.3 and are summarized in **Figure 3.3**.

FRET from the CdS donor to the amine and carboxylic acceptors has a rate constant ranging from 0.067-0.31 ns\(^{-1}\) (see **Table 3.2**). This is reflected in the TRPL measurements obtained in the 100 ns window, shown for the 4.0 nm diameter QDs in **Figure 3.2** (c) & (f). At sub-nanosecond timescales, the decay kinetics of the CdS QD donor is greatly affected by \(A_{\text{amine}}\) (**Figure 3.2**(e)), while \(A_{\text{acid}}\) has only a slight effect on this timescale (**Figure 3.2**(b)). In contrast, the carboxylic acceptor only effects changes in the lifetime of the CdS donor on much longer timescales up to 100 ns (**Figure 3.2**(c) and (f)). Assuming a Poissonian distribution of ligands that induces the same FRET quenching constant \(k_q\) for each binding event, the decay curves can be fit to extract \(k_q\) and \(m\), the average number of bound ligands.\(^{17-19}\) Parameters from this fit, \(m\) and \(k_q\), can be used to predict the steady-state behavior of the donor with \(A_{\text{acid}}\) for all three sizes (**Figure 3.3**). The predicted SSPL/SSPL\(_0\) correlate with experimental data very well, correlating two independent experiments. This good correlation confirms that FRET from the QD to the carboxylic acceptor completely describes RET at this interface.
Table 3.2 Fitting parameters for TRPL data for A_amine and A_acid experiment with classic FRET model.

<table>
<thead>
<tr>
<th>Sizes (nm)</th>
<th>k_1 (ns^{-1})</th>
<th>k_2 (ns^{-1})</th>
<th>k_3 (ns^{-1})</th>
<th>Nd_1</th>
<th>Nd_2</th>
<th>Nd_3</th>
<th>k_q (ns^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>A_amine (100ns)</td>
<td>3.4</td>
<td>0.021</td>
<td>0.12</td>
<td>0.97</td>
<td>0.14</td>
<td>0.24</td>
<td>0.65</td>
</tr>
<tr>
<td></td>
<td>4.0</td>
<td>0.026</td>
<td>0.11</td>
<td>0.53</td>
<td>0.19</td>
<td>0.39</td>
<td>0.41</td>
</tr>
<tr>
<td></td>
<td>5.0</td>
<td>0.013</td>
<td>0.08</td>
<td>0.67</td>
<td>0.11</td>
<td>0.31</td>
<td>0.62</td>
</tr>
<tr>
<td>A_acid (100ns)</td>
<td>3.4</td>
<td>0.019</td>
<td>0.067</td>
<td>0.61</td>
<td>0.29</td>
<td>0.44</td>
<td>0.28</td>
</tr>
<tr>
<td></td>
<td>4.0</td>
<td>0.023</td>
<td>0.084</td>
<td>0.60</td>
<td>0.26</td>
<td>0.38</td>
<td>0.37</td>
</tr>
<tr>
<td></td>
<td>5.0</td>
<td>0.023</td>
<td>0.13</td>
<td>1.3</td>
<td>0.14</td>
<td>0.29</td>
<td>0.59</td>
</tr>
</tbody>
</table>

Figure 3.3 Energy transfer for A_acid and A_amine. (a) For A_acid, FRET from CdS entirely explains donor quenching. Parameters extracted from the TRPL data (dashed line) can be used to fit the normalized SSPL data well, two independent experiments (see Supplementary Information). (b) For A_amine, a combination of static quenching (SQ) and FRET (dotted line) is used to reconcile the quenching of the CdS PL. The FRET only model (dashed line) is shown for comparison. Introducing the SQ component significantly improves the fitting quality. (see Supplementary Information). CdS PL was normalized with CdS emission in the absence of acceptor. Experimental data for 3.4 nm (filled black triangle), 4.0 nm (filled red circle) and 5.0 nm (filled blue square) are shown.

For the amine acceptor data, we found that FRET by itself, was not sufficient to explain the PL behavior. For a FRET only process, such as with A_acid, the increase in fluorescence of acceptor tracks the decrease in fluorescence of the QD closely.20 The inset in Figure 3.2(a) shows that when the steady-state donor PL is 45% quenched, A_acid emission is enhanced by 55%, as expected. However for A_amine, when the donor is 90% quenched, the A_amine is only enhanced by about 10% (Figure 3.2(d) inset). In order to quantitatively model the PL data, an additional static quenching (SQ) term that does not lead to emission, parameterized by \( \kappa \), is required. Figure 3.3(b) shows the FRET only model is not sufficient to predict the experimental SSPL/SSPL_0. The use of two
different decay processes improves the fitting where the relative weight ($C_0$) of SQ to FRET ranges from 10 to 25 (see **Table 3.2**), where a higher proportion of smaller QDs are statically quenched. Using this model, for the 5.0 nm QDs, we find that 9% of the quenched donors relax through FRET to an emissive acceptor, while the other 91% with bound amine ligands are quenched statically where the acceptor does not fluoresce. In contrast, for the 3.4 nm QDs, 4% of the QDs undergo FRET while 96% are quenched by a fast charge transfer mechanism. We refer to these non-emissive $A_{amine}$ as ‘dark’ acceptors.

Besides the dramatic differences in PL quenching, there are other indications that the $A_{amine}$ binding differs from that of $A_{acid}$. In both cases, the acceptor molecules’ emission shows a red shift as concentration increases. This bathochromic shift has been observed before and can be attributed to a change in the dielectric environment. But this red shift is 2-3 times larger for the $A_{acid}$ ligand compared to $A_{amine}$ (**Figure 3.4**). It is possible that the amine dye binds to ‘bare’ sites that are less well passivated by oleic acid, while the acid ligand intercalates into regions onto the NC surface surrounded by close-packed oleic acid molecules.

**Figure 3.4** Bathochromic shift of the acceptor’s emission maxima in SSPL experiments. A bathochromic shift of the acceptor’s emission maxima occurs as its’ concentration increased. This red shift is especially pronounced for $A_{acid}$ compared to $A_{amine}$.
This pronounced difference in both the SSPL and TRPL is solely caused by a change in the binding moiety. Firstly, the Förster distances between all the CdS donors and acceptors are similar, ranging from 22.1 Å to 22.8 Å, deviating by less than 2% (See Table 3.1). Förster theory predicts that both acceptors should quench the donor in the same way. Secondly, the fast quenching of the QD by the bound amine ligands may involve charge transfer. Charge transfer usually occurs on picosecond timescales, much faster than the nanosecond timescales probed by these experiments in the 100ns window. Other groups have also reported quenching of donor PL by aliphatic amines, though usually at higher concentrations of amine (when the NC to amine ratio exceeds 1:1000). In our experiment, this ratio is an order of magnitude lower.

The amine ligand preferentially binds to distinct ‘dark’ sites on the QD, resulting in both SQ and FRET from the donor QD. In contrast, the carboxylic acid ligand binds to multiple, identical sites, resulting in FRET from the QD being the sole observable. One explanation may be the static quenching from "dark" sites in the amine case is due to charge transfer that outcompetes Förster transfer for some subset of nanoparticles. Another possible explanation lies in the difference in dipole orientation of bound acid and amine on the QD surface. Therefore, the bound A_{amine} might be in an orientation with better dipole-dipole alignment with the CdS NC, or in a more rigid configuration less subject to free rotation. Note that the functional groups on both acceptors are attached to the conjugated portion by quarternary carbons that have full rotational freedom. In addition, the change in the donor quantum yield should also be considered. Selective binding will alter the surface chemistry of NP significantly thus leading to a substantial difference of donor’s quantum yield. From Förster theory, both the relative orientation of donor and acceptor dipoles and donor’s quantum yield can affect the rate of RET significantly. In all scenarios described above, the amine ligand, compared to the acid, selectively binds to certain sites on the QD surface. The
observation that \( \kappa \), the equilibrium constant for the static quenching by the amine ligand increases with decreasing particle size, suggests that the increased curvature of the QDs with diminished size results in more sites susceptible to adsorption by the amine.

3.3 Experimental section

3.3.1 Steady-state photoluminescence measurements.

![SSPL spectra for the 3.4nm and 5.0nm CdS with Aacid and Aamine; (e)-(h) Normalized donor PL and acceptor emission as a function of increasing acceptor concentration.](image)

**Figure 3.5** (a)-(d) SSPL spectra for the 3.4nm and 5.0nm CdS with Aacid and Aamine; (e)-(h) Normalized donor PL and acceptor emission as a function of increasing acceptor concentration.

3.3.2 Time-resolved photoluminescence measurements

In the 1 ns window, the bound Aamine induces a faster decay in CdS in comparison with Aacid, where no apparent change is observed. The same trend is observed in other two sizes of CdS: 3.4nm and 5.0nm, as shown in **Figure 3.6** (a)-(d). In 100ns window, both amine and carboxylic acceptor effects changes in the lifetime of the CdS donor on longer timescales up to 100 ns (**Figure 3.6**(e)-(h)).
3.3.3 Fitting using classic FRET model for both ligand.

A detailed derivation can be found in section 2.2. The final fitting result is shown below.

3.3.4 Fitting using combination of FRET and static quenching model.

\[ N_D = N_D^a + N_D^b \]
‘*N*\textsuperscript{a}\textsubscript{D}’ denotes the population of CdS NP bound to acceptors that undergoes FRET according to Poissonian statistics, while ‘*N*\textsuperscript{b}\textsubscript{D}’ is the population that binds dye and quenches, but the bound dye does not fluoresce.

\[A + D^b \rightarrow A \cdot D^b\]

\[\kappa = \frac{[A \cdot D^b]}{[A][D^b]} \tag{3.1}\]

Where \([A \cdot D^b]\) is the concentration of the non-emissive complex, \([D^b]\) is the concentration of uncomplexed donor in \(N^b\textsubscript{D}\) portion and \([A]\) is the total concentration of the added A\textsubscript{amine}. If the complexed species is non-fluorescent, the fraction of the fluorescence that remains, \(I^b_D\), is given by the fraction of the \(N^b\textsubscript{D}\) that is not complexed. The total concentration of the donor in \(N^b\textsubscript{D}\) is \([D^b]\)\textsubscript{0}.

\[[D^b]\textsubscript{0} = [D^b] + [A \cdot D^b] \tag{3.2}\]

Substitution into equation (3.2) yields

\[\kappa = \frac{[A \cdot D^b]}{[A][D^b]} = \frac{[D^b]\textsubscript{0} - [D^b]}{[A][D^b]} = \frac{[D^b]\textsubscript{0}}{[A][D^b]} - \frac{1}{[A]} \tag{3.3}\]

We can substitute the donor concentration for fluorescence intensities, and rearrangement of equation (3.3) yields\textsuperscript{22}

\[I^b_D = \frac{[D^b]}{[D^b]\textsubscript{0}} = \frac{1}{1 + \kappa[A]} \tag{3.4}\]

The final intensity of fluorescence is the sum of the intensity of CdS in \(N^a\textsubscript{D}\) and \(N^b\textsubscript{D}\) with no bound acceptor. Therefore, the fitting equation for CdS donor PL quenching is,
\[
SSPL/SSPL_0 = I_D^a + I_D^b = C \left[ \sum_{n=0}^{\infty} \frac{m^n e^{-m}}{n!} \left( \frac{N_{d1}}{k_1 + nk_q} + \frac{N_{d2}}{k_2 + nk_q} + \frac{N_{d3}}{k_3 + nk_q} \right) + C_0 \frac{1}{1 + \kappa[A]} \right] (3.5)
\]

where \(C\) are the normalizing constants. \(C_0\) is the weight for static quenching over FRET; \(\kappa\) is the equilibrium constant for forming \([A \cdot D^b]\) conjugates.

**Table 3.3. Fitting constants for static and FRET combined model fitting**

<table>
<thead>
<tr>
<th>NP sizes</th>
<th>3.4 nm</th>
<th>4.0 nm</th>
<th>5.0 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>(C_0)</td>
<td>25</td>
<td>12</td>
<td>10</td>
</tr>
<tr>
<td>(\kappa(M^{-1}))</td>
<td>94</td>
<td>61</td>
<td>24</td>
</tr>
</tbody>
</table>

### 3.4 Conclusion

In conclusion, energy and charge transfer from CdS to bound acceptors depends on the chemical nature of the adsorption. We have demonstrated that the interface between inorganic/organic components is very sensitive, and subtle differences can change the nature and rate of charge and RET dramatically. These findings are particularly relevant in ligand exchange for hybrid PV, because much like the study here, hydrazine only replaces a subset of the existing oleic acid ligands, and only hydrazine functionalized NCs show efficient multiple exciton generation (MEG).\(^{25-27}\) These findings show that synthetic control of the ligand can be used to tune charge and energy transfer in organic-inorganic hybrid devices. It provides a logical route towards next-generation hybrid PV that can potentially harness MEG and singlet fission.
3.5 References


Chapter 4  Length Dependence of Triplet Energy Transfer

4.1  Introduction

Among existing upconversion methods, sensitized triplet-triplet annihilation (TTA) based photon upconversion is the only one with demonstrated potential for harvesting incoherent photons from the sun.\(^1\)\(^-\)\(^5\) In TTA based upconversion, the sensitizer harvests the low energy photons, which are subsequently transferred to the emitting species capable of TTA. During TTA, two molecules in their triplet excited state combine to form a molecule in its singlet excited state and a molecule in its ground state, thus upconverting light. Recently, our group and others showed that inorganic nanocrystals (NCs) are viable alternatives\(^6\)\(^-\)\(^8\) to the organometallic compounds conventionally\(^9\)\(^-\)\(^11\) used as sensitizers. Even though the high density of states above the band gap in NCs may result in the reabsorption of upconverted light, the best upconversion quantum yield achieved in this hybrid upconversion system, 14.3%, is comparable to that achieved in molecule-based upconversion. The role of NCs as sensitizers makes strategic use of their intrinsic optical properties, such as a large absorption coefficient, excellent photostability and low cost, advantageous for photon upconversion.\(^12\)\(^-\)\(^13\) As the long insulating ligands on the as-synthesized NC impede efficient energy transfer, installing a transmitter ligand on NC surface is crucial for mediating triplet energy transfer across this interface.\(^7\)\(^,\)\(^14\) This transmitter accelerates triplet energy transfer (TET) to the 9, 10-diphenylanthracene (DPA) emitters by forming an energy cascade, as shown in Figure 4.1(a).
Figure 4.1 (a) Schematic of the energy transfer in this hybrid photon upconversion platform. The energy diagram depicts the triplet excitonic states of the CdSe NC, the p-phenylene (ph) bridges when n=1 and 2, and the anthracene transmitter. (b) Absorption, fluorescence spectra for 9ACA, CPA, CPPA, CP4A, CP9A ligands and 2.6 nm CdSe NCs. The spectra were taken at room temperature in hexane, the same solvent as the upconversion experiments. The green arrow indicates the 532 nm excitation wavelength.

An understanding of the mechanism of triplet energy transfer from inorganic semiconductor NC donors to the organic acceptors is essential for improving the performance of this hybrid upconversion system. Studies of energy transfer\textsuperscript{15-16} mainly focus on the kinetics of the energy transfer events and their dependence on reaction driving-force, distance, chemical environment or the linkage between the donor and acceptor.\textsuperscript{17-22} A traditional approach to explore long-range energy transfer involves the use of covalent donor–bridge–acceptor systems. However, most such studies are focused on charge or Förster energy transfer.\textsuperscript{17, 23-25} Previous work has shown surprisingly efficient energy transfer from triplets generated in acenes to lead chalcogenide nanocrystals following Dexter-type mechanism.\textsuperscript{26-27} However, while ligand exchange was necessary for the high efficiencies, it has been shown to alter NC photoluminescence quantum yield and intrinsic decay rate.\textsuperscript{28} Therefore, we are interested in elucidating this TET process
quantitatively in a model system where the acceptor molecule is covalently linked to the NCs in a well-defined manner.

This work investigates the effect of donor-acceptor distance on TET across rigid aromatic and flexible aliphatic spacers in a covalently linked CdSe NC-bridge-anthracene system. The rate of TET ($k_e$) is extracted from the upconversion quantum yield (QY) that was obtained under steady state cw illumination. For the rigid spacer, the rate constant for energy transfer is exponentially dependent on the length of the oligo-$p$-phenylene bridge, following the Dexter energy transfer mechanism. The empirical damping coefficient, $\beta$, is fitted to be $0.43\pm0.07\ \text{Å}^{-1}$. Surprisingly, different lengths of flexible aliphatic bridges have no effect on the rate of energy transfer. This interesting phenomenon may be the first experimental evidence for flexible ligands not being fully extended on a NC surface and bending over instead. These results not only further the mechanistic understanding of TET in hybrid NC-organic systems, but also facilitate the rational design and selection of the appropriate transmitters in hybrid optoelectronic systems.

4.2 Result and discussion

![Figure 4.2](image)

**Figure 4.2** The relationship between upconversion quantum yield versus the concentration of each anthracene transmitter during ligand exchange: rigid transmitters (solid square) 9ACA (red), CPA (orange), CPPA (dark yellow); flexible transmitters (hollow circle) CP4A (green) and CP9A (navy). Upconversion samples were prepared in a strictly air free manner and were excited with a 12.7 W/cm² 532 nm laser at RT.
As shown in Figure 4.1(a), a series of different anthracene ligands are linked to 2.6 nm CdSe NCs through variable-length oligo-p-phenylene or aliphatic bridges with a carboxylic acid group. The energy diagram in Figure 4.1(a) illustrates that the TET from NCs to anthracene is exergonic by roughly 0.55 eV. As the emitter species, we choose diphenylanthracene (DPA), which is commonly used in organic–organic upconversion schemes due to its long-lived, low-lying triplet state and relatively high fluorescence quantum yields (90%). Synthetic details for these novel ligands can be found in the supporting information. Their absorption and emission are shown in Figure 4.1(b). The upconversion QY was optimized by varying the concentration of anthracene ligands in the ligand exchange solution. (see Figure 4.2). The upconversion QY is defined as follows:

\[
\Phi_{UC} = 2\Phi_{ref} \times \left( \frac{\text{photons absorbed by reference}}{\text{photons absorbed by sample}} \right) \times \left( \frac{\text{photons emitted by sample}}{\text{photons emitted by reference}} \right)
\]

The average number of bound anthracene ligands per CdSe NC \(n\) was determined using UV-Vis electronic absorption spectroscopy (see section 4.3.2 for more details). Since \(n\) is small (Table 4.1), it is impossible to characterize \(n\) using NMR. The values of \(n\) \((n = 0.78-3, \; \text{Table} \; 4.1)\) obtained are consistent with previously reported studies for the binding of carboxylic acid ligands to octadecylphosphonic acid (ODPA) capped CdSe NCs. While we realize the distribution of bound ligands on NCs should follow Poissonian statistics, we do not have enough information to fully model this. The highest upconversion QY obtained for 9ACA, CPA and CPPA are 14.3%, 3.9% and 0.4% respectively and the average values are listed in Table 4.1. A similar result was also observed when the same experiments were performed on a different batch of 2.6 nm CdSe NCs (see section 4.3.3 for more details).
Table 4.1. The absorption and emission maxima for the anthracene ligands and CdSe nanocrystals (NCs) along with their extinction coefficients in hexanes at RT are listed. The average number of bound anthracene ligands (n) on a CdSe NC correspond to the value that results in the maximum upconversion quantum yield (QY). The average upconversion QY obtained by repeating the upconversion measurements under these optimized conditions is shown for comparison.

<table>
<thead>
<tr>
<th></th>
<th>$\lambda_{\text{abs}}$ (nm)</th>
<th>$\lambda_{\text{em}}$ (nm)</th>
<th>$\varepsilon$ (M$^{-1}$cm$^{-1}$) × 10$^3$</th>
<th>n</th>
<th>Upconversion QY (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Average</td>
</tr>
<tr>
<td>9ACA</td>
<td>362</td>
<td>404</td>
<td>8.68</td>
<td>2.89</td>
<td>13.0</td>
</tr>
<tr>
<td>CPA</td>
<td>366</td>
<td>405</td>
<td>6.85</td>
<td>2.34</td>
<td>3.5</td>
</tr>
<tr>
<td>CPPA</td>
<td>365</td>
<td>405</td>
<td>13.8</td>
<td>1.72</td>
<td>0.30</td>
</tr>
<tr>
<td>CP4A</td>
<td>365</td>
<td>403</td>
<td>19.1</td>
<td>1.28</td>
<td>3.0</td>
</tr>
<tr>
<td>CP9A</td>
<td>365</td>
<td>403</td>
<td>23.3</td>
<td>0.78</td>
<td>2.6</td>
</tr>
<tr>
<td>CdSe</td>
<td>518</td>
<td>534</td>
<td>62.6</td>
<td>N/A</td>
<td>N/A</td>
</tr>
</tbody>
</table>

We relate the rate of energy transfer ($k_{et}$) to the efficiency of TET ($\Phi_{ET}$). $\Phi_{ET}$ can be calculated from the measured upconversion QY, $\Phi_{UC}$, based on the following equation,

$$\Phi_{UC} = \Phi_{ET} \Phi_{TTA} \Phi_{A}$$  \hspace{1cm} (4.2)$$

because our experiments are conducted in the linear regime with regards to excitation power density and nanocrystal concentration, where TTA is the main decay pathway of the triplet excited states in DPA. $^{38-39}$ $\Phi_{UC}$, $\Phi_{ET}$, $\Phi_{TTA}$, $\Phi_{A}$ are the quantum yields of upconversion, energy transfer, triplet-triplet annihilation and acceptor fluorescence respectively (see Figure 4.1). In this work, $\Phi_{A}$, the fluorescence QY of DPA, is 0.9 based on previous studies. $^{30, 40}$ As for $\Phi_{TTA}$, standard spin statistics predict that the fraction of triplet-triplet encounters that lead to a singlet is 11.1%. However, the TTA process is usually more efficient since quintet states are not energetically accessible. $^{41-45}$ Here, we use $\Phi_{TTA} = 0.52$ based on a report by Monguzzi et. al. for DPA. $^{43, 46}$ It is assumed that DPA excited triplet state is consumed by triplet-triplet annihilation, and other monomolecular decay processes such as intersystem crossing or bimolecular processeses such as oxygen or impurity quenching are not involved (since samples are air-free). Based on the maximum upconversion QY measured, $\Phi_{ET}$ is calculated to be 30.5%, 7.8% and 0.85% for 9ACA, CPA and CPPA respectively.
The rate of energy transfer, $k_{et}$, is correlated with the efficiency of energy transfer ($\Phi_{ET}$) by equation (4.3), which is similar to that previously used by Ding et al. to calculate the yield of hole transfer from CdSe/CdS core/shell NCs to ferrocene.\(^{47}\)

$$\Phi_{ET} = \frac{n k_{et}}{k_r + k_{nr} + n k_{et}}$$  \hspace{1cm} (4.3)

In equation (4.3), $n$ is the average number of bound anthracene ligands on the surface of NCs, $k_{et}$ is the rate of energy transfer from one CdSe NC to each bound ligand, $k_r$ and $k_{nr}$ are the intrinsic radiative and non-radiative decay rates of CdSe NCs without anthracene ligands. It is assumed that the intrinsic decay rates are unchanged in the presence of the carboxylic acid functionalized ligands, an assumption verified experimentally.\(^{36, 48}\)

**Figure 4.3.** Time resolved photoluminescence measurements of CdSe NCs (black scatter plot) on (a) 1ns, (b) 1000ns time scale. The solid red curve shows the both sets of experimental data can be fit with a biexponential decay. The fitting parameters, $A_i$, $k_i$ and $\tau_i$, are given in the inset, where $i = 1$ and 2, corresponding to the first and second time constants.

Here, TET introduces a new decay channel on top of the original intrinsic decay pathways, analogous to the perturbation introduced by charge transfer. From equation (4.3), it is clear that $k_{et}$ can be calculated once $\Phi_{ET}$ and the NC’s intrinsic decay rates are known. For our CdSe NCs, the PL decays can be fitted to multiexponentials, with lifetimes of 37 ps, 286 ps, 54 ns and 182 ns respectively (Figure 4.3). So far, two groups have reported rates of TTET that differ by two orders of magnitude. If we choose the fast decay component, 286 ps for example, $k_{et}$ is calculated to be
about $2.0 \times 10^9 \text{s}^{-1}$, similar to what Castellano et. al measure with transient absorption spectroscopy. On the other hand, if we select the components on the nanosecond timescale, 54 ns or 184 ns, our calculated value, around $1.0 \times 10^7 \text{s}^{-1}$, agrees with the rate reported by Bardeen et. al. Therefore, more work must be done to understand the photophysics underpinning energy transfer between nanocrystals and molecular triplet states. Note that the intrinsic decay rates of the NC end up as a prefactor on the calculated $k_{\text{et}}$ and do not affect the value obtained for $\beta$, the Dexter damping coefficient, which is given by the slope of the plot in Figure 4.4 (see section 4.3.3 for details).

![Figure 4.4](image.png)

**Figure 4.4** The rate of triplet energy transfer ($k_{\text{et}}$, red squares) and maximum upconversion QY (blue triangles) are shown versus the phenylene bridge length of covalently bound transmitter anthracene ligands on CdSe nanocrystals. The logarithmic relation of $k_{\text{et}}$ is consistent with Dexter energy transfer and a damping coefficient, $\beta$, of $0.43 \pm 0.07 \text{Å}^{-1}$.

There is a logarithmic relationship between the donor-acceptor distance and the rate of energy transfer ($k_{\text{et}}$), consistent with Dexter energy transfer as the dominant mechanism (Figure 4.4). The distance dependence of $k_{\text{et}}$ can be described by equation (4.4), where $d$ is the length of the energy barrier and $\beta$ is an empirical damping coefficient that describes the extent of coupling through the barrier material.

$$k_{\text{et}} = k_0 \exp(-\beta d) \tag{4.4}$$

The experimentally determined $\beta$ for the CdSe-(phenylene)$_n$-anthracene system is found to be $0.43 \pm 0.07 \text{Å}^{-1}$. If we include the original, unfunctionalized ODPA-capped CdSe NCs, where
the upconversion QY is 0.026%, then $\beta$ is $0.42 \pm 0.02 \text{ Å}^{-1}$ (see section 4.3.3 for details). The same experimental result can be reproduced on another batch of 2.6 nm CdSe NCs for a $\beta$ value of $0.61 \pm 0.04 \text{ Å}^{-1}$ (see section 4.3.3 for more details). The value of $\beta$ depends on the energy offset between the donor and acceptor (0.55 eV here), as well as the height and length of the tunneling barrier between the two species. In the case of the CdSe-(phenyl)$_n$-anthracene system, the length of the phenyl bridge is systematically elongated by increasing the number of phenylene units from 0 to 2 going from 9ACA to CPA to CPPA. However, the barrier height is not constant, because the first excited triplet states of benzene and bisphenylene are 3.67 and 2.85 eV respectively,\textsuperscript{18,49-50} as drawn in Figure 4.1(a). Nonetheless, the $\beta$ value obtained here is comparable to that measured in organic donor-acceptor systems. In the case of hole transfer from a perylene-3,4:9,10-bis(dicarboximide) donor to a phenothiazine acceptor, the rate constant had a strong distance dependence with a $\beta$ value of $0.46 \text{ Å}^{-1}$\textsuperscript{51-52} However, as Dexter energy transfer can be regarded as the correlated transfer or two charges\textsuperscript{53}, $\beta$ is expected to be twice that of charge transfer for the same barrier\textsuperscript{54-57} In cases where only triplet energy transfer occurs, the Ru(bpy)$_3^{2+}$(bpy= 2,2’-bipyridine)-phenylene bridge-Os(bpy)$_3^{2+}$ system gave a $\beta$ value of $0.50 \text{ Å}^{-1}$\textsuperscript{50,58} The tunneling barrier created by the phenylene bridge between the CdSe NC and anthracene impedes efficient energy transfer, leading to a strong distance dependence. In our case, the carboxylic acid group may also contribute to the tunneling barrier. In terms of NC-molecule systems, a value of $\beta = 0.24 \text{ Å}^{-1}$ and $0.85 \text{ Å}^{-1}$ was reported for hole transfer from CdSe NC donors to ferrocene acceptors across CdS and alkyl barriers respectively.\textsuperscript{47,59} To our knowledge, this is the first report quantifying the Dexter damping coefficient characterizing energy transfer between nanocrystals and molecular triplet states. A lower $\beta$ value indicates stronger coupling, or a lower tunneling barrier\textsuperscript{60}, and the values measured here compare well considering the dielectric constants and energetic barriers introduced by the spacer.
The efficiency of triplet energy transfer can be calculated from equation (4.3) in the main text (left, $\Phi_{ET}$ in red), or from equation (4.6) below (right, $\Phi_{ET(NC)}$ in blue). $\Phi_{ET(NC)}$ determined from equation (4.6) follows the same trend as $\Phi_{ET}$, but only to a limited extent, see discussion below.

Another way of quantifying the efficiency of energy transfer, $\Phi_{ET}$, is by relating any change in NC PL to the triplet sensitization of anthracene. For clarification, we labeled it as $\Phi_{ET(NC)}$. $\Phi_{ET(NC)}$ can be calculated from the change in steady-state NC PL during the upconversion experiments where $F_{DA}$ and $F_D$ represent the CdSe emission peak intensities in the presence and absence of anthracene ligands respectively. Here, $F_D$ represents the emission of the CdSe NCs functionalized with a carboxylic acid ligand without a transmitter anthracene unit, e.g., benzoic acid, butyric acid and octanoic acid. The introduction of these carboxylic acid ligands does not appreciably change the NC PL, unlike amine or thiol based ligands.

$$\Phi_{ET(NC)} = 1 - \frac{F_{DA}}{F_D}$$ (4.6)

Figure 4.5 shows $\Phi_{ET(NC)}$ determined via equation (4.6) has the same trend as the upconversion QY, but only to a limited extent. For example, though the CPPA and ODPA ligands result in the same upconversion QY, in the presence of 2.1 mM DPA, the CdSe PL is not affected by the former while it is quenched by 10% for the latter. The low average number of bound ligands and the strong distance dependence leads to a weak effect on NC PL for ligands with a long bridge. Therefore, we cannot assign a $\Phi_{ET(NC)}$ value based on equation (4.6) for CPPA and CP4A since these ligands do not quench the NC. Indeed, even for 9ACA, the transmitter which gives the highest upconversion
QY of 14.3%, $\Phi_{ET(NC)} = 50\%$, indicating that the NC PL is only partially quenched by triplet energy transfer.

The flexible aliphatic transmitter ligands, **CP4A** and **CP9A**, give an unexpectedly high upconversion QY that shows no distance dependence. For both transmitters, the maximal upconversion QY is about 3.0% (see Table 4.1), which is similar to the optimized upconversion QY of the rigid **CPA** ligand. Given the fact that the fully extended spacer lengths for **CPA**, **CP4A** and **CP9A** are drastically different (6.2 Å, 10.9 Å and 15.5 Å respectively), the consistency in upconversion QY is quite surprising. Note that the unifying motif between these three transmitters is the single rigid phenyl group separating the anthracene moiety from the NC surface. A similar trend was also observed when we performed the same experiment on a different batch of 2.6 nm CdSe NCs (see section 4.3.3 for more details). Therefore we infer that the lack of distance dependence in the upconversion QY for the aliphatic ligands as strong evidence that these flexible molecules bend over on the surface of CdSe NC, either through thermal fluctuations or a curved ligand binding geometry.

4.3 Experimental Section

4.3.1 Ligand exchange and sample preparation

As carboxylic acid ligands cannot efficiently displace the original phosphonic acid ligands, the ligand exchange reaction was stirred vigorously until the upconversion signal did not improve, which is about 12 h in our case. After stirring, the solution was precipitated with acetone and then redispersed in 2.1 mM DPA solution in hexane for photon upconversion measurements. All upconversion experiments were strictly air free, with samples made inside a glove box and kept in the dark, in airtight fluorescence cuvettes during the entire experimental period. Different amounts of anthracene ligand were dissolved in a fixed volume of THF (100 μL), a good solvent for all the ligands. Then CdSe NCs in toluene were added. THF enables NC functionalization with conditions where ligand concentration is high and the total volume small (~200 μL in our case). In this THF-toluene solvent combination, NCs remain stable during ligand exchange without crashing out from
the solvent or a significant drop in photoluminescence (PL) QY. A small volume is preferred as it reduces the amount of acetone required to fully precipitate the CdSe NCs. While acetone is necessary as a bad solvent to separate the functionalized NCs from the ligand exchange solution, it has a negative effect on the upconversion QY since it can dissociate the bound anthracene ligands effectively. After ligand exchange, 1 mL of acetone was added to precipitate the particles. We then separated this solution into two equal volumes, spun down under exactly the same condition. One portion was used for the upconversion measurements, while the other portion was saved to characterize the average numbers of bound anthracene ligands using UV-Vis spectroscopy. For the upconversion sample, one of the pellets was redispersed in 2 mL of 2.1 mM DPA solution in hexane. The other pellet was fully dissolved in 1 mL hexane solution. Then 500 µL of the NCs solution was transferred to 3 mL hexane solvent in quartz cuvette for UV-Vis absorption measurements. Please note that due to the broad absorption feature of CdSe NC, in order to calculate the concentration of anthracene ligand accurately, the absorption spectra of CdSe NCs is first subtracted from the original data.

4.3.2 Determining average numbers of bound anthracene ligands

The absorption spectra for quantifying \( n \), the number of bound ligands per NC, are shown in Figure 4.7. The number of bound bound ligands increases in tandem with the concentration in the ligand exchange solution for both rigid and flexible ligands. The average values were obtained by measuring the upconversion QY after performing the ligand exchange at these optimized concentrations on at least three separate occasions. Interestingly, as the concentration of CP4A and CP9A in the ligand exchange solution increases from 13.2 mM to the maximal 110.9 mM, the upconversion QY drops dramatically to about 0.11%. Though we did not observe any clear shifts in the absorption spectra of the hybrid complex (see Figure 4.7), we cannot rule out the possibility that excimer formation may reduce \( \Phi_{UC} \) under higher ligand loading.
Figure 4.7 The absorption spectra of bound anthracene transmitter ligands (a) 9ACA, (b) CPA, (c) CPPA, (d) CP4A, (e) CP9A, added at different ratios relative to the CdSe NCs during ligand exchange. These spectra were used to calculate $n$, the number of bound ligands per NC. The free anthracene ligands have been removed (see text for details). The absorption spectra of the pure anthracene ligands are shown in magenta for comparison.

4.3.3 Logarithmic relationship between $k_{et}$ and phenylene bridge length.

Figure 4.8 The logarithmic relation of $k_{et}$ versus phenylene bridge length is consistent with Dexter energy transfer. A data point for the original ODPA-capped CdSe NCs is included. The Dexter damping coefficient, $\beta$, is $0.42 \pm 0.03$ Å$^{-1}$. 
Figure 4.9. The experiments in the main text were repeated on a different batch of 2.6 nm CdSe nanocrystals (NCs). (a) The optical properties of the CdSe NCs in the main text and this section. (b) The upconversion quantum yield from these NCs using the optimized ligand exchange conditions shown in Figure 4.1 and Table 4.1. (c) The logarithmic relation of $k_{et}$ versus ligand length for the rigid ligands in this experiment. The Dexter damping coefficient, $\beta$, is $0.61 \pm 0.04 \text{ Å}^{-1}$.

For the ODPA-capped CdSe NCs that did not undergo ligand exchange, $n$, the average number of DPA molecules involved in energy transfer is estimated considering the surface area of the NC and the concentration of DPA in the upconversion solution. If the radius of ODPA capped CdSe NC is estimated as the sum of the length of the ODPA ligand (2.3 nm) and the radius of CdSe core (1.3 nm), the surface area of a CdSe NC is 159.18 nm$^2$. The 9, 10-diphenyanthracene molecules is modeled as a 9.22 Å long and 13.23 Å wide rectangle, so the area occupied by each DPA molecule is estimated to be about 1.22 nm$^2$, assuming DPA’s long axis is parallel to the NC surface. The maximum number of DPA molecules on the surface of 2.6 nm diameter CdSe NC is calculated to be 130. Alternatively, taking into account the concentration of DPA (2.1 mM), the number of DPA molecules in a 4Å shell about this nanocrystal is 134, again assuming the long axis of the DPA is parallel to NC surface. Note that both these calculations provide a minimum $n$ value, hence the $k_{et}$ value for the ODPA only sample is an upper bound.

In Monguzzi et.al.’s work$^{38}$, the upconversion quantum yield is defined with a factor of 0.5 for a maximum of 0.5, as shown below,

$$QY_{SUC} = \frac{1}{2} f\phi_A \phi_{ISC} \phi_{TTA} \phi_{ET} \quad (4.5)$$

The $\Phi_{TTA}$ defined in our work is the same as $f\phi_{TTA}$ in equation (4.5), which is 0.52 for DPA. This is consistent with Sripathy et. al.$^{46}$ who showed a maximum value for $\Phi_{TTA}$ of 0.45 for DPA.

The fitted value of $\beta$ is not affected by the intrinsic decay rate used for calculating $k_{et}$, as shown below: From rearranging equation (4.3), the expression for $k_{et}$, the TTET rate constant is as follows:

$$k_{et} = \frac{\Phi_{et}(k_a + k_{nr})}{n(1 - \Phi_{et})} \quad (4.6)$$
The Dexter energy transfer expression is:

\[ k_{et} = k_0 \exp(-\beta d) \]  

(4.7)

Equating equation (4.6) and (4.7), and taking the natural log of both sides, we can obtain the following equation,

\[ \ln \frac{\Phi_{et}}{n(1 - \Phi_{et})} + \ln(k_n + k_{n+}) = \ln k_0 - \beta d \]  

(4.8)

Clearly from equation (4.8), \( \beta \) is not affected by the intrinsic decay rate of CdSe NCs.

### 4.3.4 Synthesis of anthracene ligands

All the anthracene ligands were obtained by coupling 9-bromoanthracene, 1, with various moieties through Suzuki coupling. Based on the target molecule’s polarity and solubility, we carried out two different permutations of the Suzuki coupling reaction. In Scheme S1, route (a) was applied when less polar molecules were the target, e.g. 9-(4-bromophenyl)anthracene, 2, was obtained with a yield of 64%. However, under these conditions, the direct coupling of 1 and 4-carboxyphenylboronic acid completely failed, probably due to the extreme difference in polarity between the reactants. Thus, we protected the carboxylic acid group and screened different solvents for the cross-coupling reaction (e.g. acetonitrile, tetrahydrofuran (THF), ethanol and methanol etc.). The addition of methanol gave the CPA (4-(anthracen-9-yl)benzoic acid) target compound with 90% yield. The phenyl-anthracene ligands with aliphatic linkers, CP4A (4-(4-(anthracen-9-yl)phenoxy)butanoic acid) and CP9A (9-(4-(anthracen-9-yl)phenoxy)nonanoic acid) were directly obtained by route (b) with monomers containing the carboxylic group, but a relatively low isolated yield of 32% and 20% respectively. CP4A and CP9A have a linear aliphatic chain consisting of 4 and 9 carbons respectively between the carboxylic acid binding group and the phenyl-containing anthracene core.

**Scheme S1.** Synthesis of anthracene ligands with rigid and flexible bridges.
Reagents and conditions: a) K$_2$CO$_3$, Pd(PPh$_3$)$_4$, toluene: H$_2$O=3:2, 80 °C, 10h. b) K$_2$CO$_3$, Pd(PPh$_3$)$_4$, toluene:CH$_3$OH:H$_2$O=8:3:3, 80 °C, 9h. c) KOH, THF: MeOH=1:1, 100 °C, 5h.

Compound a1 is a known compound$^{62}$: 4-bromophenol (3.0 g, 20.1 mmol, 1.0 eq), 5-bromo-1-pentene (3.0 g, 20.1 mmol, 1.0 eq), potassium carbonate (3.47 g, 25.1 mmol, 1.25 eq), potassium iodide (0.53 g, 2.01 mmol, 0.1 eq), 18-crown 6 (0.334 g, 2.01 mmol, 0.1 eq) and 100 mL acetone were mixed in two neck reaction flask. The solution refluxed for 12 h until the reaction was done. After cooling down to room temperature and removing the solvent under reduced pressure, the solution was extracted with CH$_2$Cl$_2$ and washed with water several times. The organic layer was then dried with MgSO$_4$, and the solvent was removed with a rotary evaporator. The resulting crude product was purified by silica gel column chromatography to get rid of excess 18-crown-6. A colorless oil of 3.34 g was obtained (70% yield). $^1$H NMR (400 MHz, CDCl$_3$): $^\delta$H = 7.34 (d, 2H, J= 9.0 Hz), 6.78 (d, 2H, J= 9.0 Hz), 5.83 (m, 1H), 5.02 (m, 2H), 3.93 (t, 2H), 2.22 (m, 2H), 1.87 (m, 2H) ppm.

Compound a2 was obtained in the same way as compound a1 as 3.17 g of a colorless oil (yield 74%). $^1$H NMR (400 MHz, CDCl$_3$): $^\delta$H = 7.34 (d, 2H, J=9.0 Hz), 6.78 (d, 2H, J= 9.0 Hz), 5.80 (m, 1H), 4.95 (m, 2H), 3.91(t, 2H), 2.03 (m, 2H), 1.76 (m, 2H), 1.31 (m, 10H) ppm. The proton NMR matches the reported value.$^{63}$

**Oxidation:** the oxidation of compound a1 and compound a2 was performed following a method by Borhan et al.$^{33}$

Compound b1: Compound 1a (3.0 g, 12.4 mmol, 1.0 eq) was dissolved in 62 mL of DMF (0.2 M), and 1.6 mL OsO$_4$ (0.01 eq, 2.5% in tBuOH) was added and stirred for 5 min. Oxone® (15 g, 49.6 mmol, 4.0 eq) was added in one portion and the reaction was stirred at RT for 8 h. Na$_2$SO$_3$ (100 mg, 6.0 eq w/w) was added, to reduce the remaining Os(VIII), and stirred for an additional hour. The final solution would become dark brown / black. EtOAc was added to extract the products and 1N HCl was used to dissolve the salts. The organic extract was washed with 1N HCl (3x) and brine, dried over MgSO$_4$, and the solvent was removed under reduced pressure to obtain the crude
product. Products were purified by silica gel column chromatography to give 2.3 g of a white solid (70%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta_H = 7.38$ (d, 2H, J=9.0 Hz), 6.78 (d, 2H, J=9.0 Hz), 3.99 (t, 2H), 2.58 (m, 2H), 2.12 (m, 2H) ppm. $^{13}$C NMR (500 MHz, CDCl$_3$): $\delta_C = 178.97, 157.96, 132.38, 116.39, 113.09, 66.87, 30.53, 24.39$ ppm. HRMS (-ESI/APCI) (mass m/z): 256.9829 [M-H].

Compound **b2** was obtained in the same way as compound **b1** using compound **a2** instead. A white solid was isolated (1.4 g, 63%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta_H = 7.34$ (d, 2H, J=9.0 Hz), 6.78 (d, 2H, J=9.0 Hz), 3.91 (t, 2H), 1.76 (m, 2H), 1.64 (m, 2H), 1.35 (m, 10H) ppm. $^{13}$C NMR (500 MHz, CDCl$_3$): $\delta_C = 179.51, 158.35, 132.32, 116.43, 112.71, 68.33, 34.06, 29.55, 29.42, 29.27, 29.09, 26.07, 24.77$ ppm. HRMS (-ESI/APCI) (mass m/z): 329.0639 [M*].

**Suzuki coupling:** Compound **c1** and **c2** were synthesized following a method by Miyaura et. al. $^{34}$

![Suzuki coupling reaction](image)

Compound **c1**: Compound **b1** (2.0 g, 7.7 mmol, 1.0 eq), bis(pinacolato)diboron (2.2 g, 9.0 mmol, 1.1eq), KOAc (4.5 g, 46.3 mmol, 6.0 eq), 48 mL DMSO are mixed in a flask. The reaction was degassed under Ar for 20 min and then Pd(dppf)Cl$_2$.CH$_2$Cl$_2$ (0.085 g, 0.1 mmol, 0.03 eq) was added under high argon flow. The reaction was heated at 80 °C for 8 hours. After cooling to room temperature, the reaction was extracted with EtOAc and washed with brine several times. The organic layer was then dried with MgSO$_4$, and the solvent was removed with a rotary evaporator. The resulting crude product was purified by silica gel column chromatography and EtOAc: hexane=1:1 as the eluent. A pale yellow solid was obtained after removal of the solvents (1.7 g, 73% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta_H = 7.58$ (d, 2H, J=9.0 Hz), 6.93 (d, 2H, J= 9.0 Hz), 3.99 (t, 2H), 2.37 (m, 2H), 1.93 (m, 2H), 1.27 (s, 12H) ppm. $^{13}$C NMR (500 MHz, CDCl$_3$): $\delta_C = 178.97, 161.46, 136.65, 113.95, 105.13, 83.70, 66.42, 30.58, 25.15, 24.98$ ppm. HRMS (+ESI/APCI) (mass m/z): 307.1706 [M+H]$^+$. 

Compound **c2** was obtained in the same way as compound **c1** using compound **b2** instead to give a white solid (0.88 g, 67% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta_H = 7.72$ (d, 2H, J=9.0 Hz), 6.87 (d, 2H, J= 9.0 Hz), 3.97 (t, 2H), 1.76 (m, 2H), 1.64 (m, 2H), 1.35 (m, 10H), 1.26 (s, 12H) ppm. $^{13}$C NMR (500 MHz, CDCl$_3$): $\delta_C = 179.55, 161.79, 136.55, 113.93, 105.07, 83.59, 67.78, 34.02,

Compound **CP4A, CP9A, d1** and **d2** were synthesized following a method by Cheng et. al. 32

Compound **CP4A**: A mixture of compound **c1** (147.3 mg, 0.40 mmol, 1.0 eq), 9-bromoanthracene (123.4 mg, 0.48 mmol 1.2 eq), K$_2$CO$_3$ (387 mg, 2.8 mmol, 7.0 eq) was placed in a 50 ml schlenk tube and 3.3 ml of degassed of toluene: CH$_3$OH: H$_2$O (8:3:3) were added. After degassing under argon for 20 min, Pd(PPh$_3$)$_4$ (12 mg, 0.0104 mmol, 0.026 eq) was added under argon. After heating to 80 °C under argon atmosphere for 18 h the solvent was removed to give a dark yellow residue. The solid was suspended in water and extracted with EtOAc. After drying the organic phase over MgSO$_4$ and removing the solvent, the product was purified by silica gel column chromatography to yield 45.6 mg pale yellow solid (32% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta_H$ = 8.48 (s, 1H), 8.03 (d, 2H, J= 8.4 Hz), 7.69 (d, 2H, J= 8.8 Hz), 7.46 (m, 2H), 7.35 (m, 4H), 7.12 (d, 2H, J= 8.3 Hz), 4.18 (t, 2H), 2.70 (t, 2H), 2.24 (m, 2H) ppm. $^{13}$C NMR (500 MHz, CDCl$_3$): $\delta_C$ = 179.00, 158.32, 136.90, 132.43, 131.52, 131.07, 130.64, 128.43, 127.02, 126.49, 125.34, 125.17, 114.45, 68.06, 30.78, 24.66 ppm. HRMS (-ESI/ APCI) (mass m/z): 356.1400 [M*].

Compound **CP9A** was obtained in the same way as compound **CP4A** using compound **c2** instead to give a white solid (64 mg, 20% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta_H$ = 8.48 (s, 1H), 8.03 (d, 2H, J= 8.4 Hz), 7.72 (d, 2H, J= 8.8 Hz), 7.46 (m, 2H), 7.33 (m, 4H), 7.12 (d, 2H, J= 8.5 Hz), 4.09 (t, 2H), 2.39 (t, 2H), 1.88 (m, 2H), 1.41 (m, 10H) ppm. $^{13}$C NMR (500 MHz, CDCl$_3$): $\delta_C$ = 179.25, 158.71, 137.08, 132.41, 131.55, 130.73, 130.68, 128.44, 127.10, 126.45, 125.32, 125.18, 114.48, 68.19, 34.06, 29.53, 29.37, 29.17, 26.26, 25.76, 24.85 ppm. HRMS (+ESI/ APCI) (mass m/z): 427.2340 [M+H]+.
Compound **d1**: A mixture of 9-bromoanthracene (500 mg, 1.94 mmol), 4-ethoxycarbonylphenylboronic acid (471.5 mg, 2.43 mmol), K$_2$CO$_3$ (938.4 mg, 6.79 mmol) and 16 mL of toluene: CH$_3$OH: H$_2$O =8:3:3 was mixed in a flask. The solution was degassed under argon for 20 min and Pd(PPh$_3$)$_4$ (58.3 mg, 0.05 mmol, 2.5 mol%) was added under high argon flow. The reaction then was stirred under argon for 12 h at 80°C. After the mixture was cooled to room temperature, it was extracted with EtOAc and washed with H$_2$O several times. The organic layer was then dried with MgSO$_4$, and the solvent was removed with a rotary evaporator. The resulting crude product was purified by silica gel column chromatography and CH$_2$Cl$_2$: hexane=5:1 as the eluent. A white solid was obtained (565 mg, 90% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$H = 8.53 (s, 1H), 8.26 (d, 2H, J=8.4 Hz), 8.05 (d, 2H, J=8.4 Hz), 7.58 (m, 4H), 7.47 (m, 2H), 7.36 (m, 2H), 4.49 (q, 2H), 1.47 (t, 3H) ppm. $^{13}$C NMR (500 MHz, CDCl$_3$): $\delta$C = 167.21, 143.98, 135.84, 131.52, 131.40, 129.98, 129.76, 129.54, 128.57, 127.24, 126.45, 125.82, 125.32, 61.24, 14.57 ppm. HRMS ESI-MS (mass m/z): 327.1367 [M+H]$^+$.

Compound **2**: 2 was synthesized following a previously published method. 4-Bromophenylboronic acid (469 mg, 2.3 mmol), 9-bromoanthracene (500 mg, 1.9 mmol), 17.6 mL of dry toluene, and 11.6 mL aqueous of K$_2$CO$_3$ solution (2.0 M) were placed in a 50 mL round-bottom flask. Pd(PPh$_3$)$_4$ (67.2 mg, 0.06 mmol) was added after degassing under argon for 20 min. The mixture was vigorously stirred at 80 °C for 10 hours. After cooling to room temperature, the resulting mixture was extracted with CH$_2$Cl$_2$ followed by purification by column chromatography on silica gel with hexane as the eluent to offer a white solid. The desired compound was obtained in 64% yield (414 mg). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$H = 8.51 (s, 1H; Ar H), 8.04 (d, 2H, J=8.3 Hz), 7.71 (d, 2H, J=7.4 Hz), 7.64 (d, 2H, J=9.1 Hz), 7.47 (m, 2H), 7.37 (m, 2H), 7.33 (d, 2H, J=8.8 Hz) ppm. The proton NMR matches the reported value. $^{64}$ HRMS (+ESI/ APCI) (mass m/z): 333.0269 [M-H]$^+$. 

82
Compound **d2**: A mixture of compound **2** (277 mg, 0.83 mmol), 4-ethoxycarbonylphenylboronic acid (403 mg, 2.08 mmol), K$_2$CO$_3$ (802 mg, 5.81 mmol) and 7.0 mL of toluene: CH$_3$OH: H$_2$O (8:3:3) was mixed in a flask. The reaction was degassed under argon for 20 min. Then Pd(PPh$_3$)$_4$ (48.0 mg, 0.04 mmol, 5.0 mol%) was added under argon. Then the reaction was stirred under argon for 12 h at 80 °C. After the mixture was cooled to room temperature, it was extracted with EtOAc and washed with H$_2$O several times. The organic layer was then dried with MgSO$_4$, and the solvent was removed with a rotary evaporator. The resulting crude product was purified by silica gel column chromatography and CH$_2$Cl$_2$: hexane=1:1 as the eluent. A white solid was obtained (303 mg, 75% yield). $^1$H NMR (400 MHz, CDCl$_3$): δ$_H$ = 8.53 (s, 1H), 8.18 (d, 2H, J=8.5 Hz), 8.06 (d, 2H, J=8.4 Hz, 7.84 (m, 4H), 7.71 (d, 2H, J=8.7 Hz), 7.56 (d, 2H, J=8.3 Hz), 7.48 (m, 2H), 7.37 (m, 2H), 4.43 (q, 2H), 1.45 (t, 3H) ppm. $^{13}$C NMR (500 MHz, CDCl$_3$): δ$_C$ = 166.68, 145.28, 139.21, 138.91, 136.43, 132.02, 131.50, 130.33, 130.18, 129.04, 128.54, 127.35, 127.14, 126.91, 126.81, 125.62, 125.29, 61.16, 14.55 ppm. HRMS (+ESI/ APCI) (mass m/z): 403.1717 [M-H]$^+$. 

**Ester deprotection**: Here we followed a previous published method by Kimizuka et. al.$^{35}$ The synthesis for **CPA** and **CPPA** is described below.

Compound **CPA**: To a solution of 176.3 mg (0.54 mmol) of compound **d1** in 54 mL 1:1 mixture of THF-MeOH, 12 mL of a KOH aqueous solution (2M) was added. The mixture was allowed to reflux for 5 h. THF was removed under reduced pressure and the resulting suspension was diluted with water. The precipitate formed by acidification with aqueous HCl (2M) was collected by filtration, washed several times with water yielding 135.3 mg (84 %) of a pale yellow solid. $^1$H
NMR (400 MHz, CDCl₃): δ_H = 8.54 (s, 1H), 8.33 (d, 2H, J=8.3 Hz), 8.06 (d, 2H, J=8.6 Hz), 7.59 (m, 4H), 7.48 (m, 2H), 7.37 (m, 2H) ppm. ¹³C NMR (500 MHz, CDCl₃): δ_C =171.49, 145.13, 136.42, 135.63, 131.77, 131.43, 130.47, 129.97, 128.62, 127.38, 126.43, 125.93, 125.39 ppm. HRMS (-ESI/ APCI) (mass m/z): 297.0925 [M-H]⁻

Compound CPPA: To a solution of 196 mg (0.49 mmol) Compound d2 in 49 mL 2:1 mixture of THF/MeOH, 12 mL of a 2M KOH aqueous solution was added. The mixture was allowed to reflux for 5 h. THF was removed under reduced pressure and the resulting suspension was diluted with water. The precipitate formed by acidification with aqueous HCl (2M) was collected by filtration, washed several times with water. The crude product was recrystallized in CHCl₃ and methanol mixture yielding 173.0 mg (95 %) of a pale yellow solid. ¹H NMR (400 MHz, CDCl₃): δ_H = 8.54 (s, 1H), 8.23 (d, 2H, J= 8.3 Hz), 8.06 (d, 2H, J=9.4Hz), 7.86 (d, 4H, J= 8.3Hz), 7.72 (d, 2H, J= 8.8Hz), 7.58 (d, 2H, J=7.9 Hz), 7.49(m, 2H), 7.38 (m, 2H) ppm. ¹³C NMR (500 MHz, CDCl₃): δ_C = 170.21, 146.25, 139.17, 139.08, 136.39, 132.10, 131.53, 131.03, 130.33, 128.98, 128.57, 127.45, 127.36, 126.97, 126.82, 125.66, 125.32 ppm. HRMS (-ESI/ APCI) (mass m/z): 374.1298 [M*]⁻

4.4 Conclusion

In conclusion, TET from CdSe NCs to bound anthracene ligands shows a strong distance dependence. The highest upconversion QY of 14.3% was attained for the transmitter ligand covalently bound closest to the NC surface. The rate of triplet energy transfer showed a logarithmic dependence on the distance between the CdSe donor and anthracene acceptor for rigid phenylene bridges, with an experimentally determined Dexter damping coefficient of 0.43±0.07 Å⁻¹. This work confirms that NC donors and molecular acceptors must be in close proximity for efficient correlated electron exchange necessary for high upconversion QYs. Work is underway in this laboratory to design ligands with a lower energy barrier and better chemical affinity for the NC surface.
4.5 Reference


Chapter 5  Complementary Lock and Key Ligand Binding.

5.1  Introduction

The design of ligands for nanocrystals is challenging because the high surface area to volume ratio modifies the bulk lattice in ways that are difficult to predict.\textsuperscript{1-2} Ligand development requires an understanding of the binding mechanism(s), as well as the nature of the available binding sites. The latter is difficult to characterize,\textsuperscript{3-5} due to the disordered nature of the organic-inorganic interface and the inherent distribution in the size and shape of colloidally synthesized nanocrystals. Ligands that are structurally complementary to the nanocrystal surface are critical in enhancing exciton delocalization within the hybrid structure. Here, we examine the consequence of subtle perturbations in the structure of ligands that serve as transmitters for triplet excitons from nanocrystal donors. Much like Fisher’s Lock and Key mechanism for the binding of substrates to an enzyme’s active site\textsuperscript{6}, only one of the transmitter ligands complements the nanocrystal surface, resulting in a high photon upconversion quantum yield that arises from efficient triplet energy transfer (TET).

Conjugated organic ligands can drastically enhance energy transfer from NC donor to acceptors. This is especially evident in a hybrid complex consisting of NC sensitizers and acene annihilators. For example, a combination of PbS nanocrystals and tetracene derivatives were shown to upconvert near-infrared to visible light efficiently under one sun conditions.\textsuperscript{7-9} There, low energy photons harvested by the NCs are funneled through surface anchored transmitters to free annihilators in solution. Two annihilators in their triplet-excited state collide, converting two low energy photons into one high-energy photon through triplet-triplet annihilation (TTA). In this hybrid system, TET from NC to transmitter molecules is the bottleneck limiting the photon upconversion quantum yield (QY).
Therefore, designing a transmitter ligand with high binding affinity for the NC donor in a geometry that facilitates orbital overlap is crucial in increasing the rate and the overall quantum efficiency of TET.

A series of isomeric bidentate bis-pyridine anthracene transmitter ligands were designed to fulfill these two requirements simultaneously (Figure 5.1(a)). The bidentate nature of these transmitters implies that the anthracene core is parallel to the NC surface if the ligand binds with the two pyridines. This increases the orbital overlap between the NC donor and acene acceptor, necessary for efficient Dexter energy transfer. In contrast, previous work solely involved monodentate transmitters that vary the conjugated core between geometries perpendicular to or parallel with the NC surface.\textsuperscript{8,10-13} Pyridine (Py) was selected to lock the anthracene core in a fixed geometry because it is widely used as a coordination ligand in organometallic complexes.\textsuperscript{14-15} In addition, Py shows a better binding affinity for the NC surface compared to the previously used carboxylic acid (COOH) group.\textsuperscript{16} Finally, both the COOH and Py groups do not significantly quench the NC exciton, or perturb NC photoluminescence, unlike thiols.\textsuperscript{17-19} This is important in minimizing losses in this TTA-based photon upconversion platform.

5.2 Result and discussion

\textbf{Figure 5.1} (a) The N-N distance between two pyridine groups within the three isomers is drawn together with the \{0001\} facet of wurtzite CdSe nanocrystals (NCs). The neighboring cation distances are labeled. (b) Absorption and emission spectra of three bis-pyridine anthracene isomers and 2.4 nm diameter CdSe
NCs. The spectra for both NC and three molecules are measured in hexane at room temperature. (c) Schematic of possible binding geometries and the energy transfer in this hybrid photon upconversion platform. The energy diagram depicts the triplet excitonic states of the CdSe NC, the anthracene transmitter and 9,10-diphenylanthracene annihilator.

As shown in Figure 5.1(a), the three transmitters differ in the connectivity of the pyridines with the anthracene core. One isomer is asymmetric, with one Py connected in the meta and the other in the ortho configuration (2,3-PyAn), while the other two isomers are linked at either the meta or ortho positions exclusively (3,3-PyAn and 2,2-PyAn respectively). The intramolecular N-N distances vary from 9.6 Å for 3,3-PyAn to 8.2 Å for 2,3-PyAn and 6.8 Å for 2,2-PyAn. The atomic scale differences between the pyridine groups provide the possibility that only one isomer might match the unique Cd²⁺-Cd²⁺ distances on NC surface. As transmitter ligands for photon upconversion, the 2,3-PyAn isomer yields the highest upconversion QY at 12.1±1.3%, followed by 3,3-PyAn (8.1±0.7%) and then 2,2-PyAn (2.5±0.7%). Transient absorption (TA) measurements reflect the trends in the steady state upconversion experiments, where the efficiency of TET is highest for 2,3-PyAn at 42.0% and lowest for 2,2-PyAn at 23.1%. From these results, we conclude the 2,3-PyAn isomer best complements the wurtzite CdSe NC by ‘locking’ to its surface. Figure 5.1 (b) shows the absorption and emission spectra for all three bis-pyridine anthracene isomers and the 2.4 nm diameter CdSe NCs used in this study. All the spectra are measured in hexane at room temperature. The absorption spectra share similar features, being governed mainly by the anthracene core. However, from 3,3-PyAn to 2,3-PyAn to 2,2-PyAn, the absorption maximum shows a 4 nm blue shift, as observed in a related series of phenylpyridine isomers.²⁰

Steady state photon upconversion measurements were conducted to evaluate the effect of binding geometry on TET. The energy diagram in Figure 5.1(c) illustrates that overall upconversion process. TET from NCs to the bound anthracene transmitter is exergonic by roughly 0.57 eV. In order for upconversion to occur, TET must occur from the CdSe NC photosensitizer to
the bound PyAn transmitter to the 9, 10-diphenylanthracene (DPA) annihilator. The latter is commonly used in organic–organic upconversion schemes because of its long-lived, low-lying triplet state and relatively high fluorescence quantum yield (90%).\textsuperscript{21} It shows the emission from the DPA annihilators when using three different PyAn ligands as transmitters. The upconversion QY in our study is defined as follows:

\[
\Phi_{\text{UC}} = 2\Phi_{\text{ref}} \frac{N_{\text{abs(sample)}}}{N_{\text{abs(ref)}}} \frac{N_{\text{em(sample)}}}{N_{\text{em(ref)}}}
\]

(5.1)

where \(\Phi_{\text{UC}}\) and \(\Phi_{\text{ref}}\) are the QY of upconversion sample and reference respectively. \(N_{\text{abs/em(sample/ref)}}\) are the photons absorbed/ emitted by the sample/ reference.

The optimized upconversion QYs were found by varying the transmitter density on the NC surface. This is achieved by changing the concentration of Py-An ligands during ligand exchange. Using optimized ligand exchange procedures\textsuperscript{12}, free unbound ligands are removed by precipitating NC-ligand complexes using acetone as bad solvent. The average number of bound anthracene ligands per CdSe NC, \(m\), was determined using UV-Vis electronic absorption spectroscopy. Under optimized conditions, \(m = 6.6\) and \(7.8\) for 2,3-PyAn and 3,3-PyAn respectively, while 2,2-PyAn has six times more average number of bound ligands per NC with \(m = 36.6\) (see Table 5.1). The isolated CdSe-PyAn complexes were mixed with 2.1 mM DPA and excited with a 532 nm cw laser with power density of 12.7 W/cm\(^2\). The upconverted DPA emission was detected at right angles. In this experiment, Rhodamine 6G in ethanol is used as the reference.

As the transmitter ligand shuttling triplet excitons from CdSe donors to DPA acceptors, 2,3-PyAn performed the best out of all three bis-pyridine anthracene isomers. The upconversion QY for 2,3-PyAn is as high as 12.1±1.3%, comparable to the 14.3% record with 9-anthracene carboxylic acid (9-ACA) as transmitter.\textsuperscript{12} The excitation density (\(I_{\text{th}}\)) denoting the transition from the quadratic to the linear regime for this 2,3-PyAn transmitter is 146.8 mW/cm\(^2\) for 68.7 \(\mu\)M of
functionalized CdSe NCs in 2.1 mM DPA in hexanes at RT. The upconversion QY for the other two isomers, \textit{3,3-PyAn} and \textit{2,2-PyAn}, are 8.1\textpm0.7\% and 2.5\textpm0.7\% respectively. Yanai and Kimizuka have shown that monodentate PyAn transmitters with just one pyridine for binding to the NC result in an upconversion QY of 1.4\%.\textsuperscript{22} This shows that at least two of the bidentate ligands here outperform their monodentate cousin, probably by increasing orbital overlap with the CdSe NC donor. Though both \textit{3,3-PyAn} and \textit{2,3-PyAn} have a similar binding affinity to wurtzite CdSe NCs, the latter has almost double the upconversion QY compared to the former. This indicates its binding geometry matches the CdSe surface lattice best and tightly locks the anthracene core to the surface. While \textit{2,2-PyAn} may bind stronger to the NCs (as indicated by a higher number of surface bound ligands), the upconversion QY is low, quite close to that for the monodentate ligand. This suggests that \textit{2,2-PyAn} may anchor to the surface in a monodentate fashion. This can also explain the higher number of surface bound ligands, as the monodentate geometry has a smaller footprint than the bidentate binding geometry, thus allowing the NC’s surface to accommodate more ligands.

**Figure 5.2.** Femtosecond transient absorption (TA) difference spectra in hexanes solution of (a) CdSe nanocrystals (NCs) only and (b) CdSe NCs with surface anchored \textit{2,3-PyAn}. CdSe NCs were selectively excited with a 505 nm 100 fs pulsed laser. Experimental delays span from 2.4 ps (orange) to 3 ns (purple). (c) Depletion of CdSe excited state absorption monitored by kinetic traces at 437 nm. The dots are the raw data from TA measurements for CdSe NCs only (red), CdSe NC/transmitter complexes with \textit{3,3-PyAn} (orange), \textit{2,2-PyAn} (bright green) and \textit{2,3-PyAn} (dirty green) ligands. The black solid lines are the fits for each complex. (d) An energy diagram depicting the physical processes during TA measurements. The solid lines denote the pump and probe wavelengths, dashed lines denote the relaxation processes on CdSe NCs and wavy lines denote the possible quenching process induced by ligand, such as triplet energy transfer (TET).
TA measurements were performed to determine the quantum efficiency of TET, $\Phi_{\text{TET(TA)}}$, and the rate of TET for each isomer. TA spectra were acquired up to 3.1 ns for each CdSe/PyAn complex with the highest upconversion QY.

**Figure 5.2** (a) and (b) are the TA difference spectra of the native CdSe NCs without ligand exchange and CdSe/\textbf{2,3-PyAn} complex respectively from 400-560 nm. The complete TA difference spectra spanning the visible wavelengths for all three CdSe/\textbf{PyAn} complexes can be found in the **Figure 5.4**. In all experiments, the pump laser power was low (220 nJ) such that no multi-exciton annihilation occurred within the nanocrystals. This was confirmed by power dependence experiments. All the experiments were conducted in the linear regime (see **Figure 5.3**).

![Figure 5.3](image)

**Figure 5.3** The intensity in the difference spectra of the CdSe nanocrystal ground state bleaching (monitored at 463 nm) versus different excitation powers plotted in a log-log scale. Multi-photon annihilation was observed under higher power where the slope changes from 1 to 0.5. Our experiments were performed in the linear region with a pump power of 220 nJ.

Transient kinetics of the excited state absorption (ESA) of CdSe NCs at 437 nm in **Figure 5.1**(c) reveals the quenching of NCs induced by ligand is fastest for the \textbf{2,3-PyAn} transmitter compared to the \textbf{3,3-PyAn} and \textbf{2,2-PyAn} isomers. The 1S state in CdSe NCs is comprised of five excitonic substates with labels $F = \pm 2$ (‘dark’), $\pm 1^L$ (‘bright’), $0^L$, $\pm 1^U$ and $0^U$ (listed in order of lowest to highest energies). Among them, $F= \pm 2$ (‘dark’) is optically forbidden and weakly emissive with up to ~s lifetimes (hence the label ‘dark’ state).\textsuperscript{23-24} As shown in **Figure 5.2**(d), the ESA at 437 nm is assigned to the transition from band edge states $F= \pm 1^L$ (‘bright’) and $F= \pm 2$ (‘dark’) to higher energy states on CdSe NCs. Possible channels depopulating the ESA involve electron trapping on
defect sites, stimulated emission, band edge recombination (i.e. \(F = \pm 1^L\) (‘bright’) \(\rightarrow\) \(1S_{3/2(h)}\)) and ‘dark’ state mediated band-edge recombination (\(F = \pm 1^L\) (‘bright’) \(\rightarrow\) \(F = \pm 2\) (‘dark’) \(\rightarrow\) \(1S_{3/2(h)}\)). A multiexponential model is used to fit the kinetics:

\[
\Delta A = \sum_{i=1}^{n} A_i \times \exp(-t/t_i)
\]

where \(\Delta A\) is the ESA for CdSe NC. \(A_i\) and \(t_i\) are the amplitude and corresponding decay constant for each component. To fit CdSe only, two time constants, \(t_1 = 1.05\) ps and \(t_2 = 34.6\) ns, are needed for a satisfactory fit of the data. Considering the time scales, the fast decay may correspond to the electron trapping to shallow defect sites on the surface or stimulated emission and the slower decay to direct band edge recombination, i.e. \(F = \pm 1^L\) (‘bright’) \(\rightarrow\) \(1S_{3/2(h)}\).\(^{25}\) The time constants extracted are in good agreement with previous reports.\(^{25}\) Analysis of the ESA of the CdSe NC photosensitizers functionalized with pyridine bidentate ligands with a triexponential fit given the longest component fixed, yields two other decay components with similar time scales of \(~40\) ps and \(~1\) ns for all three ligands. We note that the fastest decay process, \(t_{trap} \sim 40\) ps is slower compared to the pristine CdSe NCs and may correspond to charge trapping to deeper defects that were created during ligand exchange and cleaning.\(^{25-27}\) This change is observed across all CdSe/ PyAn complexes since the same functional group is involved. In the presence of a transmitter ligand, the new decay constant, \(t_q\), at \(~1\) ns time scales corresponds to an additional decay pathway introduced by surface bound PyAn transmitters, most probably due to TET from the \(F = \pm 2\) (‘dark’ state on NC) \(\rightarrow\) \(T_{1,1}\) (the triplet state on anthracene) or other decay processes induced by the disruption of the original ligand shell. The values for \(t_{trap}\) and \(t_q\) are listed in Table 5.1 for each ligand. Detailed fitting parameters can be found in

Table 5.2. As the solid line in Figure 5.2(c) shows, the fits are robust. In related work, Mongin et. al. extracted \(t_{TET}\) arising from CdSe NCs and surface bound 9-ACA from the ground state bleach (GSB) of the NCs with a stretched exponential.\(^{13}\) Here, we focus on the depleted ESA of the NCs,
because its decay kinetics is directly related to the physical process of TET to the surface bound PyAn.

**Table 5.1.** The quantum yield of photon upconversion (Φ_{UC}), and the efficiency of triplet energy transfer (TET) (from both upconversion and transient absorption (TA) spectroscopy, Φ_{TET(UC)} and Φ_{TET(TA)} respectively), and the average number of bound ligands per CdSe (m) are listed. From TA data, analysis of the kinetics of the NC donor provides the decay time constants of surface trapping and quenching on the NC induced by PyAn ligands, t_{trap} and t_{q}. Analysis of the kinetics of T_{1L→T_{nL}} on the PyAn transmitters gives the time constant and rate of TET (t_{TET} and k_{TET} respectively) from CdSe NCs.

| Parameters obtained from fitting kinetic traces of excited state absorption at 437 nm using a multiexponential decay function. Data is from transient absorption kinetics of CdSe nanocrystals with and without surfaced bound three bidentate pyridine ligands suspended in hexane (λ_{ex} = 505 nm). |
|---|---|---|---|---|---|
| CdSe | 0.073 | 1.1 | 0.93 | 34600 | NA | NA |
| CdSe/3,3-PyAn | 0.084 | 50.1 | 0.69 | 34600 | 0.16 | 1050 |
| CdSe/2,3-PyAn | 0.15 | 51.1 | 0.57 | 34600 | 0.18 | 785 |
| CdSe/2,2-PyAn | 0.11 | 31.2 | 0.64 | 34600 | 0.14 | 800 |

The kinetics of the triplet excited state formed on the PyAn transmitters can be monitored at 445 nm, an isobestic point in the TA spectra. While the T_{1L→T_{nL}} transition on anthracene is normally around 433 nm, in this work, the ESA of both the transmitter and NC overlap, resulting in an isobestic point at 445 nm. It is well known that the excited state energy levels of anthracene are very sensitive to small changes in molecular structure. Changes in TA kinetics hypsochromic to this isobestic point are dominated by ESA of the CdSe NCs, while difference spectra bathochromically shifted from 445 nm are assigned to the ESA of the triplet excited state on the anthracene ligand. The overall T_{1L→T_{nL}} transition time decay constant at ~445 nm are 800 ps, 785 ps and 1050 ps for 2,2-PyAn, 2,3-PyAn and 3,3-PyAn respectively. We notice that the decay time constant of the ESA at 437 nm of the nanocrystal photosensitizer in the CdSe/ PyAn complexes (t_{q}) is inversely correlated to the growth in the absorption of the triplet excited states on the transmitters at 445 nm (t_{TET}). This is a strong evidence that the quenching on NC induced by PyAn is due to TET. Detailed fitting procedures see section 5.3.4. Using TA spectroscopy, Mongin et. al. showed
$k_{TET}$ from CdSe NC to surface bound 9-ACA is about $2.0 \times 10^{9}$ s$^{-1}$, which is on the same order of magnitude with the value obtained in this study. Note that the average number of bound ligands, $m$, in their case is about 12. Using time-resolved photoluminescence measurements, Piland et al. found the rate of energy transfer is $1.5 \times 10^{7}$ s$^{-1}$ in a similar system, which is about two orders of magnitude smaller. This lower rate of TET is perhaps due to the lower number of surface bound transmitter ligands (~2). We have considered electron transfer from ligands to CdSe NCs as another possible energy transfer mechanism. However, the absence of peaks at 629 nm, 681 nm or 748 nm for the anthracene radical cation$^{30,31}$ or 596 nm and 732 nm for the anthracene radical anion$^{32}$, rules out the possibility of sequential charge transfer as a possible mechanism for TET for CdSe/PyAn complexes (see Figure 5.4).

**Figure 5.4** Picosecond TA difference spectra of CdSe nanocrystals (NCs) that have surface anchored (a) 2,3-PyAn (b) 3,3-PyAn, (c) 2,2-PyAn ligands in a hexane solution. The CdSe NCs were selectively excited with a 505 nm pulsed laser. Experimental delays span from 2.4 ps (orange) to 3 ns (purple). The red line indicates background scattering from the pump source before time 0.

The efficiencies of TET from NC to PyAn obtained from TA measurements, $\Phi_{TET(TA)}$, are 42.0%, 38.1% and 23.1% for 2,3-PyAn, 3,3-PyAn and 2,2-PyAn respectively, correlating directly with the upconversion QY. $\Phi_{TET(TA)}$ was extracted from the kinetics at 445 nm of the CdSe/PyAn complexes after accounting for the contribution of the NC (See section 5.3.4 for details). As expected, the 2,3-PyAn isomer with the highest upconversion QY has the highest efficiency of TET, $\Phi_{TET(TA)}$, and it quenches the CdSe NC donor the fastest (lowest $t_q$). In addition, the 2,2-PyAn transmitter with the lowest upconversion QY has the lowest $\Phi_{TET(TA)}$. However, the 2,2-PyAn
quenches the CdSe NC donor more effectively than the 3,3-PyAn isomer (Figure 5.2(c) or Table 5.1), despite the fact that it has a lower upconversion QY. This observation is consistent with reports of the super-linear dependence of NC emission on ligand functionalization, and that NC photoluminescence can only be related to ligand binding at high surface coverage, not the low density of transmitter ligands in this work.16, 33

Figure 5.5. The efficiency of TET measured by transient absorption spectroscopy, $\Phi_{\text{TET(TA)}}$ (black circle) for each bis-pyridine anthracene transmitter correlates with the corresponding photon upconversion quantum yield (red square).

Another way of calculating the quantum efficiency of TET is from the photon upconversion quantum yield obtained under cw irradiation, which is a convolution of the following factors in equation (5.3),34,35

$$
\Phi_{\text{UC}} = \Phi_{\text{TET(UC)}} \Phi_{\text{TTA}} \Phi_{\text{A}}
$$

(5.3)

where $\Phi_{\text{UC}}$, $\Phi_{\text{TET(UC)}}$, $\Phi_{\text{TTA}}$, $\Phi_{\text{A}}$ are the quantum yields of upconversion, TET, TTA for DPA and DPA fluorescence respectively. If we assume $\Phi_{\text{A}}=0.9$ and $\Phi_{\text{TTA}}=0.52$ for DPA based on previous reports,21,36 the calculated $\Phi_{\text{TET(UC)}}$ is 25.8%, 17.3% 5.3% for 2,3-PyAn, 3,3-PyAn and 2,2-PyAn respectively. Note that, in our system, $\Phi_{\text{TET(UC)}}$ can be regarded as the overall TET efficiency and is composed of two individual TET steps, i.e. TET from the NC light absorber to PyAn transmitter, $\Phi_{\text{TET(NC\rightarrow PyAn)}}$, and from PyAn transmitter to DPA annihilator, $\Phi_{\text{TET(PyAn\rightarrow DPA)}}$, as shown in equation (5.4):

$$
\Phi_{\text{TET(UC)}} = \Phi_{\text{TET(NC\rightarrow PyAn)}} \times \Phi_{\text{TET(PyAn\rightarrow DPA)}}
$$

(5.4)
Therefore, since the TA measurements only characterize the TET process from NC to surface bound transmitters, $\varphi_{TET (NC\rightarrow PyAn)}$, it makes sense that $\Phi_{TET(TA)}$ is larger than $\Phi_{TET(UC)}$ (Table 5.1). However, $\varphi_{ET(PyAn\rightarrow DPA)}$ should be close to 1 since the concentration of DPA is 2.1 mM and TTA is diffusion limited here.\(^{29,37}\) The discrepancy may arise from the fact that upconversion QY is measured in the presence of the annihilator, while $\varphi_{TET}$ from TA is in the absence of the DPA emitter. The DPA annihilator is an energy sink for the triplets transferred to the PyAn transmitters that increases the efficiency of TET.

5.3 Experimental section

5.3.1 Ligand exchanged with pyridine ligands and sample preparation

During ligand exchange experiments, 25 µL CdSe ([CdSe] = 506.7 µM) is added to certain aliquot of ligands (depending on the ratio required) dissolved in fixed volume of 100 µL CHCl₃. The final concentration of CdSe in the ligand exchanged solution is 101.3 µM. This ligand exchanged solution was stirred vigorously for 12 h when 1 mL of acetone was added to precipitate the particles. We then separated this solution into two equal volumes, spun down under exactly the same condition (7830 rpm for 10 min). Here, only one cleaning cycle was performed as we found further cleaning greatly decreases the upconversion QY of the sample prepared, probably due to the introduction of trap states on NCs or the removal of too many transmitters. One portion was used for the upconversion measurement, while the other portion was saved to characterize the average numbers of bound anthracene ligands using UV-Vis spectroscopy. For the upconversion sample, the pellet was redispersed in 2 mL of 2.1 mM DPA solution in hexane. Then the sample with optical density of 0.2~0.3 at the excitation wavelength was sealed in an air-free Teflon-capped Starna cuvette and steady state upconversion measurement was performed. For ultrafast TA experiments, we used 2 mm quartz cuvettes with optical densities of 0.4~0.5 at the excitation wavelength (505 nm). All upconversion experiments were strictly air free, with samples made
inside a glove box and kept in the dark, in airtight fluorescence cuvettes during the entire experimental period.

Two batches NC with similar size of 2.3 and 2.4 nm were synthesized using this method and used in this study. In steady state upconversion measurement, 532 nm cw laser was selected as the excitation for the 2.4 nm NC (first exciton at 514 nm) and 488 nm cw laser was used for 2.3 nm NC (first exciton at 501 nm). The optimal conditions for steady state upconversion experiment were found mainly using 2.4 nm NC and the samples for TA experiment were prepared using the 2.3 nm CdSe NC. The best upconversion QY were reproducible when using different batches NC, demonstrating the robustness of this system.

5.3.2 Measurement and calculation of average bound ligands

After cleaning, the isolated CdSe/Py complex was fully dissolved in 1 mL hexane solution. Then 500 μL of this solution was transferred into 3 mL hexane solvent in quartz cuvettes for UV-Vis absorption measurements. An example of the absorption spectra of the isolated CdSe/Py complex is shown in Figure 5.6. In order to calculate the concentration of anthracene ligands accurately, the broad absorption feature of CdSe NC has to be correctly accounted for. Therefore, the absorption spectra of CdSe NCs is first subtracted from the original data. Using the corresponding extinction coefficients for both pyridine ligands and NCs (Table 5.3), the average number of bound ligands is obtained.
Figure 5.6. The absorption spectra of isolated CdSe-PyAn complex for 2,3-PyAn (black), 2,2-PyAn (red) and 3,3-PyAn (olive) respectively. All these three samples were used for TA measurement and spectra were taken after experiment. Comparing to CdSe only (blue), there is no peak shift in CdSe-PyAn, indicating that CdSe is stable and did not degrade during the whole process, including ligand exchange, sample cleaning and TA measurement.

Table 5.3 extinction coefficients, absorption and emission maxima for all bis-pyridine anthracene ligands and two different batches of CdSe NCs.

<table>
<thead>
<tr>
<th></th>
<th>(M$^{-1}$cm$^{-1}$)*</th>
<th>Absorption maxima (or first excitonic peak for NC) (nm)</th>
<th>Emission maxima (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3,3-PyAn</td>
<td>1.82×10$^4$</td>
<td>372</td>
<td>408</td>
</tr>
<tr>
<td>2,3-PyAn</td>
<td>1.28×10$^4$</td>
<td>371</td>
<td>426</td>
</tr>
<tr>
<td>2,2-PyAn</td>
<td>1.11×10$^4$</td>
<td>369</td>
<td>429</td>
</tr>
<tr>
<td>DPA</td>
<td>1.40×10$^4$</td>
<td>372</td>
<td>404</td>
</tr>
<tr>
<td>CdSe 2.3 nm</td>
<td>6.10×10$^4$</td>
<td>501</td>
<td>510</td>
</tr>
<tr>
<td>CdSe 2.4 nm</td>
<td>5.06×10$^4$</td>
<td>516</td>
<td>524</td>
</tr>
</tbody>
</table>

*All the samples were measured in hexane solution under ambient conditions.

5.3.3 Ultrafast Transient Absorption Spectroscopy

Time-resolved experiments were performed using the Ti:Sapphire chirped pulse amplified system Spitfire-ACE (Spectra Physics, Newport Corp, 6 mJ @ 800 nm, 100 fs, 1 kHz) and Transient Absorption Spectrometer (TAS, Newport Corp.). The amplifier system is pumped using an Empower® Q-switched DPSS laser and seeded by a Mai Tai SP oscillator (90 fs, 80 MHz). The outcome of the regenerative amplifier was split in multiple paths. One beam was coupled to optical parametric amplifiers (OPA, Lightconversion TOPAS™) to generate a pump pulse at 505 nm (100 fs pulse duration). A small portion of the fundamental 800 nm beam was picked off and sent through a delay line and then focused into a 2 mm CaF$_2$ crystal to generate a white light continuum. The
generated supercontinuum is then focused onto the sample and overlapped with the pump beam. The transient spectra were detected with fiber-coupled CCD-based monochromator (Oriel, Newport).

**5.3.4 Calculation of efficiency of triplet energy transfer**

**Figure 5.7** (a) Kinetic traces at 445 nm mainly correspond to the excited state absorption of T1L→TnL transition of anthracene transmitter molecules in CdSe/PyAn complexes. The background signal from the ESA of CdSe NC only spectra (red) is subtracted from the decay traces of the CdSe/PyAn complexes (black) to obtain the ESA of the triplet formed on PyAn (blue). The CdSe NC only spectrum (red) is normalized to have the same ΔA with the CdSe/PyAn sample (black) at CdSe ground state bleaching peak (we choose 461 nm in this case) and the decay at 445 nm for CdSe NC only sample after scaling is regarded as background. (b) Fits for ESA of the PyAn triplet state are in solid lines for NC-ligands complexes with 3,3-PyAn (red), 2,3-PyAn (black) and 2,2-PyAn (blue). The fitting parameters for each CdSe-isomer complex are listed in the inset, where A1 is the amplitude, tTET is the time constant for the formation of the first triplet excited state on PyAn ligand and y0 is the fitting offset. The tTET correlates well with CdSe NC quenching induced by PyAn ligands, tQ.

The efficiency of triplet energy transfer from NC to PyAn can be determined using ultrafast TA experiments. The ΔA at 501 nm (ground state bleach) and the corresponding ground state molar extinction coefficients for the CdSe nanocrystals (ε(501nm) = 51,684 M⁻¹cm⁻¹) were used to determine the concentration of excited states generated. The concentration of PyAn in its triplet state ([³PyAn*]) formed upon triplet energy transfer from NC was determined using the maximum ΔA at 445 nm (i.e. y0 in the fitting parameters in the inset in **Figure 5.7**(b)) and its corresponding triplet molar extinction coefficient (ε = 2000 M⁻¹cm⁻¹). The triplet molar extinction coefficient was estimated from the triplet molar extinction coefficient of anthracene. Finally, the triplet state quantum efficiency is defined as the ratio of the concentration of CdSe excited states upon laser
excitation and the concentration of $[^3\text{PyAn}^*]$ generated from triplet energy transfer, as shown in equation (5.5):

$$\Phi_{TET(TA)} = \frac{\Delta \Lambda(^3\text{PyAn}^*)/\varepsilon(^3\text{PyAn}^*)}{\Delta \Lambda(CdSe^*)/\varepsilon(CdSe^*)} \quad (5.5)$$

The calculated results are listed in Table 5.1.

![Figure 5.8](image.png)

**Figure 5.8** Determination of threshold for excitation intensity.

Log–log plot of intensity of upconversion signal versus 488nm pump power density for the 2.3 nm diameter CdSe/2,3PyAn complex in 2.1 mM DPA hexanes. The transition from the quadratic (slope = 2) to linear (slope = 1) regimes is clearly shown and the threshold for excitation power density in this system is determined to be 146.8 mW/cm$^2$. The sample were prepared under optimized conditions as described above.

### 5.3.5 Synthesis of bidentate pyridine ligands

**Synthesis of 9,10-di(pyridin-3-yl)anthracene (3,3-PyAn)**

![Scheme 1](image.png)
9, 10-dibromoanthracene (500 mg, 1.5 mmol), 3-pyridineboronic acid (405 mg, 3.3 mmol) were added into a 50 mL round-bottom flask. Then 3.1 mL of 4.84 M K₂CO₃ solution, 13.6 mL toluene and 3.1 mL ethanol were added. The mixture was degassed under argon for 20 min before Pd(PPh₃)₄ (86.0 mg, 0.075 mmol) was added under high argon flow. The mixture was vigorously stirred at 80 °C for 12 hours. After cooling to room temperature, the resulting mixture was extracted with CH₂Cl₂ followed by purification by column chromatography on silica gel with 1:1 = CH₂Cl₂: ethyl acetate as the eluent to offer a light yellow solid (332.4 mg, 83.9% yield). The product was recrystallized in CH₂Cl₂ before used for ligand exchange. ¹H NMR (300 MHz, CDCl₃) δ 8.85 (d, J = 8.0 Hz, 2H), 8.75 (s, 2H), 7.85 (m, 2H), 7.76 – 7.58 (m, 6H), 7.45 – 7.36 (m, 4H) ppm. ¹³C NMR (600 MHz, CDCl₃) δ 151.9, 151.8, 149.2, 139.0, 138.9, 134.8, 133.8, 130.2, 126.6, 125.9, 123.6, 123.6 ppm. HRMS (+ESI/APCI) (mass m/z) calcd for C₂₄H₁₇N₂ [M+H]⁺ : 333.1394, Found: 333.1541.

Synthesis of 2-(10-(pyridin-3-yl)anthracen-9-yl)pyridine (2,3-PyrAn)

Boronic acid anthracene (a) was synthesized following a patent by Yoon et. al. with a 62.4% yields. ³⁸

2-(Anthracen-9-yl)pyridine (b) was synthesized by modifying a previous synthesis by the Chang group.³⁹ 9-Boronic acid anthracene (500 mg, 2.3 mmol), 2-bromopyridine (27.3 mg, 1.73 mmol), 1.36 g Na₂CO₃ was added to a 50 mL round-bottom flask. Then 17.4 mL of toluene, ethanol
and water in a ratio of 7:1.5:7 were added. Pd(PPh₃)₄ (60.0 mg, 0.052 mmol) was added after degassing under argon for 20 min. The mixture was vigorously stirred at 80 °C for 10 hours. After cooling to room temperature, the resulting mixture was extracted with CH₂Cl₂ followed by purification by column chromatography on silica gel with 40:1 = CH₂Cl₂ : ethyl acetate as the eluent to offer a pale yellow solid (622.5 mg, 81.4 % yield). ¹H NMR (400 MHz, CDCl₃) δ 8.90 (d, J=5.8 Hz, 1H), 8.53 (s, 1H), 8.03 (d, J= 8.6 Hz, 2H), 7.92 (m, 1H), 7.57-7.51 (m, 3H), 7.46-7.37 (m, 3H) ppm, 7.37-7.33 (m, 2H). The proton NMR matches the reported value.⁴⁰

2-(10-bromoanthracen-9-yl)pyridine (c) was synthesized following a previously published method with a 78.0% yield.⁴¹ Compound b (500 mg, 2.22 mol) was dissolved in 26.7 mL anhydrous dimethylformamide. 395.0 mg (23.5 mmol) N-bromosuccinimide was added and the solution were degassed under argon for 20 min. Reaction was stirred under room temperature for 4 h before quenching with water. The product was extracted with CH₂Cl₂ twice. Then the combined organic layer was washed with water 5 times. The organic layer was then dried with MgSO₄, and the solvent was removed with a rotary evaporator. The resulting crude product was purified by a flash chromatography using pure CH₂Cl₂ as the eluent. A light yellow solid was obtained (565 mg, 78.0% yield). ¹H NMR (400 MHz, CDCl₃) δ 8.90 (d, J = 5.0Hz, 1H), 8.60 (d, J = 8.9 Hz, 2H), 7.92 (m, 1H), 7.59 -7.55(m, 2H), 7.53-7.46 (m, 4H), 7.40 – 7.36 (m, 2H) ppm. The proton NMR matches the reported value.⁴²

2,3-PyAn was synthesized following a previously published method by Cho et al.⁴³ 500 mg (1.34 mmol) of compound c, 214.0 mg (1.74 mmol) 3-pyridineboronic acid and 1.48 g (10.72 mmol) K₂CO₃ were mixed in a 25 mL flask with 7.2 mL dioxane and 2.8 mL water. The solution was degassed under argon for 20 min before 54.7 mg (0.067 mmol) PdCl₂(dppf)CH₂Cl₂ was added. The mixture was vigorously stirred at 80 °C for 10 hours. After cooling to room temperature, the resulting mixture was extracted with CH₂Cl₂ followed by purification by column chromatography
Synthesis of 9,10-di(pyridin-2-yl)anthracene (2,2-PyAn)\textsuperscript{44}

9,10-Anthracenediboronic acid bis(pinacol) ester (d) was synthesized and purified according to a previously published method by Yang et. al.\textsuperscript{44}

2,2-PyAn 230.0 mg (0.543 mmol) of compound d and 195.5 mg (1.23 mmol) 2-bromopyridine were added to a 25 mL flask with 4.6 mL 2.0 M K$_2$CO$_3$ solution and 9.2 mL tetrahydrofuran. The solution was degassed under argon for 20 min before 68.5 mg (0.059mmol) Pd(PPh$_3$)$_4$ was added. The mixture was vigorously stirred at 80 °C for 10 hours. After cooling to room temperature, the resulting mixture was extracted with CH$_2$Cl$_2$ followed by purification by column chromatography on silica gel with 1:1 CH$_2$Cl$_2$: ethyl acetate and 0.5% trimethylamine as the eluent to offer a light yellow solid. The product was recrystallized in CH$_2$Cl$_2$ before used for future ligand exchange experiments (23.8% yield). $^1$H NMR (400 MHz, CDCl$_3$) δ 8.98 – 8.88 (m, 2H), 7.93 (m, 2H), 7.66 – 7.50 (m, 6H), 7.46 (m, 2H), 7.33 (m, 4H) ppm. $^{13}$C NMR (600 MHz, CDCl$_3$) δ 158.6, 150.3,
150.2, 136.6, 136.4, 129.9, 129.8, 127.1, 127.1, 126.4, 125.7, 122.6 ppm. HRMS (+ESI/APCI) (mass m/z): calcd for C_{24}H_{17}N_{2} [M+H]^+ : 333.1394, Found: 333.1524.

5.4 Conclusion

In conclusion, the binding geometry greatly affects the efficiency of TET from NC to bound ligands. The best binding geometry results in a significantly higher upconversion quantum yield, as reflected in the increased efficiency of TET given by TA measurements. This study indicates that even though the surface chemistry of NC is ill-defined and difficult to accurately predict, it is still oriented in a specified manner. Careful design of surface ligands to match the NC surface can maximize exciton delocalization between inorganic NCs and organic molecules. The use of bidentate ligands here suggests a new paradigm in the design of ligands for nanocrystal surfaces to maximize charge or energy transfer across these hybrid surface.
5.5 References


Chapter 6  Supporting information

6.1 Instrument

**General instrumentation:** Proton NMR (¹H) spectra was recorded on Varian Inova-300 MHz or 400 MHz spectrometers; carbon NMR (¹³C) spectra were recorded on a Varian Inova-500 MHz or 600 MHz spectrometer. The ¹H and ¹³C chemical shifts (δ) are reported in parts per million and the residual solvent peak was used as an internal standard at room temperature. High resolution mass spectrometry (HRMS) was recorded on an Agilent LCTOF using APCI/ESI ionization. Absorption spectra were recorded on a Jasco-V670 UV-Vis absorption spectrophotometer. Samples were prepared in the glove box with air-free cuvettes. Upconversion fluorescence spectra were recorded on an Ocean Optics Inc. JAZ spectrometer. 532 nm or 488 nm light was obtained from a Coherent Sapphire laser, with an output power of 10 mW.

**Time-resolved photoluminescence measurement:** Fluorescence lifetime data were taken using front face detection with a Hamamatsu C4334 streakscope picosecond streak camera with a time resolution of 15 ps. The 400 nm excitation pulse was generated by frequency doubling the 800 nm pulse from a 1 kHz Coherent Libra regenerative amplifier. Scattered pump light was removed by placing a 400 nm long wave pass filter and 420 nm color filter on the input lens before the streak camera. The fluorescence was detected at 54.7° relative to the pump to eliminate rotational diffusion effects. Measurements of the fluorescence decay at different laser intensities yielded similar decays, indicating that exciton-exciton annihilation did not influence the results.

**Upconversion optical set up:** upconversion fluorescence spectra were recorded at a right angle to the excitation with an Ocean Optics Inc. JAZ spectrometer. A Coherent 488 nm OBIS or 532 nm Sapphire laser with an output power of 10.0 mW and final power density is 12.7 W/ cm² was used. A 500 mm focal length lens was used to focus the laser onto the cuvette. The laser source is focused within 1 mm from the front side of the cuvette. This front corner excitation scheme limits the path
length of the excitation and emitted light to 1 mm or less inside the cuvette, which minimizes the attenuation of the excitation beam and reabsorption of the upconverted light. A lens with focal length of 30 mm was used to couple the signal from upconversion sample into the Ocean Optics Inc. fiber optics. The distance from the sample to the lens, and the lens to the optical fiber are both 60 mm (twice the focal length of the lens). The corresponding notch filter (Semrock) is used to block the scattered laser light and was inserted right before the optical fiber. The upconversion quantum yield was calculated using Rhodamine 6G as a reference with quantum yield of 0.95 in ethanol.

The upconversion quantum yield ($\Phi_{uc}$) is defined by equation (6.1) as outlined previously.  \(^1\)

$$\Phi_{uc} = 2 \times \Phi_{RG6} \times \frac{n_{DPA}^2}{n_{RG6}^2} \times \frac{[\text{Area}]_{DPA}}{[\text{Area}]_{RG6}} \times \frac{1 - 10^{-A_{RG6}}}{1 - 10^{-A_{CG6}}} \tag{6.1}$$

where $\Phi_{RG6}$ is the quantum yield of R6G, $n_{DPA}$ and $n_{RG6}$ represent the refractive indices of the solvents for the DPA upconversion sample and R6G, which are hexane and ethanol, respectively. $[\text{Area}]_{DPA}$ and $[\text{Area}]_{RG6}$ are the integrated areas of the fluorescence peaks of DPA and R6G. $A_{CG6}$ and $A_{RG6}$ stand for the absorbance of CdSe NCs and R6G at 532nm.

### 6.2 Chemicals

Chemical reagents were purchased from Aldrich Chemical Co, Strem, TCI America, Alfa Aesar or Combi-blocks and were used as received. Cadmium oxide, octadecylphosphonic acid (ODPA), trioctylphosphine oxide (TOPO) and trioctylphosphine (TOP) were purchased from Alfa Aesar, Strem and TCI America respectively. CdS NP synthesis, octadecene (ODE) and oleic acid were purchased from Aldrich Chemical and TCI America respectively. 9,10-diphenylanthracene (DPA) was purchased from TCI America. Dry and degassed toluene and dichloromethane were obtained from JC Meyer’s solvent purification system.
6.3 Synthesis of nanocrystal

Synthesis of CdS nanocrystal: 0.128 g of cadmium oxide (1.00 mmol), 3.390 g of oleic acid (12.00 mmol), and 10 g of ODE (90%) were put under vacuum and heated to 100 °C for 1 hour. Then the mixture was heated to 300°C under Ar until a colorless to pale yellow clear solution was formed. It was then cooled to a 240 °C in an Ar atmosphere. 0.016 g (0.5 mmol) of S powder dissolved in ODE was quickly injected under Ar. The reaction was heated for certain amount of time depending on the desired final sizes. For example, reaction was heated at 240 °C for 2 min to obtain CdS nanoparticle with size of 4.0 nm. Then solution was quickly cooled down to room temperature with compressed air. As-prepared CdS nanocrystals were transferred to the glove box and cleaned with acetone and toluene at least three times. The final pellet was dissolved in toluene and stored inside the glove box for future use. The concentration was determined by measuring the O.D. at the first exciton peak and calculated according to Yu et. al. In order to make sure the NC is fresh for the measurements, all the SSPL and TRPL experiments were performed within a month after the preparation of this NC. TEM of 5.0 ± 0.47 nm CdS is in Figure S1. The quantum yield of these particles is 0.19.

![Figure 6.1. TEM of CdS nanocrystals with diameter of 5nm used in experiment. Scale bar is 10 nm.](image)
**Synthesis of CdSe nanocrystal:** CdSe nanocrystals (NCs) were synthesized and purified by our previously published procedure.\(^2\) Trioctylphosphine oxide (TOPO) (3.0g), octadecylphosphonic acid (ODPA) (0.280g) and CdO (0.060g) were mixed in a 25mL three neck flask, exposed to vacuum and heated to ca. 150°C for 1 hour. Then, under Ar (g), the solution was heated to about 330°C to dissolve the CdO. At this point, 1.5 g of trioctylphosphine (TOP) was injected and the temperature was increased to 370°C. Then the Se:TOP solution (0.058g Se + 0.360g TOP) is injected. About 3 s after injection, the reaction flask was cooled down quickly with compressed air. After the synthesis, as-prepared CdSe NCs were transferred to the glove box and cleaned with methanol and toluene at least three times. The final pellet was dissolved in toluene and stored inside a argon glove box for future use. The NC concentration and diameter was determined by measuring the absorbance at the first exciton absorption maxima and calculated according to Yu et. al.\(^3\) The photoluminescence quantum yield of the NC prepared using this method was measured to be around 0.10 using Rhodamine6G (quantum yield = 0.95) as the standard. The surface of as-synthesized NC is capped with octadecylphosphonic acid ligands.

![Figure 6.2](image.png)

**Figure 6.2** Transmission electron microscopy (TEM) image of the as-synthesized ODPA-capped CdSe (2.4 nm) nanoparticles. Scale bar is 10 nm.
6.4 References

