

Charge-transfer between TCNQ and different sizes of InP quantum dots

by

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B.S., Liaoning University, 2015

A THESIS

submitted in partial fulfillment of the requirements for the degree

MASTER OF SCIENCE

Department of Chemistry
College of Arts and Sciences

KANSAS STATE UNIVERSITY
Manhattan, Kansas

2018

Approved by:

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Abstract

Quantum dots (QDs) are novel semiconductors of interest for applications because of their special tunable properties. Among the many types of QDs, InP QDs attract attention because they do not have toxic-heavy-metal elements such as Cd or Pb. Charge-transfer (CT) is important in applications of InP QDs. CT consists of two or more molecules and some of them donate electrons and others accept those electrons. An understanding of CT between QDs with tetracyanoquinodimethane (TCNQ) is important for applications of QDs in photovoltaic and photocatalytic materials. TCNQ is an organic electron acceptor and CT complexes of TCNQ exhibit metallic electric conductivity. Previous research about CT between QDs and TCNQ examined PbS and CdSe QDs, but toxic-heavy-metals limit future application of these materials. So, it is important to research CT between InP QDs and TCNQ. This thesis examines how the amount of InP QDs (QD:TCNQ ratio) and diameters of InP QDs affect the CT between InP QDs and TCNQ.

In this thesis, InP QDs are synthesized by a microwave-assisted ionic liquid (MAIL) method and InP QDs of different sizes are isolated using size-selective precipitation. Then, TCNQ-InP QD solutions are prepared with different ratios, with and without light, and with InP QDs of different sizes. These InP QDs and InP QDs-TCNQ samples are characterized using UV-Vis-NIR absorption, photoluminescence (PL), time-correlated single photon counting (TCSPC), and FT-IR spectroscopies.

In Chapter 2, the details of synthesizing InP QDs, size selection, and preparation of different TNCQ-InP QD solutions are presented. Then, factors that affect the interaction between InP QDs and TCNQ and possible reasons for these factors are discussed.

Based on calculations and experimental results, the carbon atom with the biggest amount of positive charge in TCNQ and phosphorous in InP QDs are likely the acceptor and donor, respectively. CT is affected by the amount of InP QDs in solution, and more InP QDs will reduce more TCNQ. The CT is also affected by the size of the InP QDs and enhanced by light.

Table of Contents

List of Figures	vi
List of Tables	viii
List of Symbols	ix
List of Abbreviations	x
Acknowledgments.....	xi
Chapter 1 - Introduction.....	1
Quantum Dots	1
Charge transfer.....	3
Synthesis of QDs	4
Size-selective precipitation	5
References.....	10
Chapter 2 - Charge-transfer between InP QDs and TCNQ.....	12
Introduction.....	12
Experiment.....	13
Results and Discussion	16
References.....	33
Chapter 3 - Conclusion	34

List of Figures

Figure 1.1 Spectra of InP QDs of different size from reference 3	1
Figure 1.2 The relationship between size and bandgap for QDs	2
Figure 1.3 UV-Vis spectra of InP QDs after size-selective precipitation from reference 14	6
Figure 1.4 The structure of TCNQ from reference 21	6
Figure 1.5 UV-Vis (left) and IR (right) spectra of TCNQ in different states from reference 21 and 22 respectively	7
Figure 2.1 Schematic for preparing photon induced samples	15
Figure 2.2 Absorption spectra of InP QDs from reactions at 280 °C (red) and 260 °C (blue)	17
Figure 2.3 IR spectra of TCNQ with the InP QDs synthesized at (a) 280 °C and (b) 260 °C	18
Figure 2.4 UV-Vis and emission spectra of InP QDs (synthesized at 280 °C) before size-selective precipitation	19
Figure 2.5 UV-Vis and emission spectra of InP QDs (synthesized at 280 °C) after size-selective precipitation (Diameter: 3.58 nm; 3.38 nm; 3.29 nm from top to bottom)	20
Figure 2.6 Lifetimes of three types of InP QDs (blue: $\lambda_{1st} = 483$ nm; red: $\lambda_{1st} = 491$ nm; black: $\lambda_{1st} = 513$ nm)	21
Figure 2.7 Luminescence kinetic scanning spectrum of InP QDs with TCNQ	22
Figure 2.8 Lifetimes of InP QDs and InP QD-TCNQ (black: InP QDs; red: InP QDs + TCNQ; Emission of InP QDs was monitored at 565 nm)	23
Figure 2.9 Precursors of InP QDs with TCNQ	24
Figure 2.10 Charge distribution on the surface of TCNQ	25
Figure 2.11 Simulated IR spectra of TCNQ and P^{3-} with 5 Å and 3 Å distance	25
Figure 2.12 Vibration models for different motions	26
Figure 2.13 Cartoon of InP QDs capped with palmitic acid and TCNQ in solution	27
Figure 2.14 IR spectra for TCNQ with different volume of InP QDs (peaks C and D are from reduced TCNQ, E is from pristine TCNQ)	28
Figure 2.15 InP QD-TCNQ samples in different conditions (peaks C and D are from reduced TCNQ)	29

Figure 2.16 IR spectra of different sizes of InP QDs with TCNQ (peaks C and D are from reduced TCNQ, D is from pristine TCNQ).....	30
Figure 2.17 Energy levels of TCNQ and InP	32

List of Tables

Table 2-1 Diameters of different sizes of InP QDs (synthesized at 280 °C)	19
Table 2-2 The lifetime of different InP QD samples	22

List of Symbols

$I(0)$	PL at the initial time
$I(t)$	PL at time t
τ	Lifetime
B_i	Amplitude
D	Average diameter
λ	Wavelength
m	The mass of electrons
m^*	The mass of particles
a_0	Bohr radius of the hydrogen atom
ε	The dielectric constant of the material
T_{1P}	The spin-lattice relaxation time in the rotating frame

List of Abbreviations

QDs	Quantum dots
CT	Charge transfer
InPA	Indium palmitate
TCNQ	Tetracyanoquinodimethane
FT-IR	Fourier-transform infrared spectroscopy
UV-Vis	Ultraviolet-visible
PL	Photoluminescence
NC	Nanocrystal
ODE	Octadecene
TOP	Trioctylphosphine
TOPO	Trioctylphosphine oxide
InMA	Indium with myristate ligands
FWHM	Full width at half maximum
MAIL	Microwave-assisted ionic liquid
TMS	Trimethylsilyl
MV	Methylviologen
P3HT	Poly(3-hexylthiophene-2,5-diyl
QY	Quantum yield

Acknowledgments

The thesis would not be possible to be finished without lots of help which I received from many people.

Foremost, I am very thankful to my advisor Dr. Emily McLaurin from Chemistry department of Kansas State University, for teaching me knowledge about chemistry not just about quantum dots, supporting my ideas, encouraging me, tolerating my bad English proficiency. I appreciate her to provide me the chance to start my graduate student career, work on quantum dots project and let me love quantum dots.

I appreciate all groupmates from McLaurin's Group, Dr. Nate Coleman, Mohammad S. Yazdanparast, Raghavender Siramdas, Bemnet Kebede, Stephanie Lee, Lacey Beck, Cesar Aparicio and Jacob Iverson. Without your kind help, I cannot imagine how I can start my project and adapt the life in the new environment.

I also would like to thank Dr. Stefan Bossmann, Dr. Tendai Gadzikwa and Dr. Viktor Chikan who teach me lots of knowledge about chemistry from various fields. Thanks Michael Hinton and Tingting Liu who provide lots of help to my TA work.

Besides, I would also like to thank Amila Abeysekera, Chamara Gunawardana, Chris Satterfield, Jianxiong Li, Kanchana Samarakoon, Nandini Sarkar, Yang Song, Zhen Liu who provide help in my courses, researchers, and life.

Finally, I am deeply grateful to my parent, for giving birth to me, bringing up me and supporting me to chase my dream.

Chapter 1 - Introduction

Quantum Dots

Quantum dots (QDs) are a kind of novel material which can emit light with tunable wavelength. The bandgap energy of QDs depends on their size.^{1,2} Thus, the wavelength of emission light will also be related to size, as shown in Figure 1.1 and Figure 1.2.³ Thus, QDs attract attention.

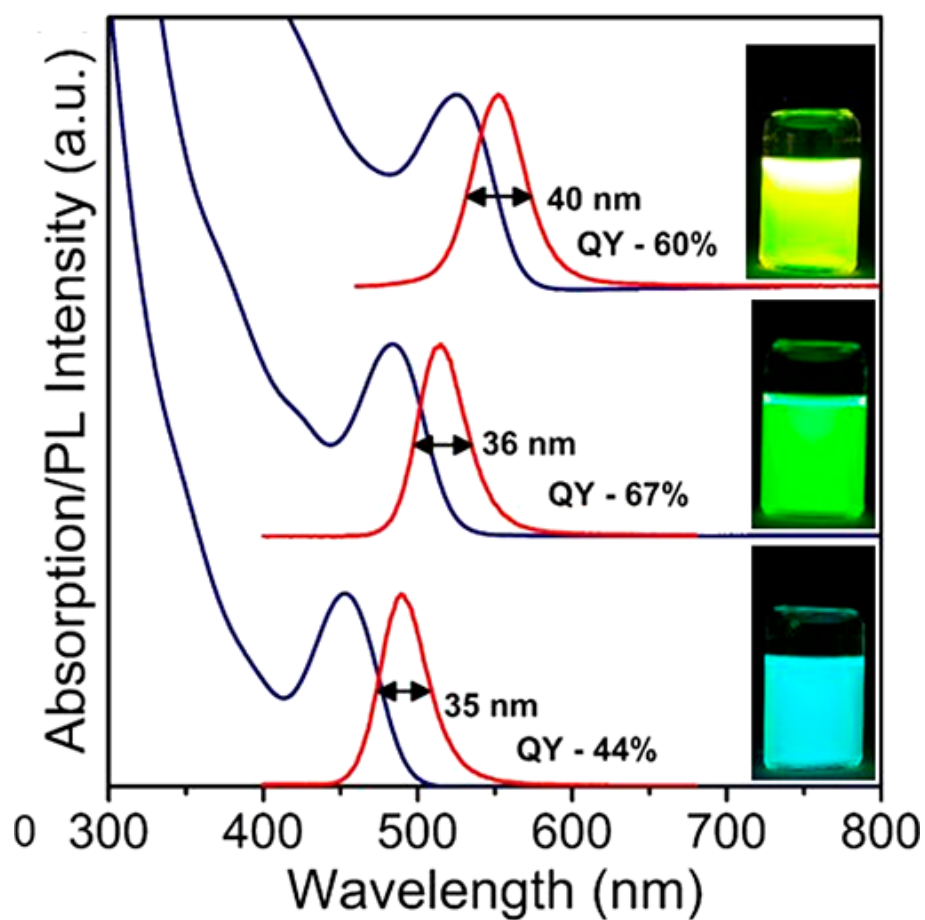


Figure 1.1 Spectra of InP QDs of different size from reference 3

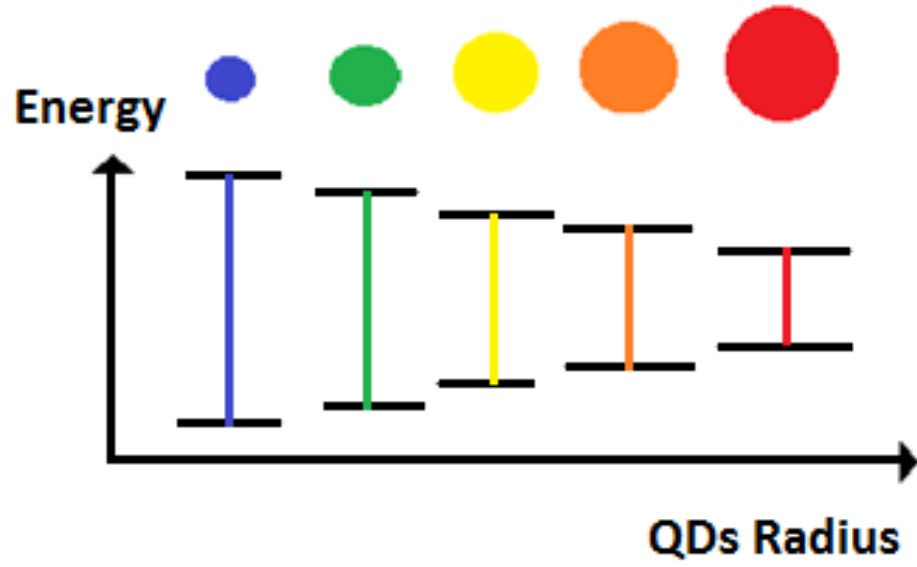


Figure 1.2 The relationship between size and bandgap for QDs

Quantum confinement results in a band energy change due to the shrinking of a bulk semiconductor.⁴ This effect occurs when the size of a nanoparticle is smaller than its Bohr radius.

$$a_B = \varepsilon \frac{m}{m^*} a_o \quad (1)$$

In eq 1, m is the mass of electrons, m^* is the mass of particles, a_o is Bohr radius of the hydrogen atom, and ε is the dielectric constant of the material. Once the size of the nanoparticles is smaller than its own Bohr radius, the band energy will be affected by quantum confinement.⁵ The movement of electrons in the crystals will be confined in specific directions. Due to the confinement, the energy band in bulk crystals will start to separate.⁶ Finally, the band gap will change to several energy levels. Thus, its electrons transition energy will increase which will cause a blue shift in the absorption spectra. For example, the band gap of bulk InP

semiconductor is 1.35 eV, but for InP QDs with 2.5 nm diameter, the band gap is approximately 2.47 eV.⁷ Compared with bulk InP, it is a large blue-shift.

Based on the number of confinement directions, nanocrystals (NCs) are divided into three types: 1) Two-dimensional objects; 2) One-dimensional objects; 3) Zero-dimensional objects.⁸ For two-dimensional objects, electron movement is limited in just one axis. For one-dimensional objects, the number will be two. For zero-dimensional objects, it has limitations in all three axes.⁹ Based on this, QDs are zero-dimensional and spherical with radii smaller than its Bohr radius.¹⁰

Charge transfer

Charge transfer (CT) consists of two or more molecules and some of the molecules will be donors who are responsible for donating electrons, and some them will work as acceptors which will accept electrons.¹¹ If the LUMO of acceptors matches with HOMO of donors, the process may happen. The process is very useful for solar cells, which can improve the efficiency of energy conversion of solar cells. However, the process is not well understood.

For CT of QDs, the types of CT can be classified based on the type of acceptor: 1) QDs—Inorganic compounds; 2) QDs—Organic compounds; 3) QDs—QDs. At present, many pairs of QDs and organic compounds have been studied for CT. In these pairs, QDs can be either the donor or acceptor.

Synthesis of QDs

QDs are a kind of NC, and their synthesis follows the principles of nucleation and growth.¹² Once the concentration of monomers is over the critical value, nucleation starts.¹³ To be a NC, the minimum size of nucleation is needed for a given condition and a given reaction.

The Nozik group from the University of Colorado Boulder successfully synthesized InP QDs using InCl_3 , $\text{Na}_2\text{C}_2\text{O}_4$, CH_3CN , $\text{P}(\text{SiMe}_3)_3$ and TOPO/TOP mixture.¹⁴ However, the process required more than three days. The Peng group used octadecene (ODE) as solvent, alkyl indium as the indium precursor and $\text{P}(\text{SiMe}_3)_3$ as the phosphorus precursor.¹⁵ In this method, ODE was used as the solvent, which was cheaper and lower-toxicity than TOPO/TOP. By this method, the synthesis could be done in several hours. The properties of InP QDs were very good, the fwhm of the absorption peak of InP QDs from this method was about 0.22 eV, which was narrower than InP QDs from the Nozik group whose fwhm was more than 0.32 eV. However, there is still a deficiency in the method, the temperature for growth of InP QDs is 270 °C.¹⁵ At this temperature, InMA_3 is easy to decompose to In_2O_3 which will make it difficult to react indium with $\text{P}(\text{SiMe}_3)_3$.¹⁶ The Strouse group pioneered microwave reactor methodologies to synthesize InGaP, InP, and CdSe QDs.¹⁶ Using this method, the rate of formation of QDs can be increased further and the material quality and monodispersity of QDs can also be enhanced. By further *in situ* active ion etching, the quantum yield (QY) can reach 47%.¹⁷⁻¹⁸ The McLaurin group adapted this method to synthesize InP QDs successfully.¹⁹ In this microwave-assisted ionic-liquid (MAIL) method, the time to get InP QDs from InP precursor is just 15 mins. Compared with three days from the Nozik group, and several hours from the Peng group, this method is efficient.

To improve the quality of InP QDs from synthesis, much research about the synthesis mechanism of InP QDs has been done. The Bawendi group found that most of the precursor of

phosphorous was depleted in the nucleation step of the synthesis of InP QDs, so there was not enough P for InP QDs to grow.¹² Then, the growth of InP QDs depended on ripening of non-molecular InP QDs species. This might be the reason why InP QDs did not have good size distribution.¹³ The results from Cossairt group showed that magic-sized clusters (MSCs) were the key intermediates in the synthesis of InP QDs. InP QDs form from the heterogeneous growth of MSCs.²⁰ Unfortunately, the mechanism of synthesis of InP QDs is still not clear. Many groups are still working on making it clear.

Size-selective precipitation

No matter which synthesis is used to prepare InP QDs, the size distribution of InP QDs is not very good. The fwhm of absorption peak of InP QDs will be more than 50 nm.¹⁴ Size-selective precipitation is a useful method to get InP QDs with narrow size-distribution and isolate InP QDs of different size. The method was used for InP QDs by the Nozik group and the resulting UV-Vis absorption spectra are shown in Figure 1.3.¹⁴ Flocculation of particles in solution needs to overcome the energetic barrier. Particles with different size have a different energetic barrier. If additional solvent is added to the InP QD solution, the energetic barrier of the particles will decrease, especially for the largest particles. The largest particles will flocculate first, then by centrifugation the largest particles are separated. By repeating this process, InP QDs of different size can be separated.

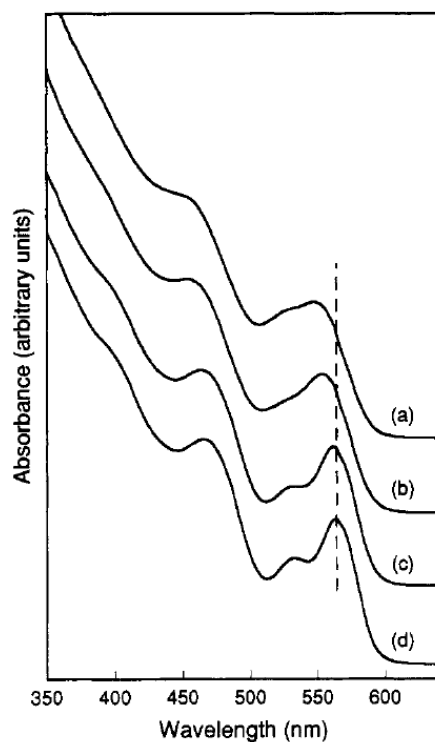


Figure 1.3 UV-Vis spectra of InP QDs after size-selective precipitation from reference 14

TCNQ is an organic electron acceptor (shown in Figure 1.4) with many advantages. TCNQ is a strong π -acid, so it easily accepts electrons.²¹ CT complexes of TCNQ exhibit metallic electric conductivity.²¹ Thus, TCNQ complexes can transfer electrons efficiently, which will help to improve the efficiency of solar cells. In addition, TCNQ in different states has distinct absorption features in the UV-Vis-NIR and mid-IR (Figure 1.5), which make the characterization of CT complexes of TCNQ easy.^{21,22}

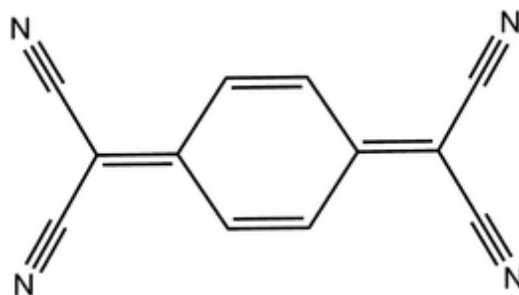


Figure 1.4 The structure of TCNQ from reference 21

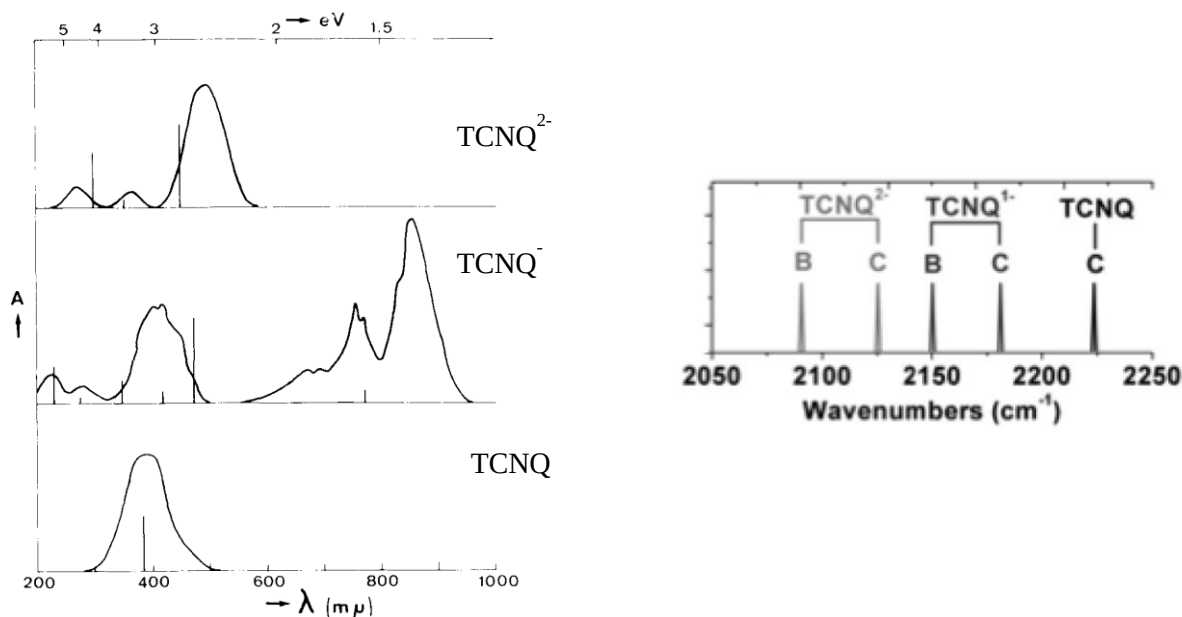


Figure 1.5 UV-Vis (left) and IR (right) spectra of TCNQ in different states from reference 21 and 22 respectively

The Weiss group has done some research about CT between QDs and TCNQ. The Weiss group studied CT between PbS and TCNQ.²⁴ The absorption of PbS, PbS-TCNQ and TCNQ reduced by voltage were measured. After TCNQ was reduced, the reduced TCNQ peaks appear in the UV-Vis-NIR spectrum. In the PbS QDs UV-Vis-NIR spectrum, these peaks were not observed. After PbS QDs were added to the TCNQ solution, reduced TCNQ peaks appeared again. The IR spectra results agree the result from UV-Vis-NIR that TCNQ is reduced. After PbS QDs were added to the TCNQ solution, peaks from reduced TCNQ appeared. The intensity of these peaks was related the ratio of TCNQ and PbS.

Then, precursors of PbS were mixed with TCNQ. In the IR spectra of Pb-oleate with TCNQ, there was only the peak from pristine TCNQ. In the UV-Vis-NIR spectra of Pb-oleate with TCNQ, there were no new peak as well, but in the UV-Vis-NIR spectra of TMS sulfide

with TCNQ, peaks from reduced TCNQ could be observed. It means that TMS sulfide reduces TCNQ. So, in PbS-TCNQ solution, TCNQ was reduced by sulfur in PbS.

After TCNQ was added to PbS QDs, some paramagnetic centers formed on the surface of PbS QDs based on the NMR spectrum. The intensity of $1/T_{1\rho}$ matched the intensity of the peak of reduced TCNQ in the IR spectra indicating all of the paramagnetic centers were from TCNQ. These results showed that TCNQ accepted electrons from PbS. Finally, the number of TCNQ anions per QDs was calculated.

After CdSe was added to TCNQ, the reduced TCNQ peak appeared in the UV-Vis-NIR spectra. The same peak appeared in the UV-Vis-NIR spectra of TOPSe with TCNQ, which means that TCNQ got electrons from Se in CdSe.²³ The IR spectra of TCNQ and mixtures of CdSe and TCNQ were measured and the results were similar to results from the UV-Vis-NIR spectra suggesting CdSe reduces TCNQ. The IR spectra were simulated for TCNQ and CdSe at different distances. Based on the simulated IR spectra, the distance of TCNQ and CdSe in solution could be estimated.²³

However, in these studies, both PbS and CdSe contain toxic heavy-metal elements. This limits the application of these materials. InP QDs are a good candidate to substitute PbS and CdSe because there is not a toxic-heavy-metal element.

Some groups did research about CT between InP QDs with some organic compounds.^{25,26} The Lian group researched CT between InP QDs and Methylviologen (MV).²⁵ In the research, InP QDs and InP QDs shelled with CdS were used. InP QDs and InP QD-MV samples were measured using transient absorption spectroscopy. After MV was added to InP solution, the decay time of InP QDs excited state became shorter. The result showed that CT occurred between InP QDs and MV.

Then, InP shelled with CdS and InP shelled with CdS mixed with MV samples were measured using transient absorption spectroscopy. After MV was added to InP QDs shelled with CdS, the decay time of the InP QDs excited state became shorter. This meant that CT occurred between InP QDs shelled with CdS and MV. In addition to this result, another interesting phenomenon was observed. Despite the decay of the InP QDs excited state decreasing after MV was added, the effect for InP QDs shelled with CdS was smaller than the effect for InP QDs without a shell. The result showed that CT was related to the surface of the InP QDs.

The Soci group researched CT between InP QDs and P3HT.²⁶ In their research, InP QDs with diameters of 2.5 nm and 4.5 nm were used. They characterized the transient absorption spectra of the InP QDs. Then, InP QDs with different sizes were added to P3HT and the transient absorption spectra of these samples were measured. After the InP (2.5 nm) were added into the P3HT solution, the decay time of excited state of P3HT became shorter, indicating electron transfer from InP QDs (2.5 nm) to P3HT is insufficient. After InP QDs (4.5 nm) were added to the P3HT solution, the decay time of excited state of P3HT became longer which means some long-lived charges formed. These results showed that the CT was related to the size of InP QDs.

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Chapter 2 - Charge-transfer between InP QDs and TCNQ

Introduction

Although the charge-transfer (CT) between InP QDs and TCNQ is very important, there is no research about the process. Based on previous research from other groups about CT between QDs and organic compounds¹⁻⁴, some hypotheses for the CT between InP QDs and TCNQ are: 1) CT between InP QDs and TCNQ is enhanced by light; 2) smaller InP QDs have more ability to CT with TCNQ; 3) CT will increase as the amount of InP QDs in solution increases; 4) poor surfaces of InP QDs reduce the CT between InP QDs and TCNQ. To get evidence for these hypotheses, there are some challenges: 1) TCNQ does not fluoresce so CT cannot be observed by monitoring the emission of TCNQ; 2) the size distribution of InP QDs is large and to research if the CT is size-dependant having InP QDs with small size distribution is necessary; 3) InP QD emission is strongly quenched after mixing with TCNQ so CT is difficult to observe by monitoring the decay of the InP emission.

We synthesized InP QDs by a microwave-assisted ionic-liquid (MAIL) method from the McLaurin group.⁵ Then, InP QDs of different sizes were separated using size-selective precipitation. The UV-Vis results show that InP QDs of different size were obtained. Then, TCNQ-InP solutions were prepared in different ratios and with and without light. InP QDs of different size were also mixed with TCNQ. The UV-Vis-NIR abs, photoluminescence (PL), and FT-IR results show that the CT can be affected by the amount of InP QDs, light, and size of InP QDs.

Experiment

Materials. All the chemicals used are commercially available and were used without further purification; Indium acetate ($\text{In}(\text{OAc})_3$, 99.99%-In) and *tris*(trimethylsilyl)phosphine ($\text{P}(\text{TMS})_3$, min. 98% (10 wt% in hexanes)) from Strem Chemicals, 1-Butyl-3-methylimidazolium tetrafluoroborate (BMIM BF_4 , $\geq 98\%$) and 7,7,8,8-Tetracyanoquinodimethane (TCNQ, 98%), Chloroform-D (99.8%) from Cambridge Isotope Laboratories, Chloroform (Ethanol as Preservative/Certified ACS) from Fisher Chemical, palmitic acid (PA, $\geq 99\%$), Decane(anhydrous, $\geq 99\%$) and Acetone (for HPLC, $\geq 99.9\%$) from Sigma-Aldrich.

Indium Palmitate (InPA). A two-necked 100 mL round-bottom flask was used as the reaction vessel. One neck was attached to Schlenk line with a condenser; the other one was sealed by a septum. The flask was evacuated and then, 0.605 g, PA was added under N_2 overpressure. The system was heated in an oil bath at 105 °C for 5-10 mins. After cooling back to room temperature, the flask was filled with N_2 and 0.207 g $\text{In}(\text{OAc})_3$ was added. After the system was evacuated again, the flask was heated in an oil bath at 150 °C until pressure in the flask went back to baseline. All of the solid that formed on the wall of the flask was melted by heat gun. After cooling InPA back to room temperature, the setup was detached and moved to the glove box. Then, 47 mL decane was added and the solution was left stirring for 24 h.

InP Precursor. $(\text{TMS})_3\text{P}$ (10 wt% in hexanes) (1.15mL) was dispersed in 3 mL decane and transferred to the InPA RB flask slowly. After the color of the solution changed to orange, the solution was transferred to a Schlenk tube and connected to a Schlenk line. The solution was then heated in an oil bath at 65 °C until the solution was clear, then the tube was moved back to the glovebox.

Microwave-Assisted InP QDs Synthesis. In the glovebox, 3 mL InP precursor and 78 μL BMIm BF_4 were combined in a 10 mL glass microwave vessel. The vessel was capped, moved out of the glovebox, and put into the microwave. The mixture solution was heated to 280 $^\circ\text{C}$ using the heat as fast as possible method at 800 W set-power for 15 mins and then cooled to 55 $^\circ\text{C}$ using compressed air.

The InP QD solution was transferred to a centrifuge tube and 2 mL acetone was added and was oscillated. The solution was cloudy. The solution was centrifuged to work at 5400 RPM for 5 mins. After 5 mins, there was some InP QD precipitate on the wall of the centrifuge tube, and the solution was orange and clear. The clear solution was transferred to a new centrifuge tube and InP QD precipitate was resuspended in chloroform. Then 2 mL acetone was added to the new centrifuge tube and the above procedures were repeated until the solution in the initial centrifuge tube was colorless.

TCNQ solution. InP QD UV-Vis spectra were measured and used to calculate their concentration by the formula in D.V. Talapin Ph.D. thesis.¹ Then, the weight of TCNQ required for InP QD:TCNQ molar ratios of 1:450 and 1:800 were calculated. The TCNQ was weighed accurately and dissolved in chloroform. The solutions were stored in darkness and kept for no more than two days.

Photon-induced samples. To keep samples excited by UV light continuously, a UV lamp was used. InP QDs and TCNQ were mixed in the same ratio. Two sets of samples were kept in amber vials in the dark. Two sets of samples were kept in glass vials with a 365 nm UV lamp for 24 h as shown in Figure 2.1.

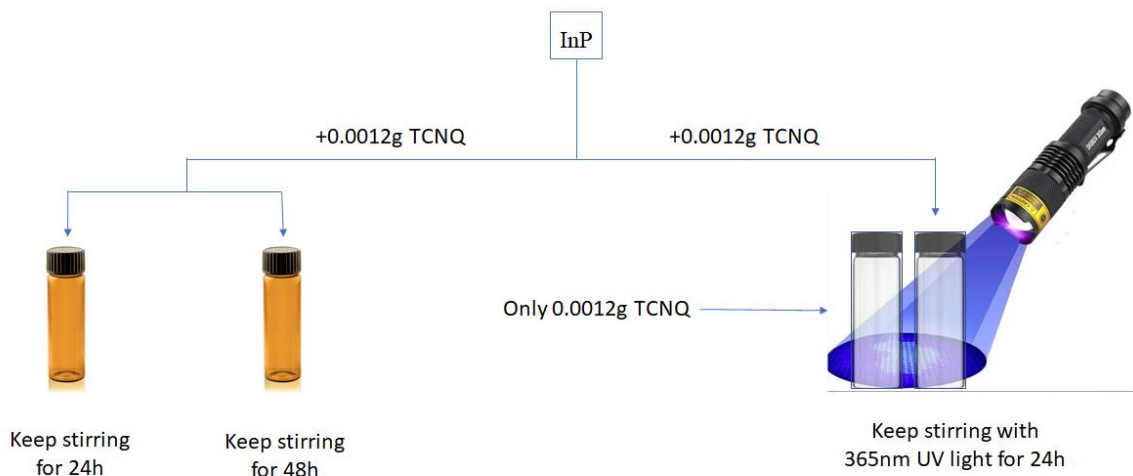


Figure 2.1 Schematic for preparing photon induced samples

Physical Measurements. Microwave syntheses were done using an Anton Paar Monowave 300 Microwave Reactor and an IR sensor (for temperature). UV-Vis absorption spectra were recorded with an Agilent Cary 5000 UV-Vis-NIR spectrophotometer. FT-IR spectra were recorded with a Thermo Nicolet NEXUS 870 FT-IR. PL spectra were recorded using a PTI Quanta Master 400 fluorometer. Lifetime and luminescence kinetic scanning were recorded by Edinburgh Instruments Lifespec II. The lifetime data were fitted by the exponential equation.

$$I(t) = I(0) \sum_{i=1}^n B_i e^{-\frac{t}{\tau_i}}$$

$I(0)$ and $I(t)$ represent the PL at the initial time and time t . τ represents the lifetime of a sample in a special emission wavelength by one channel. B_i is the amplitude of each lifetime. The final lifetime is the average of these lifetimes. $\bar{\tau}$ represent the average lifetime of the sample.

$$\bar{\tau} = \frac{\sum_{i=1}^n B_i \tau_i^2}{\sum_{i=1}^n B_i \tau_i}$$

Results and Discussion

InP QDs were synthesized by a microwave-assisted ionic-liquid (MAIL) from the McLaurin group.⁵ Then UV-Vis-NIR absorption spectra show that InP QDs of different sizes were obtained after size-selective precipitation. The lifetime and luminescence kinetic scanning result suggest the occurrence of CT between TCNQ and InP QDs. The IR spectra shows that light can enhance the CT between TCNQ and InP QDs. The more InP QDs, the more TCNQ is reduced. The smaller InP QDs have better ability to reduce TCNQ. The lifetime results show that InP QDs of different sizes have different surfaces.

To research if the CT between TCNQ and InP QDs is size-dependant, InP QDs of different sizes are required. The simplest method to obtain InP QDs of different diameters is to change the reaction temperature using the established microwave-assisted ionic-liquid (MAIL) method.⁵ InP QDs were prepared as described in the experimental section. Briefly, two microwave vessels containing 3 mL InP precursor and 78 μ L BMIm BF₄ were prepared. These vessels were capped, moved out of the glovebox, and put into the microwave. The mixtures were heated to 280 °C or 260 °C using the heat as fast as possible method at 800 W set-power for 15 mins and then cooled to 55 °C using compressed air. The absorption spectra of the two samples is shown in Figure 2.2.

After these InP QDs were mixed with TCNQ solution, the TCNQ peaks change in the IR spectrum. For the InP QD (280 °C)-TCNQ sample, there are peaks at 2181 cm^{-1} and 2202 cm^{-1} from reduced TCNQ and a peak at 2225 cm^{-1} from pristine TCNQ. In the IR spectrum of InP QD (260 °C)-TCNQ, the positions of the peaks from reduced TCNQ are at 2190 cm^{-1} and 2204 cm^{-1} as shown in Figure 2.3. The position of peaks from QDs-TCNQ complex in both of samples in IR spectra is different. So another method is needed to obtain monodisperse InP QDs of

different sizes. Size-selective precipitation is a good method for obtaining a subset of monodisperse QDs.

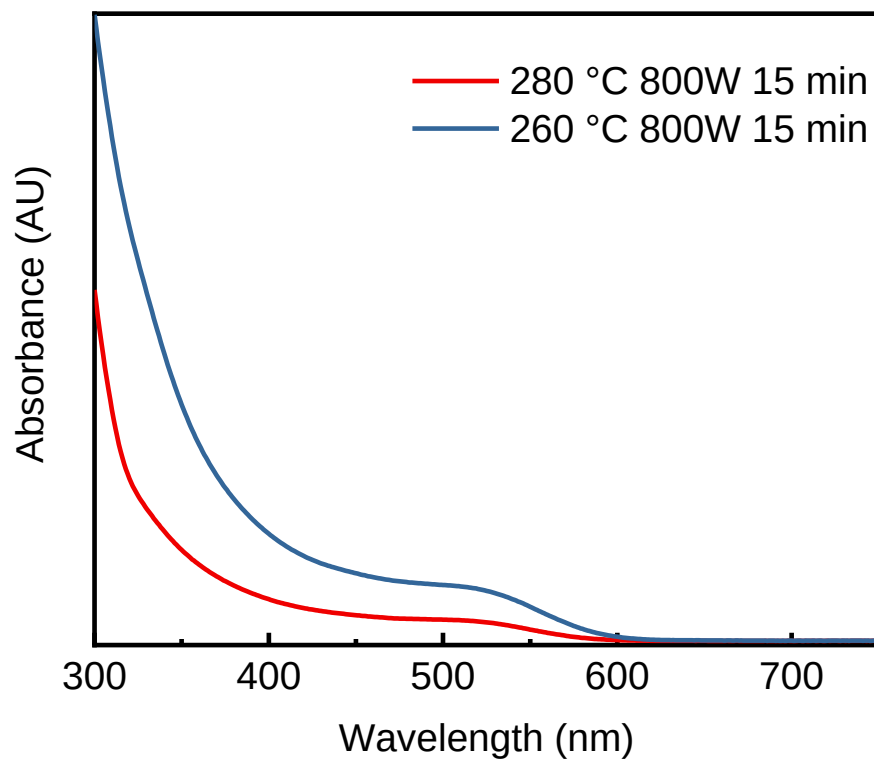


Figure 2.2 Absorption spectra of InP QDs from reactions at 280 °C (red) and 260 °C (blue)

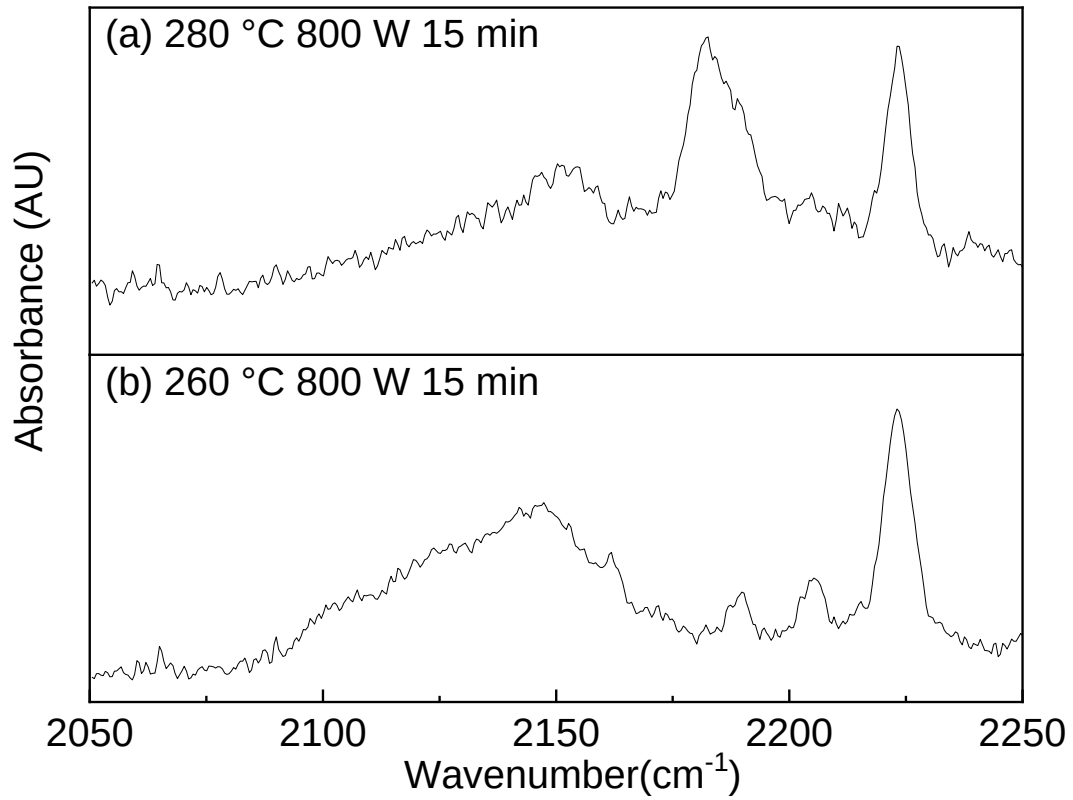


Figure 2.3 IR spectra of TCNQ with the InP QDs synthesized at (a) 280 °C and (b) 260 °C

Figure 2.4 shows the UV-Vis and emission spectra of the InP QDs synthesized at 280 °C before size-selective precipitation. Initially, the absorption peak of InP QDs is very broad with about 0.276 eV fwhm. After size-selective precipitation, three sizes of InP QDs are isolated (Figure 2.5). The fwhms are narrowed to approximately 0.14 eV (Table 2-1.).

Based on the UV-Vis spectra of InP QDs, the average size of InP QDs particles can be estimated using equation from the Ph.D. thesis of Talapin, D. V.⁶

$$D = (-3.7707 * 10^{-12})\lambda^5 + (1.0262 * 10^{-8})\lambda^4 - (1.0781 * 10^{-5})\lambda^3 + (5.4550 * 10^{-3})\lambda^2 - (1.3122)\lambda + 199.9$$

D represents the average diameter of InP QDs and λ is the 1st absorption feature the QDs.

Table 2-1 Diameters of different sizes of InP QDs (synthesized at 280 °C)

Number	Absorption of InP QDs (nm)	Average diameter of InP QDs (nm)
1	513	3.58
2	491	3.38
3	491	3.38
4	483	3.29

Because the amount of # 4 InP QDs is far less than # 1 and # 2, prepare a solution with TCNQ with 1:450 ratio, the weight of TCNQ is very small. It is hard to weight the TCNQ and prepare TCNQ solution accurately. So I increase the ratio to 1:800. Thus, I choose InP QDs of 3.38 nm diameter to work in both ratios.

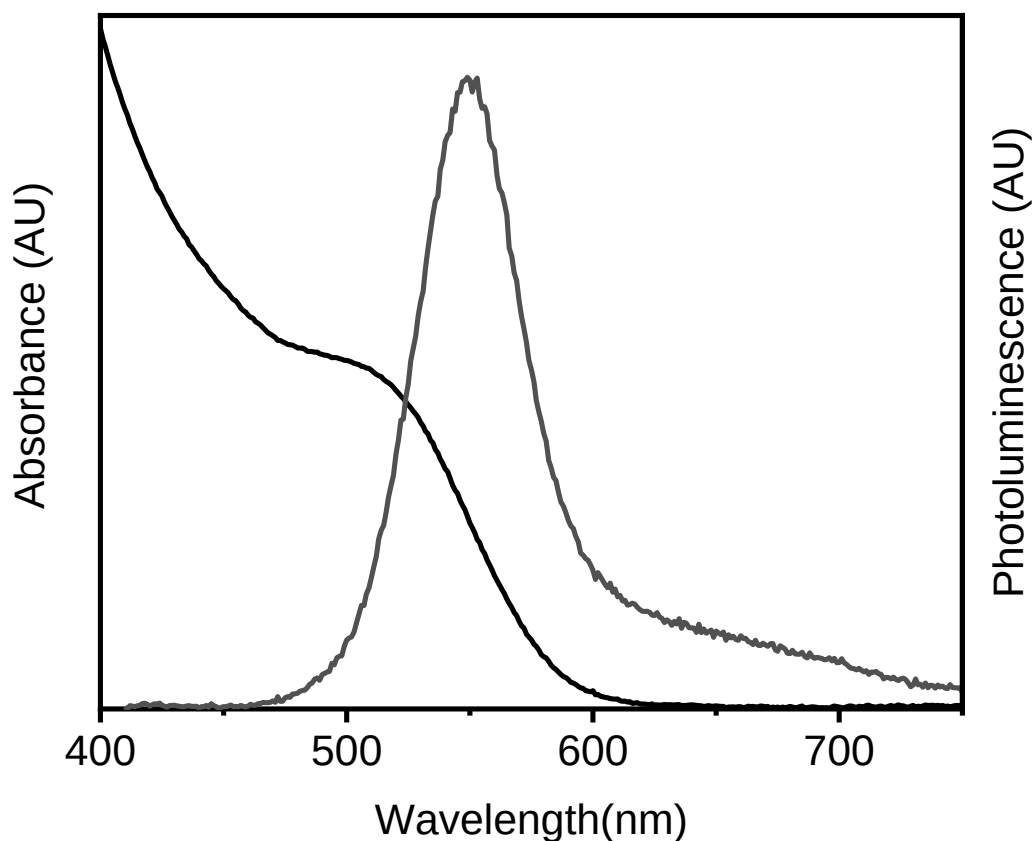


Figure 2.4 UV-Vis and emission spectra of InP QDs (synthesized at 280 °C) before size-selective precipitation

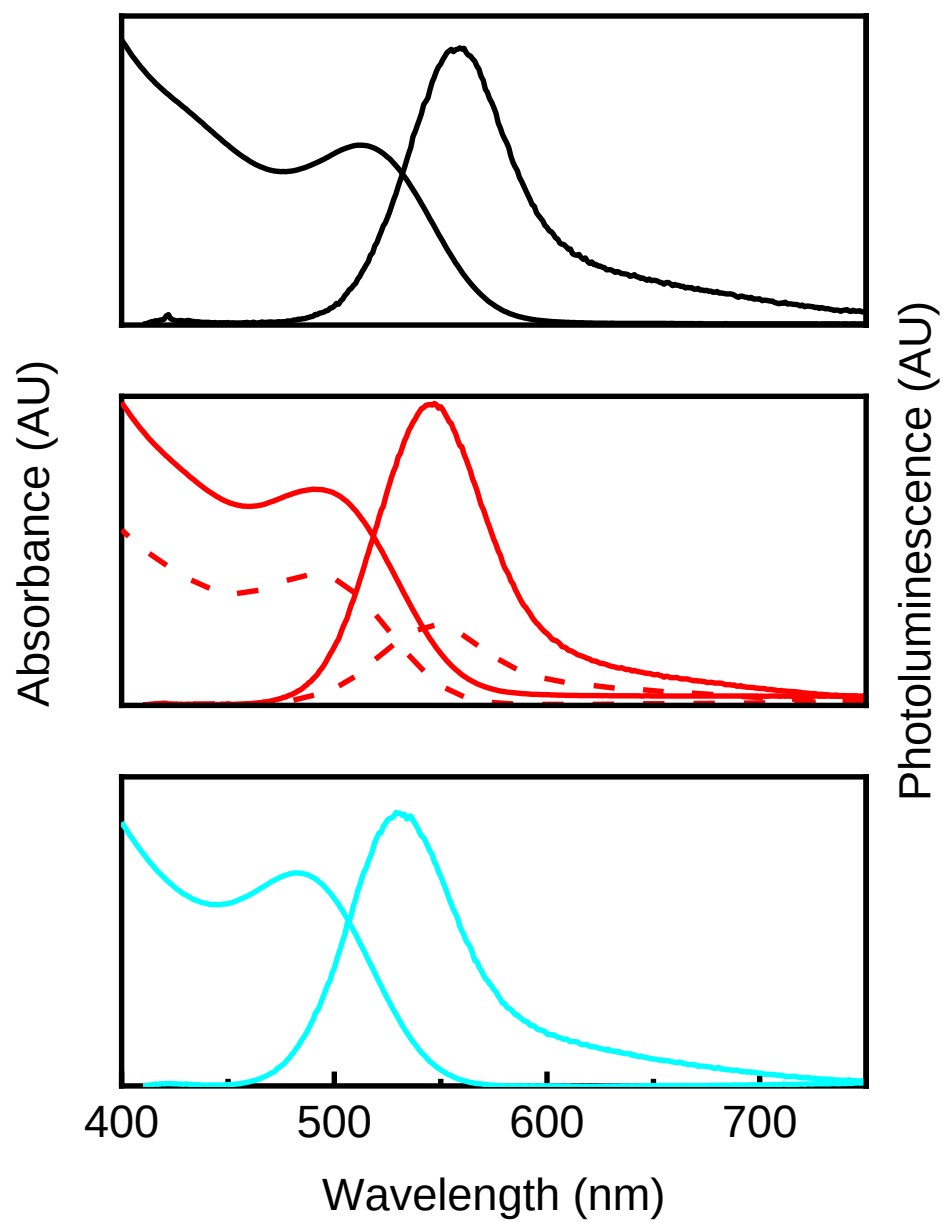


Figure 2.5 UV-Vis and emission spectra of InP QDs (synthesized at 280 °C) after size-selective precipitation
(Diameter: 3.58 nm; 3.38 nm; 3.29 nm from top to bottom)

The luminescence of the InP QDs of different sizes was measured using TCSPC spectroscopy. The data is shown in Figure 2.6. The results are fitted to a biexponential. QDs may have two or more decay times, because of different channels for electrons and holes to recombine. QDs usually have two decay times, one is shorter and the other is longer. The shorter lifetimes is from the core emission of QDs, and the longer lifetime is from the surface emission of QDs.⁷ The fitted results are shown in Table 2-2. and τ_1 is assigned to the core emission, and τ_2 to surface emission. The InP QDs of different size have similar τ_1 and τ_2 , indicating they have similar emission.

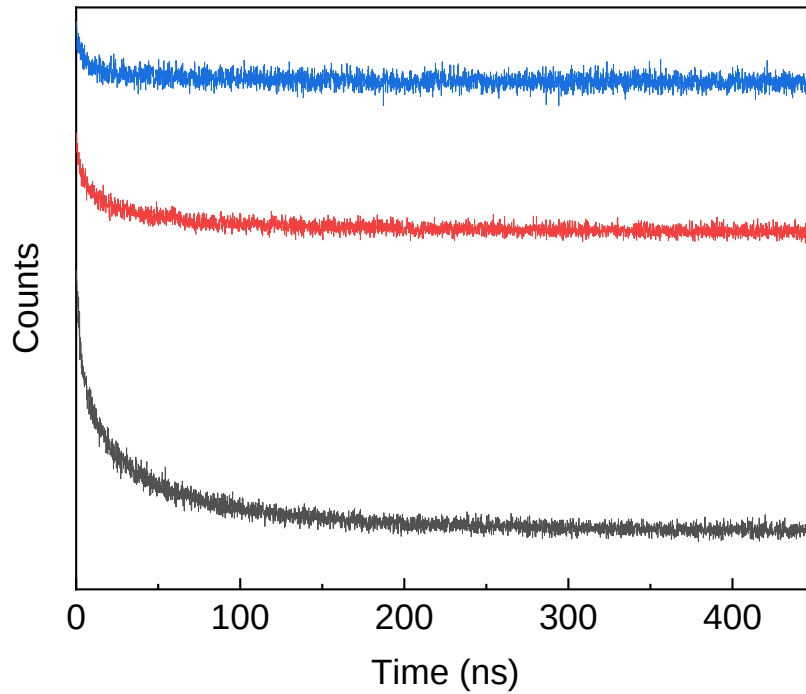


Figure 2.6 Lifetimes of three types of InP QDs (blue: $\lambda_{1st} = 483$ nm; red: $\lambda_{1st} = 491$ nm; black: $\lambda_{1st} = 513$ nm)

Table 2-2 The lifetime of different InP QD samples

1St Abs of InP QDs	τ_1 (ns)	B_1	τ_2 (ns)	B_2	τ (ns)
513 nm	6.60 $\pm$ 0.20	0.039 $\pm$ 0.001	59.79 $\pm$ 0.72	0.028 $\pm$ 0.000	52.7
491 nm	6.20 $\pm$ 0.38	0.015 $\pm$ 0.001	61.72 $\pm$ 2.03	0.009 $\pm$ 0.000	53.8
483 nm	6.02 $\pm$ 0.40	0.009 $\pm$ 0.001	65.96 $\pm$ 6.32	0.003 $\pm$ 0.000	53.1

At the initial time, there was just InP QDs in the solution. Then, at 1000s and 2600s, TCNQ solution was added. After TCNQ was added, the number of photons emitted by the InP QDs decreased (Figure 2.7). This means that the InP QDs are not able to emit the same number of photons possibly because some of the electrons are captured by TCNQ.

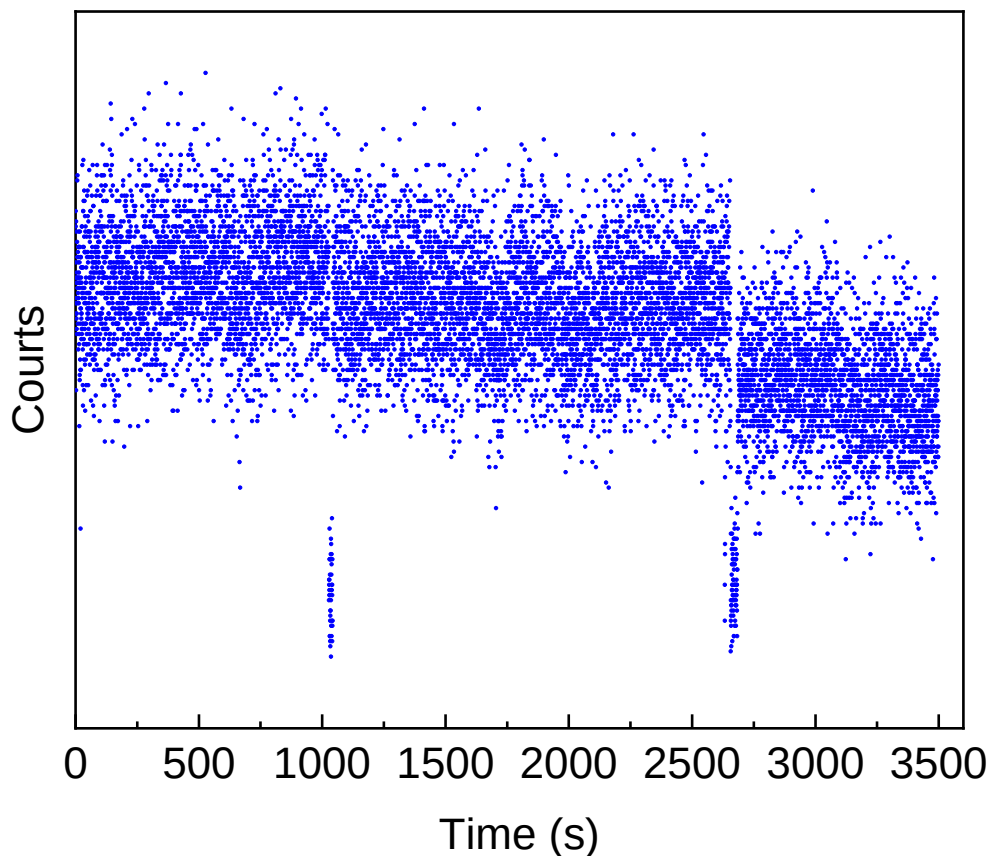


Figure 2.7 Luminescence kinetic scanning spectrum of InP QDs with TCNQ

Lifetime results for the quenched and unquenched samples are fitted to a biexponential (Figure 2.8). The average lifetime of InP QDs is 50.1 ns, and InP QDs in the TCNQ-InP QD mixture samples is just 0.855 ns indicating TCNQ quenches the excited state of the InP QDs.

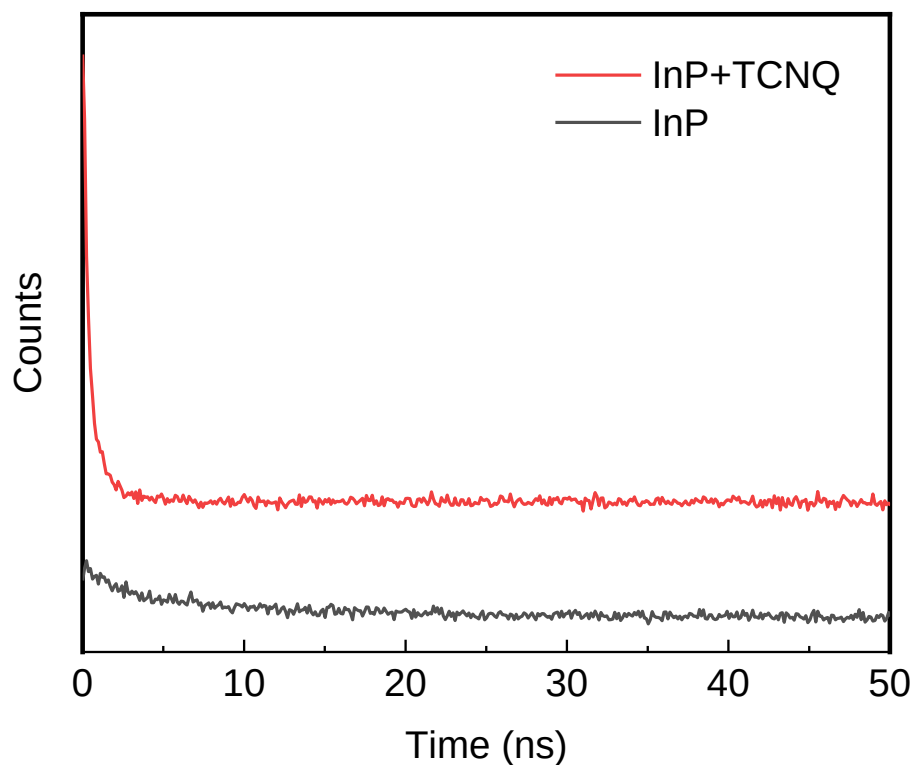


Figure 2.8 Lifetimes of InP QDs and InP QD-TCNQ (black: InP QDs; red: InP QDs + TCNQ; Emission of InP QDs was monitored at 565 nm)

For CT, it is important to determine who is the donor and who is the acceptor because it is important to know where electrons are from and where electrons will go. Thus, precursors of InP were mixed with TCNQ. The ratio of $(\text{TMS})_3\text{P}$ to TCNQ is 488:1 and $\text{In}(\text{OAc})_3$: TCNQ is 120:1.

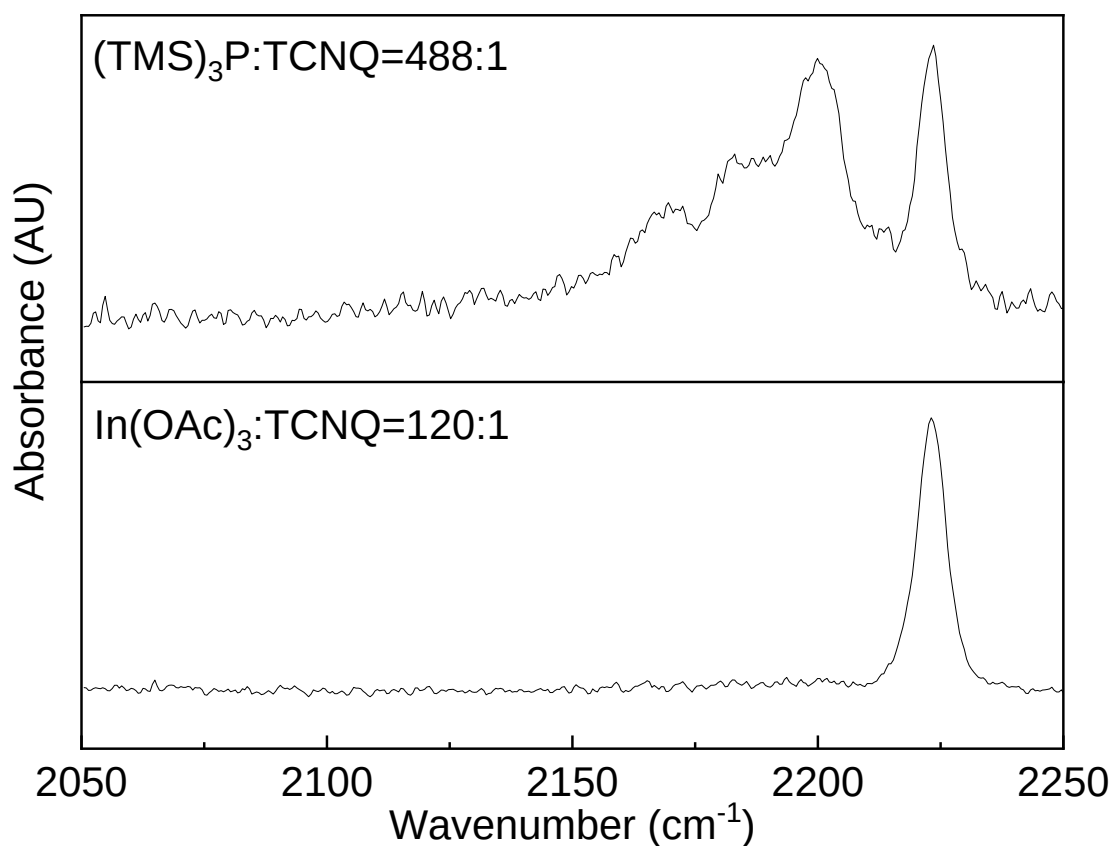


Figure 2.9 Precursors of InP QDs with TCNQ

In the IR spectrum of the $\text{In}(\text{OAc})_3$: TCNQ solution, the peak at 2225 cm^{-1} is from TCNQ, and no new peak appeared. So, $\text{In}(\text{OAc})_3$ cannot reduce TCNQ. In the $(\text{TMS})_3\text{P}$: TCNQ solution IR spectrum, except for the peak at 2225 cm^{-1} , there are peaks at 2200 cm^{-1} and 2168 cm^{-1} . Both of them are from reduced TCNQ. Thus, InP QDs is a donor, and TCNQ gets electrons from P in InP QDs. The cartoon of InP QDs capped with palmitic acid ligand and TCNQ in solution is shown in Figure 2.13.

Then, simulations were used to calculate the charge distribution on the surface of TCNQ using DFT (B3YLP method) with 6-311G++ basis.

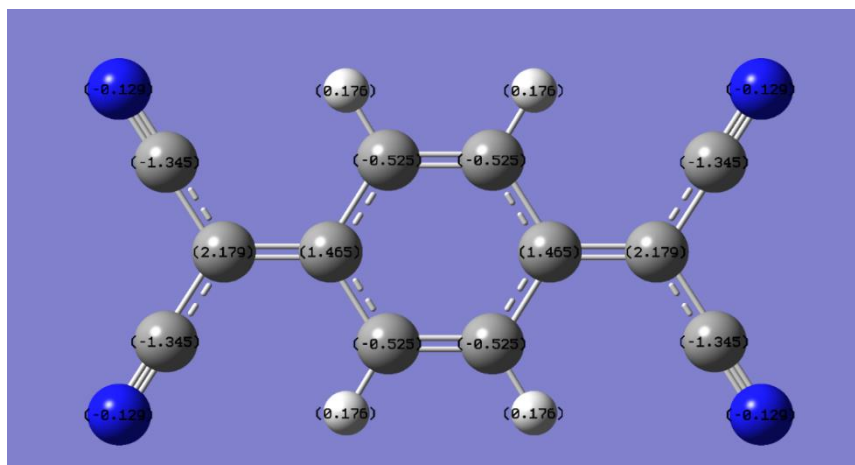


Figure 2.10 Charge distribution on the surface of TCNQ

Because TCNQ is the acceptor, the most positive part of the molecule will lean to get electrons. Based on Figure 2.10, the most positive parts are the carbons at the two branches. The two carbons will get electrons from InP QDs.

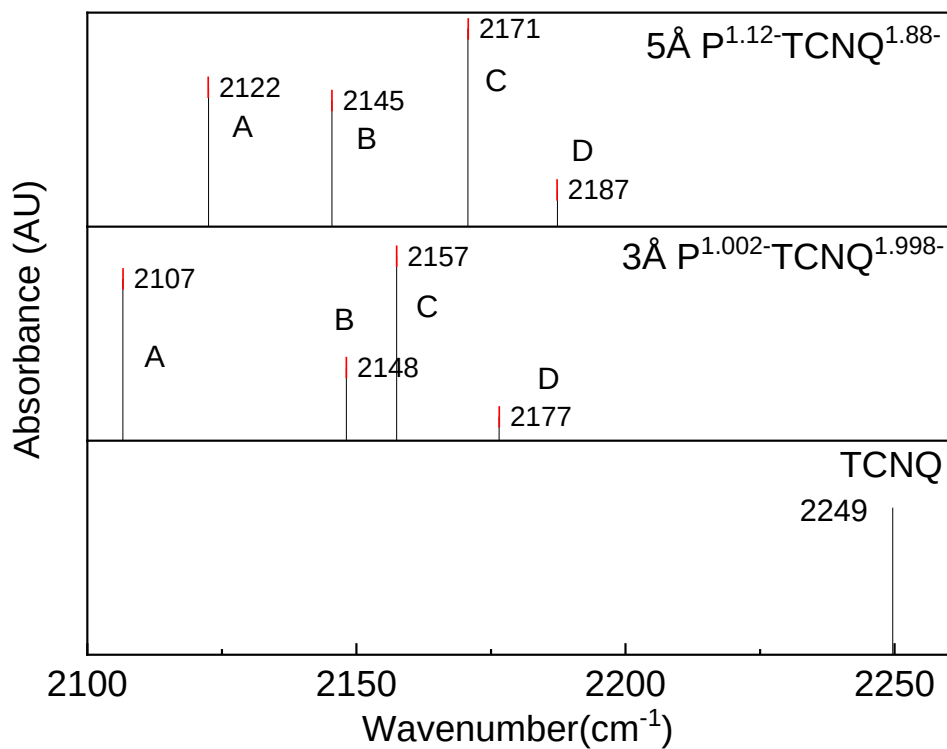


Figure 2.11 Simulated IR spectra of TCNQ and P³⁻ with 5 Å and 3 Å distance

IR spectra of TCNQ and P^{3-} in different distances are simulated and shown in Figure 2.11. Each simulated peak is matched with its vibration model. In addition, charge distribution on the surface of P and TCNQ complexes are also simulated.

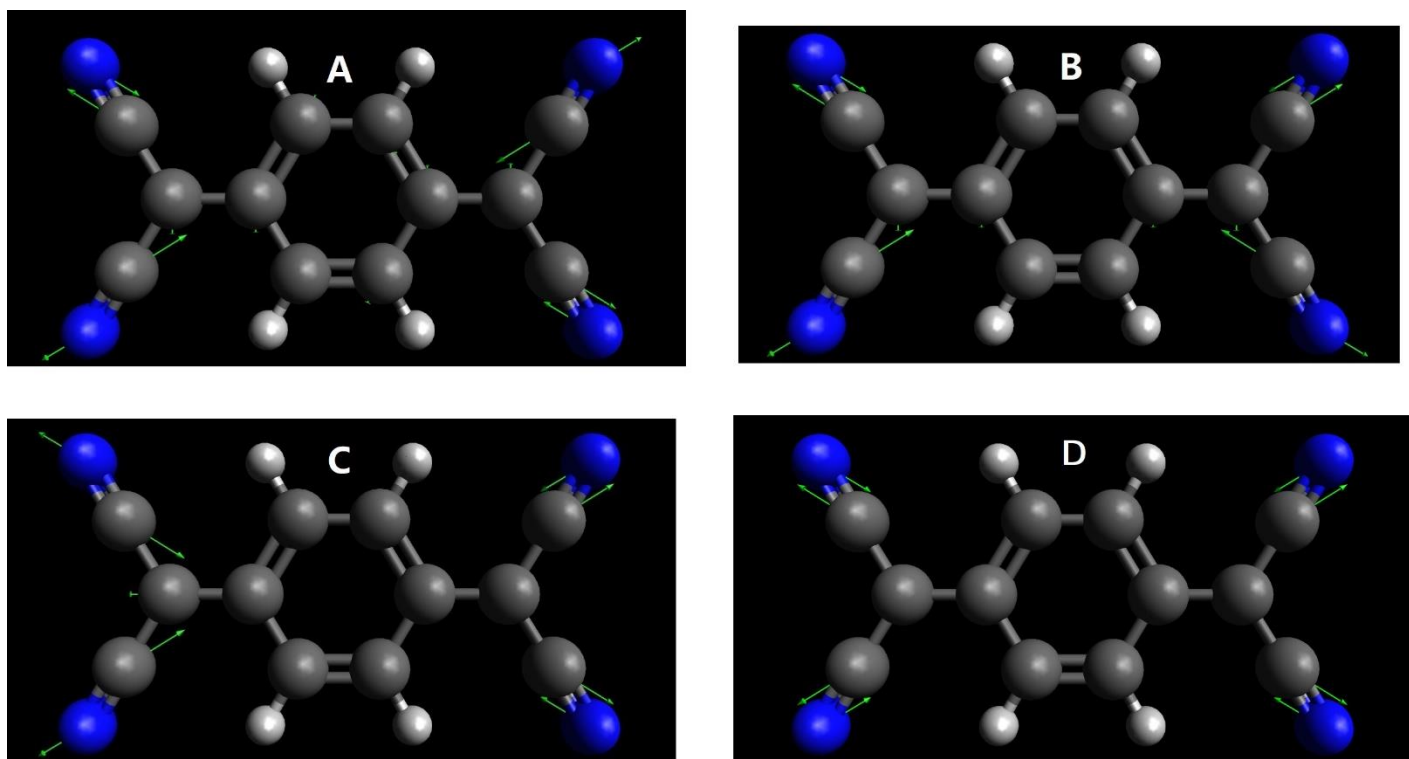


Figure 2.12 Vibration models for different motions

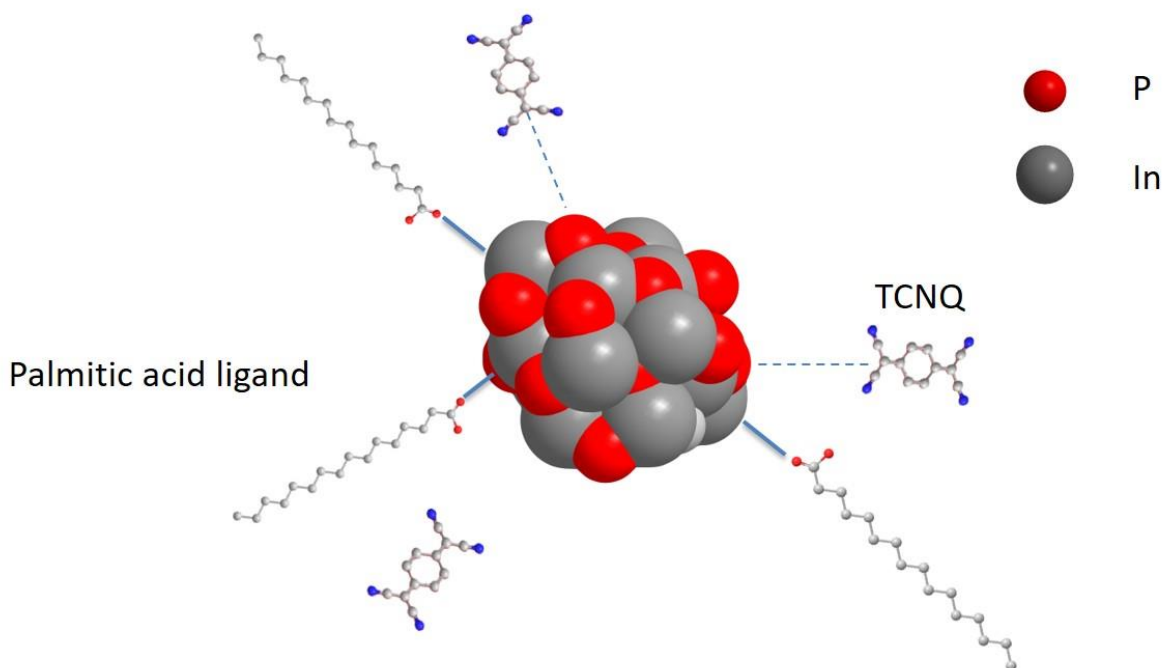


Figure 2.13 Cartoon of InP QDs capped with palmitic acid and TCNQ in solution

The TCNQ and InP QD samples with different ratios were prepared. Before InP QDs were added to the TCNQ solution, there is only a peak from pristine TCNQ at 2225 cm^{-1} . After InP QDs were added to the TCNQ solution, the peaks C and D from reduced TCNQ appear. With increasing volume of InP QDs, the intensity of peaks C and D increases and E decreases. This demonstrates the more InP QDs will reduce more TCNQ. The result shows that the amount of InP QDs will affect the CT between InP QDs and TCNQ. Based on the simulation results from Figure 2.11, the distance between the InP QDs and TCNQ is close to $5\text{ \AA}$.

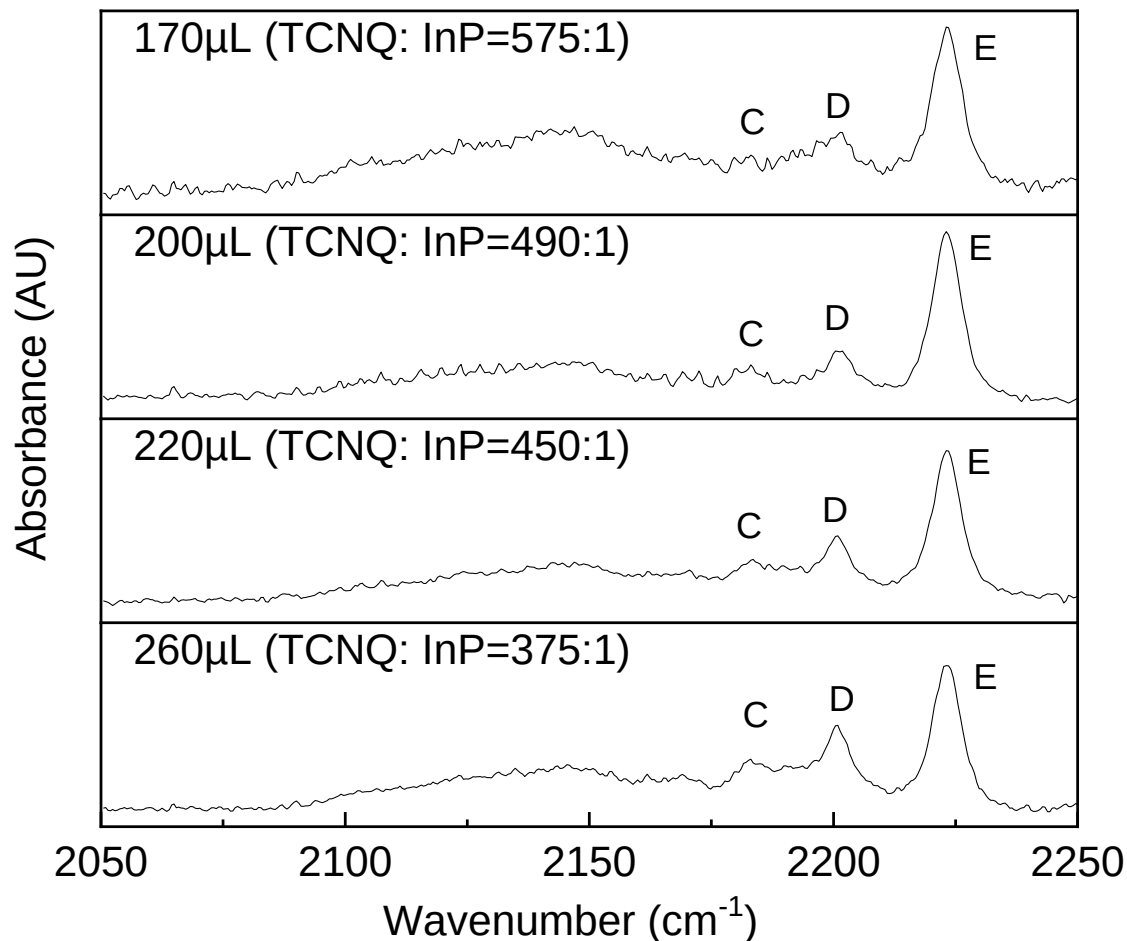


Figure 2.14 IR spectra for TCNQ with different volume of InP QDs (peaks C and D are from reduced TCNQ, E is from pristine TCNQ)

The InP QDs with TCNQ samples were put in several different conditions as shown in Figure 2.1, to check if light can affect the CT. IR spectra of these samples are shown in Figure 2.15. Before InP QDs are added to the TCNQ solution, none of the TCNQ is reduced, so the pristine TCNQ is not affected by light. After InP QDs were added to the TCNQ, peaks C and D from reduced TCNQ appear. For the InP QD-TCNQ sample kept in darkness for 24 h, little of the TCNQ is reduced by InP QDs. The reaction time for the second sample is 48 h, and the intensities of peaks C and D are similar to the intensities of peaks C and D in the first sample.

For the sample kept under light, the intensities of peaks C and D are much stronger than the intensities of peaks C and D for the samples kept in darkness. This result shows that light can enhance the CT between InP QDs and TCNQ.

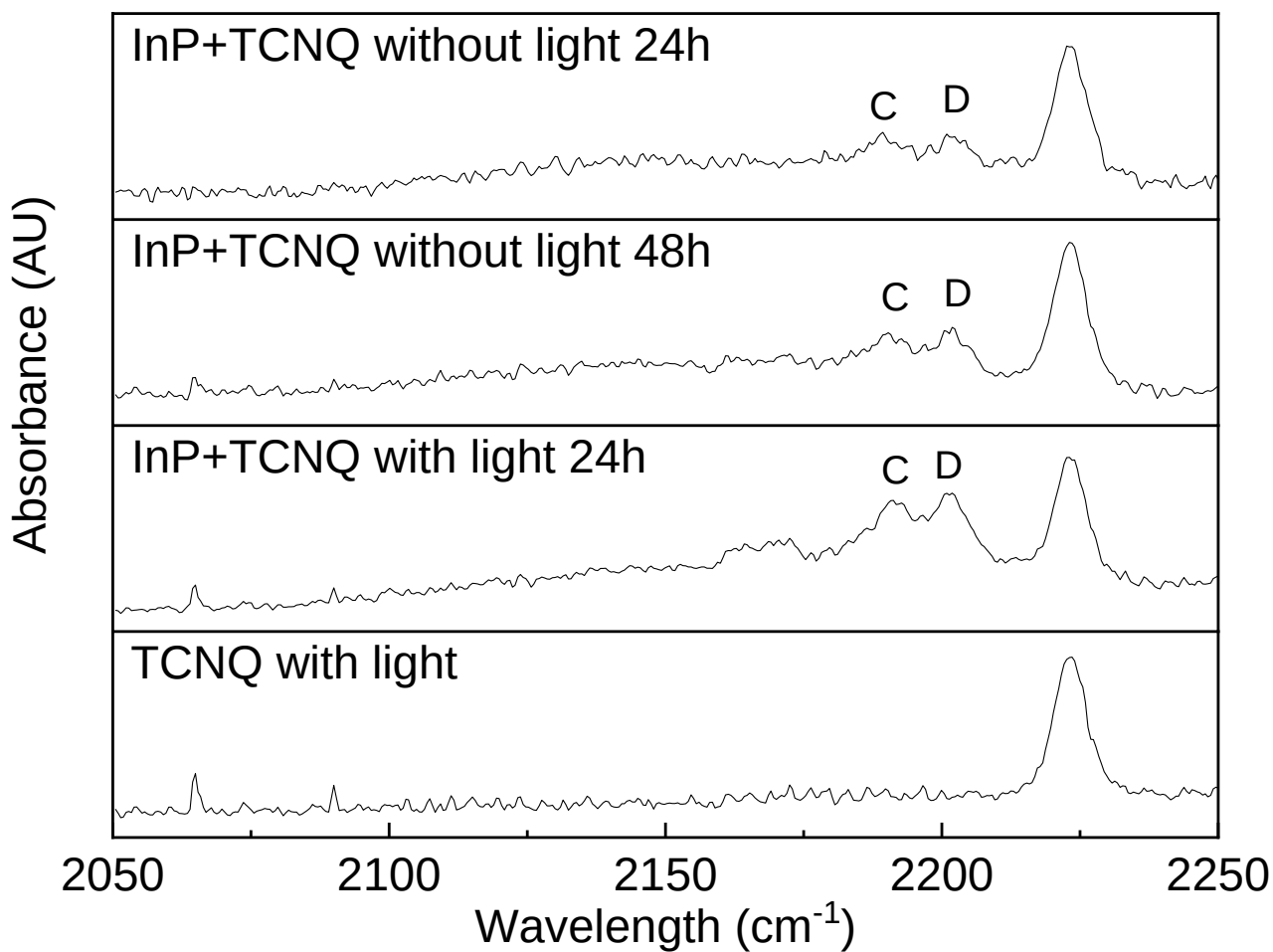


Figure 2.15 InP QD-TCNQ samples in different conditions (peaks C and D are from reduced TCNQ)

The IR spectra of these samples are shown in Figure 2.16. All of these spectra are similar. The Peak at 2225 cm⁻¹ is from pristine TCNQ. Peaks at 2203 cm⁻¹ and 2209 cm⁻¹ are from reduced TCNQ. The difference among these spectra is the intensity of the peak of reduced TCNQ. In the first two graphs, the ratio of TCNQ and InP QDs is the same, but the intensity of

peaks C and D in the first graph is stronger than them in the second graph, indicating the InP QDs of the diameter of 3.29 nm can reduce more TCNQ than InP QDs of the diameter of 3.38 nm. In the third and fourth graphs, the ratio of TCNQ and InP QDs is the same. The intensity of peak C and D in the third graph is stronger than them in the fourth graph, which means that InP QDs of the diameter of 3.38 nm can reduce more TCNQ than InP QDs of the diameter of 3.58 nm. The result indicates the intensity of peaks C, D is proportional to the size of the InP QDs.

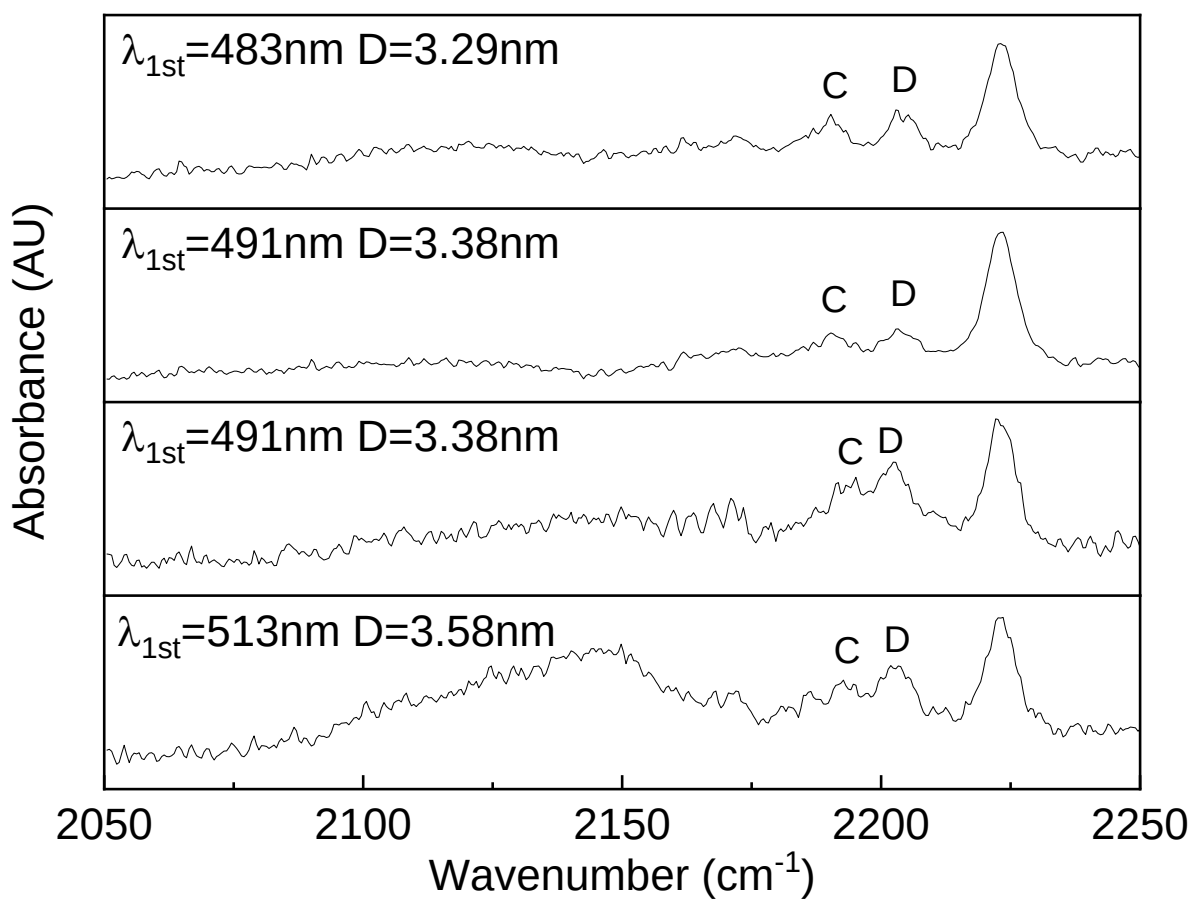


Figure 2.16 IR spectra of different sizes of InP QDs with TCNQ (peaks C and D are from reduced TCNQ, D is from pristine TCNQ)

A prerequisite for CT is matched energy levels. From literature, the HOMO of InP QDs about 3.5 nm in diameter is at -5.94 eV and the LUMO of TCNQ is at about -5 eV.^{9,10} After TCNQ and InP QDs are added to solution, the TCNQ approaches the InP QDs, then they can form a complex. The HOMO of InP QDs and LUMO of TCNQ may couple with each other to form two new energy levels. There is some evidence for the hypothesis, the reaction is irreversible. If energy levels do not couple together, electrons from the HOMO of InP QDs jump to LUMO of TCNQ directly, then these electrons are in the unstable state, they will go back, then the reaction should be reversible. In addition, the InP QD-TCNQ mixture has absorption at 850 nm which is equal to 1.46 eV but based on Figure 2.17, the difference of the LUMO of TCNQ and the HOMO of InP QDs is just 0.8 eV which is smaller than 1.46 eV. For InP QDs of smaller size, it has a smaller percent of surface emission in overall emission which means that InP QDs of smaller size has a bigger ratio of the anion to the cation, indicating there is more phosphorus on the surface of InP QDs of smaller size. In CT, TCNQ approach to phosphorus on the surface of InP QDs to get electrons. Thus, more phosphorus will increase the chance of TCNQ getting electrons from InP QDs.

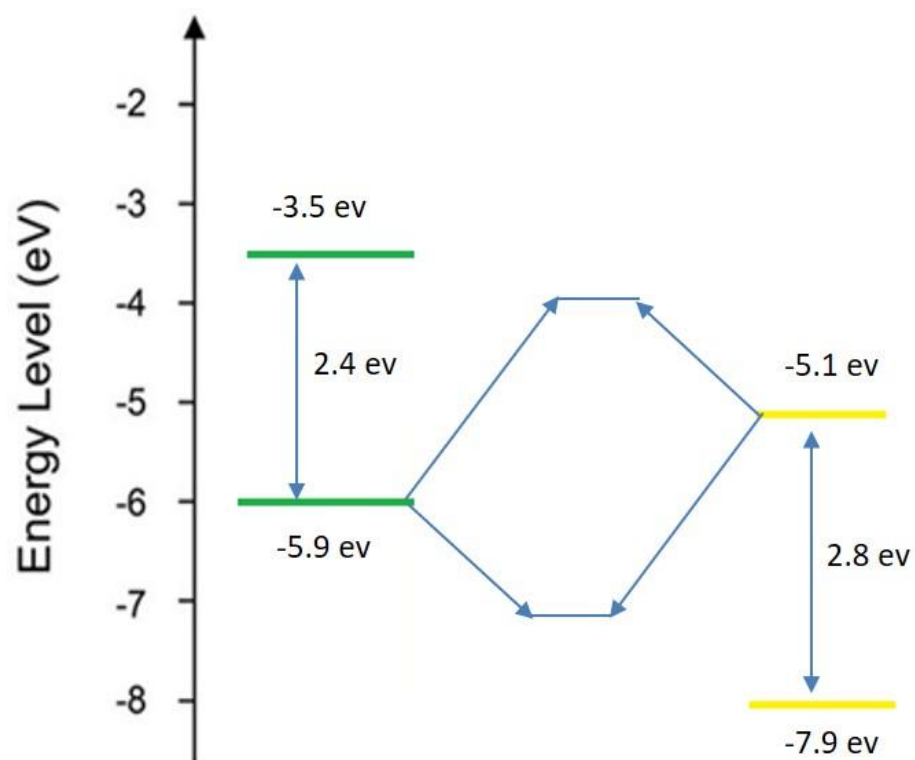


Figure 2.17 Energy levels of TCNQ and InP

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Chapter 3 - Conclusion

This thesis shows entire effort to understand the CT between InP QDs and TCNQ. It is fundamental to bring promising applications of InP QDs or some other QDs in photovoltaic or photocatalytic materials into our daily life. The CT can increase the ratio of electrons utilized in InP QDs which can help solar cells or other devices.

In the thesis, InP samples are synthesized by a microwave-assisted ionic liquid (MAIL) method, then InP QDs of different size are isolated from the same InP QDs by size-selective precipitation. The precursors of InP QDs are mixed with TCNQ. The results show that phosphorous precursor can reduce TCNQ. So, in CT between TCNQ and InP QDs, the acceptor is TCNQ, and the donor is InP QDs, and the C with the biggest positive charge in TCNQ and P in InP QDs are likely the acceptor and donor respectively. The TCNQ-InP QDs are prepared with different ratios, the IR spectra of these solutions show that the amount of InP can affect the CT between InP QDs and TCNQ, because the more InP QDs, the more P to donate electrons. Then, InP QD-TCNQ solution in the same ratio is prepared and kept in different conditions, such as different reaction times and with/without light. The IR spectra of these solutions show that the CT between TCNQ and InP QDs can be affected by light. Finally, TCNQ with the InP QDs of different size are prepared. Based on the IR spectra of these samples, the smaller InP QDs have better ability to reduce TCNQ. The lifetime results of the InP QDs of different size show that the emission of the samples is similar.

In the future, the relationship between the surfaces of InP QDs and CT need to be studied further. A useful method to do this research is to shell the surface of InP QDs and check if the InP QDs can still donate electrons to TCNQ.