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Interfacial Assembly of Nanoparticles with Soft Templates for Photovoltaic Applications

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Abstract

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Controlling the assembly of nanoparticles into well-defined functional systems remains a challenge. The main difficulty is that the majority of bulk nanoparticle processing methods result in nanoparticle aggregation and phase separation. In this thesis, we describe a soft-templating strategy to direct the assembly of semiconducting cadmium selenide (CdSe) tetrapods (TPs) into a wire-like and network structure and their application in heterojunction photovoltaic devices. In particular, the templating occurs at the air/water interface and transferred to a substrate via the Langmuir-Blodgett (LB) technique.

First we show how a small amphiphilic molecule, such as 1-palmitoyl-2-oleoyl-sn-glycero-3-phosphocholine (POPC) lipids, can serve as a soft template to control the arrangement of CdSe TPs at the air/water interface. CdSe TPs aggregate into uncontrolled disc-like structures when deposited onto the air/water interface; however, with the presence of POPC, wire-like structures are observed upon compression. Larger templating agents, such as the conjugated polymer, poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV), was also shown to be able to template CdSe TPs.
This conjugated polymer is of particular interest because of its relatively stability at the air/water interface and its application in organic solar cells. We also discovered a mixed solvent technique, which can manipulate the morphology of MEH-PPV formed at the air/water interface. When MEH-PPV was deposited using a mixed solvent combination of chloroform and chlorobenzene, ring-like structures formed by MEH-PPV were observed at the air/water interface. These ring structures showed very interesting optical properties such as red-shifted light absorption compared to pure solvent cases, tunable band gaps and birefringence. This unique assembly behavior is due to the difference of spreading coefficients and evaporation rates between chloroform and chlorobenzene.

The soft-templating method was used to build up heterojunction photovoltaics. When CdSe TPs and MEH-PPV are mixed together in chloroform and deposited on the air/water interface, large CdSe TP network structures were formed. This structured film can be transferred onto a solid substrate multiple times via LB technique to build up the photoactive layer of a solar cell. It was observed that the power conversion efficiencies (PCEs) of the devices generated via the LB technique outperformed the conventional spin-coating method, due to the percolating network presented in the photoactive layer. We also set the best reported PCE record from the LB-aided device under the combination of CdSe TPs and MEH-PPV in this thesis. With these studies, there are now a number of possibilities of utilizing the air/water interface with soft templates and the Langmuir-Blodgett technique, which can lead to solutions for real world applications.
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1 Introduction

This thesis elucidates the assembly and application of soft materials, such as lipids and conjugated polymers, with hard materials, such as cadmium selenide (CdSe) tetrapods (TPs), at the air/water interface. By using the Langmuir-Blodgett (LB) technique, amphiphilic molecules are utilized as soft templates to manipulate the packing and assembly of nanocrystals. This method allows for the precise control of CdSe TPs structures over multiple length scales. Understanding the assembly mechanism of CdSe TPs enables us to combine CdSe TPs with different templating agents to build up a desired configuration. This work also resulted in the discovery of an unique method to control the organization of a conjugated polymer, poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV), at the air/water interface using different solvent combinations. Lastly, we apply this templating technique to fabricate a heterojunction hybrid solar cell and characterize the improvement on the power conversion efficiency (PCE) of the solar cell compared to conventional spin coating methods.
1.1 Materials at the air/water interface

1.1.1 Langmuir film, Langmuir-Blodgett and Langmuir-Schaefer technique

The Langmuir-Blodgett (LB) technique was originally used for probing the phase behavior of the amphiphilic molecules at the air/water interface [1-3]. Amphiphilic molecules have one hydrophobic end, i.e. hydrocarbon chain, and one hydrophilic end, such as carboxyl group (-COOH) (Figure 1.1a), amino group (-NH₂) or hydroxyl group (-OH). When amphiphilic molecules assemble at the air-water interface, the hydrophobic group is oriented out of the water surface, while the hydrophilic group is immersed in the water phase. The surface tension can be related to the partial derivative of Gibbs free energy with respect to the surface area when at thermodynamic equilibrium, as shown in the following equation [4]:

\[
\gamma = \left( \frac{\partial G}{\partial A} \right)_{T,P,n}
\]

where \( \gamma \) is surface tension of water; \( G \) is Gibbs free energy and \( A \) is the surface area.

By dissolving the amphiphilic molecules into the volatile solvent like chloroform or hexane, we can easily spread these molecules at the air-water interface to form an insoluble monolayer on the water surface. A monolayer consisting of a single layer of molecules is denoted as a Langmuir film. The association behavior of amphiphilic molecules at the air-water interface is not only determined by the physical and chemical
properties of hydrophobic and hydrophilic parts, respectively, but is also dictated by the shape and size of two ends. Additionally, if the polar head group carries any charge, then electrostatic force needs to be considered as well.

Using a trough, we can control the area occupied by each amphiphilic molecule. By decreasing the area occupied per molecule, phase transitions take place at the 2-D air/water interface, analogous to a three-dimensional (3-D) system. Normally we measure the surface pressure ($\pi$) in a monolayer as:

$$\pi = \gamma_0 - \gamma$$  \hspace{1cm} (1.2)

where $\gamma_0$ is the surface tension in the absence of monolayer and $\gamma$ is the surface tension of monolayer presented. The surface tension of water is 72.8 mN/m at 20 °C. This high value of surface tension, compared to other liquids, makes water a good subphase candidate in a monolayer experiment. Figure 1.1b shows a typical scheme of surface pressure ($\pi$) as a function of area per molecule ($a$) of amphiphiles at air/water interface [5]. In a typical $\pi$-$a$ isotherm, the x-axis, $a$, which is area per molecule (or called mean molecular area), is defined by the effective surface area ($A$) divided by the total number of molecules:

$$a = \frac{A}{cN_AV}$$  \hspace{1cm} (1.3)
where \( c \) is the specific molar concentration of the solution and \( V \) is the volume of the solution.

At the beginning, molecules are first spread on the interface so that the distance between molecules is large where there is little interaction between molecules. This is often referred to as the gas state. In this state, molecules are not oriented and are often found lying at the interface. As the distance between molecules decreases, a more ordered structure arises, which is the liquid phase. The smaller area per molecule that is occupied, the more ordered structures appear: the solid state shows the most oriented structure of amphiphiles. If we continue compressing the surface after the solid state has formed, the monolayer collapses. One may find the so-called liquid-expanded phase (LE) and liquid-condensed phase (LC) between the three main stages as shown in Figure 1.1b. The appearance of liquid-condensed phase is decided by the molecular structure of the amphiphilic molecule, such as the length of the hydrocarbon chain, and the temperature of the subphase [6] (Petty1996). Normally when the molecular structure of the amphiphilic molecules is less branched, meaning the molecules can pack as close as possible to each other under compression, the greater chance that a liquid-condensed phase can be observed (Petty1996).
Figure 1.1. (a) Schematic of an amphiphilic molecule. The hydrophilic end of the amphiphilic molecule here is carboxyl group (-COOH). It can be amino group (-NH$_2$), hydroxyl group (-OH) or other functional groups; (b) schematic illustration of surface pressure ($\pi$) versus mean molecular area ($a$) of amphiphilic molecules. Note that the liquid-expanded phase (LE) or liquid-condensed phase (LC) can both appear in the isotherm, depending on the structure of the amphiphilic molecule; (c) illustration of the compressing experiment and the LB transfer.

In Figure 1.1c, a schematic of a typical experiment is shown. The amphiphilic molecules is deposited on the water surface as in the 2-D gas phase as mentioned earlier, and then two moving barriers start to compress the monolayer. The transfer step takes place when the surface pressure of the monolayer reaches a relatively stable point. Once
vertically transferred the monolayer onto a solid substrate, the dried monolayer is known as a Langmuir-Blodgett (LB) film [1-3, 7, 8]. By repeating the transfer step with different transfer fashion, multiple layers are able to be built up as Y- (centrosymmetric), X- and Z- type (non-centrosymmetric) LB multi-layer (Figure 1.2). In this thesis, we only built up Y-type multi-layers. Another approach to transfer the Langmuir film onto a solid substrate is called Langmuir-Schaefer (LS) technique [9] when transferring the thin film from the water surface horizontally. It can be accomplished with dipping or lifting. This technique was utilized when studying the assembly behavior of poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV), a common conjugated polymer, at the air/water interface. More detail on the experimental setup will be elaborated in Chapter 2 and Chapter 4.
Figure 1.2. Schematic of different transfer fashions: (a) X-; (b) Y- and (c) Z-type LB multi-layer; (d) LS-dipping and (e) LS-lifting.

1.1.2 Nanocrystals at the air/water interface

Recently, the LB technique has been applied to the assembly of nanocrystals, such as nanoparticles [10-12] and nanorods [13], where it has been shown how nanorods can be used to mimic the phase transition of liquid crystals in a 2-D system ([13], p. 4361, as shown in Figure 1.3). In the study of Chung et al. [10], they were able to direct silver nanoparticles to form wire-like structures at the air/water interface under specific spreading solution concentration and surface pressure, controlling the width of the wire and spacing between wires as well; Fried et al. [11] built up a uniform two-dimensional array of magnetite and cobalt-ferrite nanoparticles by carefully tuning the pH value of the
subphase and the particle concentration. This well-defined array of magnetic nanoparticles has potential applications in information-storage media and new magnetoresistive materials with the suitable particle composition. Their research also reveals how important the monodispersity of the nanoparticles is to obtain a high quality two-dimensional array. This paper demonstrates the advantages of using the LB technique, as a “bottom-up” method, on the assembly of nanocrystals that one can control the packing of nanocrystals precisely in nanoscale and produce large area of uniform film of desired structures in micrometer-level at the same time.

![Figure 1.3](image)

**Figure 1.3.** Transmission electron microscopy (TEM) images of the LB films of BaCrO$_4$ nanorods transferred at different surface pressure: (a) isotropic; (b) partial two dimensional (2-D) nematic arrangement; (c) 2-D smectic arrangement; (d) multi-layer of
nematic arrangement and (e) schematic illustration of phase transition of nanorods at the air/water interface (adapted from Kim et al. [13]).

Several more interesting structures of nanocrystals were observed at the air/water interface. Song et al. [14] showed synthetic methods and characterization of different morphologies of Pt nanocrystals – cubes, cuboctahedra and octahedra. After the deposition of Pt cube nanocrystals at the air/water interface, Pt cube nanocrystals coverage on the water surface can be tuned by the surface pressure – higher surface pressure, higher surface coverage. They conclude that the surface coverage of Pt nanocrystals cannot reach a high enough value to have the close-packed two-dimensional structures as what Fried et al. [11] found with the nanoparticles, but surface uniformity is achievable. Another interesting result was that when the film on the water surface was transferred onto a solid substrate, the surface morphology formed by Pt octahedral nanocrystals was totally different from the one in Pt cube nanocrystals; surprisingly in the case of Pt cuboctahedra nanocrystals, the surface morphology here shared both features discovered in the previous two. This finding leads to more opportunities in designing a new type of two-dimensional metal catalyst, again contributed by the LB technique.

Goodman et al. [15] extended the application of the LB technique to Cadmium telluride (CdTe) TPs. This is the first paper that examined the assembly behavior of tetrapod-shaped nanocrystals at the air/water interface, where they found that the phase behavior of CdTe TPs at the air/water interface cannot be explained by the classic gas-liquid-solid phase transition model (Petty1996). They observed that CdTe TPs formed
ribbon-like structures, as depicted in Figure 1.4, and large aggregates along with those ribbons. When applying more external force on the thin film, larger aggregates were recorded but the thickness of the ribbon structures remained constant. In my research, the same conclusion regarding the conflict between the classic gas-liquid-solid phase transition was obtained by observing the assembly behavior of CdSe TPs at the air/water interface: the thin film of CdSe TPs did not collapse when reaching the theoretical critical area for CdSe TPs. However, due to the types of ligands coated on TPs and the various sizes of TPs, we observed disc-like structures formed by CdSe TPs (will be shown in Chapter 3), instead of ribbon structures formed by CdTe TPs. Undeniably, the driving force of forming either disc-like or ribbon structures is related to how the solvent evaporates, where chloroform was used as the solvent candidate. The effect of solvent is discussed in Chapter 4 in regards to 2-D assembly behavior of MEH-PPV. Another main difference between the interfacial behavior CdSe and CdTe TPs is that we can precisely manipulate the thickness of thin film of CdSe TPs by tuning the surface pressure because of the smaller size of CdSe TPs, while the thickness of thin film of CdTe TPs is fixed. More comparison between these two TPs will be discussed in the following chapters.
1.1.3 Polymers at the air/water interface

The assembly behavior of polymers at the air/water interface has attracted much attention as well. Amphiphilic polymers, for example, poly (L-lactid acid) (PLLA) [16], and diblock copolymers [17-19] that consist of hydrophilic group and hydrophobic group are two main subjects. For diblock copolymer, poly(styrene)-b-poly(ethylene oxide) (PS-b-PEO) has be intensively studied at the air/water interface. Devereaux et al. [20] reported the assembly behavior at the 2-D system of this diblock copolymer with 7 % PEO by mass, forming three different features: continents (planar aggregates), dots (circular aggregates) and spaghetti (rodlike aggregates) as shown in Figure 1.5. They discovered that the concentration of the spreading polymer solution is the key factor to determine the predominant feature at the air/water interface when three features were found together all the time. They also looked into the effect of surface pressure and the compressing rate on the features, which did not have as great of an effect on structure assembly compared to the spreading solution concentration.
Figure 1.5. AFM images (4 μm × 4 μm) of transferred LB films of poly(styrene)-b-poly(ethylene oxide) (PS-b-PEO) diblock copolymers (Mw = 51k, 7% PEO by mass). There are three types of featured surfaces observed: row 1, continents (planar aggregates); row 2, dots (circular aggregates); row 3, spaghetti (rodlike aggregates). The deposition variables for each image are $\pi = 2$ mN/m, concentration = 1 mg/mL, and compression speed = 10 mm/min except as follows: (1A) concentration = 1.7 mg/mL, (1B) concentration = 3.5 mg/mL, (1D) concentration = 1.7 mg/mL, (2A) $\pi = 1$ mN/m, (2B) $\pi = 4$ mN/m, (2C) compression speed = 20 mm/min, (2D) $\pi = 4$ mN/m, (3B) $\pi = 0.5$ mN/m, (3C) $\pi = 6$ mN/m, and (3D) concentration = 0.5 mg/mL (adapted from Devereaux et al. [20])


Cheyne et al. continued to report and propose the possible mechanism of resulted features from PS-b-PEO [21] at the air/water interface. Two molecular weight of PS-b-PEO were tested: 141k with 11.4 wt % PEO, and 185k with 18.9 wt % PEO. Compared to Devereaux et al., these PS-b-PEO diblock copolymers were more hydrophobic. The spreading concentration again was the crucial parameter that influenced the morphologies at the air/water interface. For 141k, higher concentrations resulted in more overlap and entanglement between PS-b-PEO polymer chains (as a 3-D system), resulting in more dots and spaghetti features found on at the air/water interface (on 2-D) while rings and chains were newly-observed structures under critical concentration. On the other hand, there were no rings and chain-like structures found but dots and spaghetti across the tested concentration range for 185k. They proposed that dewetting induced the structure formation of PS-b-PEO at the air/water interface as shown in Figure 1.6. At the beginning, the spreading solution was deposited at the air/water interface and formed relatively uniform tin layer. As time goes by, the depositing solvent evaporates and the thickness of thin film drops. At the critical point, the thin film ruptures and the “holes” become larger with time. The edge of the holes accumulated more and more polymer chain, and eventually met the frontiers of other holes, forming the network-like structures.
Mitsuishi et al. [22] have applied the LB technique to establish polymer nanosheets of poly(N-dodecylacrylamide) (pDDA), shown in Figure 1.7. As shown in Figure 1.7a, the C=O and N-H bonds provided good hydrogen bonding between polymer chains on the same layer, while the long hydrocarbon side chains stabilized the interaction between layers. Figure 1.7b depicts the SEM image of free-standing polymer nanosheets after depositing the LB film for 700 layers (Y-type of LB films). This study inspired us to further pursue templates that can help to order CdSe TPs at the air/water interface. In the following section, we continue to introduce soft template organization.
1.2 Template Organization

To prevent aggregation and help the stability of dispersed particles in the bulk solution, a coating of hydrophobic ligands on the nanocrystal surface is widely used [23]. When nanocrystals are deposited on the water surface, the issue of instability may arise. In the study of spontaneous fractal aggregation of gold nanoparticles at the air/water interface, from Cheng et al. [24], they noticed that the fatty acid coated on the gold nanoparticle surface might detach from the particle and dissolve into the water, causing the bare gold nanoparticle surfaces to be exposed to each other. In order to minimize the surface energy, neighboring gold nanoparticles coalesced together, instead of remaining dispersed on the water surface. In the case of CdTe TPs ([15], p. 2046), the dewetting phenomena of the CdTe TPs film was found, which drove CdTe TPs to form ribbon structures, as shown in Figure 1.4, without further control.

Figure 1.7. (a) Scheme of constructing polymer nanosheets of pDDA; (b) SEM image of free-standing pDDA nanosheets (adapted from Mitsuishi et al. [22])
Subsequently, template organization was developed as a solution to this practical issue (Hassenkam et al. [25], Hansen et al. [26], Markovich et al. [27], Volinsky et al. [28]). In this technique, amphiphilic molecules are used as soft template agents to stabilize the target material, e.g., nanocrystals, at the air/water interface. Surfactants such as lipids and amphiphilic polymers are intensively adopted as template substances. Hassenkam et al. [25] used dipalmitoylphosphatidylcholine (DPPC) as the template substance to direct the assembly of dodecanethiol-capped gold nanoparticles at the air/water interface. They proposed that DPPC lifted gold nanoparticles up to minimize the contact between water and dodecanethiol to decrease the energy loss; by replacing parts of dodecanethiol with hydrophilic coatings in the control experiment, they found that the stabilization function provided by DPPC is diminished, because now the gold nanoparticles compete with DPPC to cover the water surface. Their proposed mechanism helped better understand how CdSe TPs and other templating agents interact. First, 1-palmitoyl-2-oleoyl-sn-glycero-3-phosphocholine (POPC) is used as a templating agent, whose molecular structure is similar to DPPC. Second, there are hydrophobic ligands like dodecanethiol on the CdSe TPs surface as well. Consequently, I discovered parallel results between the fluorescence lipid control experiment, where the fluorescent signal was detected from all over the surface except the areas made of CdSe TPs, meaning POPCs are located between water and CdSe TPs. More detail will be elaborated in Chapter 3.

In addition to lipids, amphiphilic polymers are another favored category for use as a templating agent. Hansen et al. [26] used two types of poly(p-phenylenes), which has one phenolic group and one hexyl (C₆PPPOH) or dodecyl (C₁₂PPPOH) side chain, to manipulate the orientation of gold nanoparticles at the air/water interface. By having
different side chain lengths, C₆PPPOH and C₁₂PPPOH possess totally distinct behavior either at the interface or on the solid substrate by spin coating. C₆PPPOH was able to organize stable multi-layer Langmuir-Blodgett films while C₁₂PPPOH was not; ordered honeycomb structures constructed by C₁₂PPPOH were found by spin coating it on the solid substrate as less ordered structures formed in the C₆PPPOH case [29, 30]. Interestingly, Hansen et al. proved that C₁₂PPPOH was the better templating agent for gold nanoparticles that can provide the ordered pattern at given surface pressure on the water interface, as shown in Figure 1.8. After passing the critical point, the ordered configuration destroyed. The noticeable finding in Hansen et al. [26] signifies the importance of choosing the template substance between the candidates, even from the same series of materials, and the proper transferred point to have a desired structure, where we also acquired the similar conclusion from the system of POPC/CdSe TPs.

**Figure 1.8.** AFM (left) and TEM (right) images of the Langmuir-Blodgett films of C₁₂PPPOH/gold nanoparticles (67 wt %) transferred at 40 mN/m (adapted from Hansen et al. [26]).
In the research of Markovich et al. [27], they tried to order the packing of dodecanethiol-capped gold nanoparticles in diacetylene monolayer templates at the air/water interface. Figure 1.9 indicates that gold nanoparticles aligned right next to the condensed diacetylene template; after plasma etching, diacetylene and dodecanthiol coating on the gold nanoparticle surface were removed, and only gold nanoparticles were left in the LB film. Plasma etching offers the possibility of removing undesired ligands in the thin film. Furthermore, by replacing one end of diacetylene with another carboxyl group, the packing of gold nanoparticle changed from nanowires to nanoislets, where the structures again remain intact after plasma etching. More detail about ligand exchange process will be shown in Chapter 2 and 5.

**Figure 1.9.** (a) TEM images of gold nanoparticles in diacetylene templates (0.11 mole % gold nanoparticles). The black strips are the gold nanoparticles assemblies and the slightly darker part is diacetylene; AFM images of gold nanowires, recorded after plasma
etching; (b) TEM images of gold nanoparticles in diacetylene with two carboxyl groups templates (0.14 mole % gold nanoparticles); AFM images of gold nanoislets, recorded after plasma etching. The scale bar is 50 nm (adapted from Markovich et al. [27]).

1.3 Heterojunction Hybrid Solar Cells

The silicon-based solar cells, including single- and polycrystalline-type, have dominated the current photovoltaic industry. It is known as the first generation of the solar cell, while the second generation of the solar cell consists Cu(InGa)Se$_2$ (CIGS) and CdTe thin films. The silicon-based solar cell has the theoretical power conversion efficiency (PCE) around 31% [31]. The highest PCE record of solar cells has been pushed to 44.7% in September 2013 by German Fraunhofer Institute for Solar Energy Systems [32]. Figure 1.11 is the up-to-date chart about the best research-cell efficiencies, collected by National Renewable Energy Laboratory (NREL) in 2013. The third generation type of solar cell, the dots marked as red in Figure 1.10, has been developing since the 90s, including dye-sensitized solar cell (DSSC), organic photovoltaic (OPV), heterojunction hybrid solar cells. The organic part of the hybrid solar cell can be a number of conjugated polymers, including MEH-PPV, poly(3-hexylthiophene-2,5-diyl) (P3HT), poly(2-methoxy-5-(3′,7′-dimethyl-octyloxy)-p-phenylenevinylene) (OC1C10-PPV) and poly[2,6-(4,4-bis-(2-ethylhexyl)-4H-cyclopenta[2,1-b;3,4-b′]dithiophene)-alt-4,7-(2,1,3-benzothiadiazole)] (PCPDTBT) and others [33-36], while the inorganic part of it consists of semiconductor nanocrystals of various shapes, for example, CdTe
nanoparticles/nanorods, CdSe nanoparticles/nanorods/tetrapods/hyperbranched nanocrystals, and CdS, PbS and PbSe nanoparticles [34–36].

In this thesis, the main focus is the assembly of CdSe TPs. The first batch of CdSe TPs was synthesized and reported by Manna et al. in 2000 [37]. Since then, more and more synthesis methods and photovoltaic devices made of CdSe TPs have been reported. Sun et al. [38] studied how nanocrystal shape influenced PCE of solar cells. CdSe nanorods and tetrapods (both in chloroform/pyridine) were mixed with OC11C10-PPV (in 1,2-dichlorobenzene). They found that the device made of CdSe tetrapods had a higher external quantum efficiency (EQE) (45 %) than the one with CdSe nanorods (23 %). The thickness of the photoactive layer was 160-180 nm, giving the PCE of the solar cell of 1.8 % under standard AM1.5 illumination. The best result of the hybrid solar cell based on CdSe TPs was reported by Dayal et al. in 2010 [39]. They mixed CdSe TPs (in chloroform/pyridine) and PCPDTBT (in trichlorobenzene) and obtain the highest PCE of 3.2 % by far.

These nanocomposite thin films promise to be the next generation of low cost photovoltaic [31] by combining the ease of processibility using solution-based methods onto a variety of substrates with the broad light absorption spectrum that can be achieved by varying the nanoparticle size [34, 35, 40, 41]. Theoretically hybrid photovoltaics should be able to harvest more light than organic photovoltaics [35, 36], but thus far, power conversion efficiencies (PCE) for hybrid photovoltaics have remained low [34, 41]. A lot of issues arise, such as the interfacial contact between polymers and nanoparticles. In paper from Greenham et al. [42], it was found that if the TOPO ligand on CdSe nanoparticles was replaced, the contact between CdSe nanocrystals and MEH-
PPV became better and the EQE was larger than the system without ligand exchange treatment. We will reveal more details related to the ligand exchange in the following chapter.

Many groups have studied how to control the morphology of the photoactive layer, specifically on the polymer crystallization, by tuning the annealing temperature and time afterwards [43-45]. Structures such as pillars and nanotubes inside the photoactive layer resulted in better contact and better direction for electron/holes transfer within the electrodes [46-48]. In this thesis, it is demonstrates how controlling the packing of CdSe TPs in the photoactive layer using soft template technique at the air/water interface, improves the PCE of the heterojunction hybrid solar cells.
Figure 1.10. Chart of best research-cell efficiencies up-to-date (adapted from NREL website). The third generation of solar cell mentioned in this thesis falls into the category of “Emerging PV” (red) in this chart.

1.4 Summary

In summary, the LB technique has been approved as a powerful “bottom-up” tool to build up large areas of uniform nanoscale structures from nanoparticles, nanorods, cube-shaped nanocrystals and tetrapod-shaped nanocrystals at the sub-micrometer or micrometer level. To have further control and stabilization of the assembly of those nanocrystals at the air/water interface, a template organization is introduced in this thesis. We choose POPC as the template substance to manipulate the assembly of CdSe short TPs since POPC has similar molecular structure as DPPC, which has been intensively
studied in the literature. Further tests enable us to understand how POPC affects the morphologies formed by CdSe TPs. According to my research, the assembly behavior of CdSe TPs is different from that previously reported. The assembly behavior of amphiphilic polymers and diblock copolymers also offered a platform to conduct a soft templating organization strategy at the air/water interface. By being able to understand the possible arrangement of CdSe TPs at the air/water interface using MEH-PPV as a template agent and an electron donor, I was able to engineer a hybrid solar cell. In the following chapters, I am going to depict the design of this system and show how we can obtain the desired configuration of TPs at the air/water interface.
2 Materials and Experimental Methods

In this chapter, we are going to introduce general information about the materials and experimental techniques used in this thesis. More specific experimental detail will be addressed in the corresponding chapters. The experimental techniques used for assembling, monitoring and characterizing thin films of either, CdSe TPs/lipids, conjugated polymers, and CdSe TPs/conjugated polymers, from the air/water interface include the Langmuir trough, the Brewster angle microscopy (BAM), the atomic force microscopy (AFM) and the transmission electron microscopy (TEM). Other optical properties were characterized using an ultraviolet-visible (UV-vis) spectrophotometer for absorption spectra and the spectrofluorometer for photoluminescence (PL) emission tests. Parts of the fabrication process of the hybrid solar cell described in Chapter 5 are elaborated in this chapter as well.

2.1 Materials

The chemical synthesis method for producing CdSe TPs is described in [49]. We acquired CdSe TPs from Professor Wong’s research group. We stored the CdSe TPs in chloroform (CF) for storage. There were two different sizes of TPs synthesized and used in this thesis. As shown in Figure 2.1a, the arm length of the short TP (sTP) is around 11
nm and the diameter of the arm is 4.5 nm; while in Figure 2.1b, the long TP (LTP) has the arm length of 30-40 nm and the arm diameter of ~2 nm. In Chapter 3, the assembly behavior of the short TPs at the air/water interface is tested and in Chapter 5, we will continue to compare the size effect on the performance of the solar cell. The lipid used for soft-templating of tetrapods is 1-palmitoyl-2-oleoyl-sn-glycero-3-phosphocholine (POPC) (Figure 2.2a), obtained from Avanti Polar Lipids, Inc. (Alabaster, AL). POPC is dissolved in CF and stored in refrigerator (−4 °C). Before starting the experiment, the POPC solution was taken out from the refrigerator and kept at ambient conditions for at least 20 minutes to allow the temperature of the stored solution back to room temperature. The POPC solution was also put in the ultrasonicator for 10-20 seconds before mixing with the CdSe TPs dispersion.

The conjugated polymer used in Chapter 4 and 5 is poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) (average Mn = 150,000-250,000, Mw/Mn = ~5) as shown in Figure 2.2b, one of the common conjugated polymers used in organic light-emitting diodes (OLEDs) [50-54] and photovoltaic devices (PVs) [33, 55-59]. MEH-PPV, chlorobenzene (CB) and CF mentioned above were all purchased from Sigma-Aldrich (St. Louis, MO, USA). MEH-PPV was dispersed either in CF or CB at concentrations between 2.5 - 3.0 mg/mL. The solution was stirred for at least one day and filtered through a 0.45 μm filter. In Chapter 4, we study how different solvent combinations affect the morphology formed by MEH-PPV at the air/water interface. For the hybrid solvent case, the CF and the CB solution were mixed immediately before the experiment.
In the fabrication of a hybrid solar cell, we utilized titanium dioxide (TiO$_2$) as the buffer layer on the cathode. More details about the procedure will be shown in Section 2.3.2. The chemicals used for making the TiO$_2$ film including titanium tetraethoxide, ethanol and hydrochloric acid were all purchased from Sigma-Aldrich too.

![TEM images](image)

Figure 2.1. TEM images of (a) short CdSe TPs; (b) long CdSe TPs
Figure 2.2. The lipid and the conjugated polymer: (a)1-palmitoyl-2-oleoyl-sn-glycero-3-phosphocholine (POPC); (b) poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV)

2.2 Instruments and Techniques

2.2.1 Langmuir Trough

As mentioned in Chapter 1, the surface pressure is a function of area per molecule at a constant temperature. Practically, we apply two moving barriers to reduce or increase the area per molecule by compressing or expanding the available surface. The Langmuir trough we were using is a KSV 2000 (KSV Instrument Ltd., Finland), having the effective surface area of 75900 mm². Figure 2.3a shows an illustration of a Langmuir trough [60]. The trough is made of Teflon, avoiding any leakage of water over the edge; the moving barriers comprise of Delrin, a hydrophilic material that prevents water from
passing beneath the barriers. The surface pressure is measured using a Wilhelmy plate, which is generally consist of thin Platinum or paper etc., coupled with an electrobalance. There are three forces exerting on the plate: surface tension, the weight of plate downward, and the buoyance force upward, as shown in Figure 2.3b [5]. We can write the force balance as:

\[ F = \rho_p g l_p w_p t_p + 2\gamma (t_p + w_p) \cos \theta - \rho_l g t_l w_l h_l \] .................................(2.1)

where \( l_p, w_p \) and \( t_p \) are the dimensions of the plate; \( \rho_p \) and \( \rho_l \) are the density of plate and subphase, respectively; \( \theta \) is the contact angle of the subphase on the solid plate and \( h_l \) is the immersed depth of the plate. The change in force between a pure subphase system and the same subphase with the presence of monolayer can be measured, from which we could obtain from the following equation:

\[ \Pi = -\Delta \gamma = \frac{-\Delta F}{2w_p} \] .................................(2.2)

where we assume it is completely wetting, e.g. \( \cos \theta = 1 \), and \( w_p \) is much larger than \( t_p \).
2.2.2 Brewster Angle Microscopy (BAM)

Being able to image structure formation at the air-water interface is useful because it allows us to monitor structural changes in real time. Brewster angle microscopy (BAM) is based on index of refraction changes and has been applied to the study of lipids, polymer, surfactants, and nanocrystals at the air-water interface [61-65].

Normally we expect to see refraction and reflection happen when shining a laser beam at an interface. However, at the Brewster angle, there’s no reflection of the incident light from the interface, or more precisely, there is a minimum p-polarized reflectance from the interface (Figure 2.7). We are able to calculate the Brewster angle from the relationship below:
\[
\tan \theta_b = \frac{n_s}{n_a}
\]  

(2.3)

where \( \theta_b \) is Brewster angle; \( n_s \) and \( n_a \) are refractive index of subphase and air, respectively. At the air/water interface, the Brewster angle is equal to 53.1 degree. Therefore, when working at this angle, the signal from water will exhibit a minimum value and practically, appear as the dark part in the image.

Once a film of molecules is present at the air-water interface, those entities will reflect the incident light, which allows us to capture the incident light from those molecules and identify those structures at interface. Figure 2.8 shows a typical BAM image of dioctadecylamine (DODA) [63]. The lighter islands are DODA that can easily be distinguished from the water background as recording the surface pressure at the same time. We mounted the KSV 2000 Langmuir trough onto a BAM (Accurion, GmbH, Germany) to monitor images of the thin films in real time (Figure 2.10). In Chapter 3 and 4, we utilized this technique to monitor CdSe sTPs/POPC and MEH-PPV thin film at the air/water interface.
Figure 2.4. Scheme of Brewster angle (adapted from KSV [60]).

Figure 2.5. BAM images of DODA: (a) $T = 23.9 \, ^\circ \text{C}, \pi = 5.0 \, \text{mN/m}$, 5 min after pressure jump; (b), (c) and (d) are at $T = 24.6 \, ^\circ \text{C}, \pi = 1 \, \text{mN/m}$ with time after pressure jump of 100 min, 6 hour 10 min and 6 hour 12 min, respectively. The horizontal full width of each image is 430 $\mu$m (adapted from Flores et al. [63]).

2.2.3 Atomic Force Microscopy (AFM)

Though we can observe the large scale structure changes by BAM, we typically have to specify the optimal point for transferring the thin film at the air-water interface onto a
solid substrate. To verify the quality of the transferred thin film, we use the atomic force microscopy (AFM) to measure the thickness and the morphology of the thin film.

A Nanoscope IIIA atomic force microscopy (Digital Instruments, Plainview, NY) is used. Figure 2.6 shows the scheme of basic principle of AFM [66, 67]. As shown in Figure 2.6a, the main parts of AFM are the incident laser, cantilever, tip, sample stage, scanner and the detector, which consists of a mirror and a photodiode. The tip is mounted onto a cantilever spring, while the sample is mounted on the piezoelectric scanner. The incident laser shines on the tip and the reflected light is directed onto a photo-detector. AFM images are generated by scanning the sample surface in both the X- and Y-direction. In this project, we operated the AFM in “tapping mode”. The tip oscillates in a constant frequency. When the tip starts to “scan” the sample surface, the moving part is the piezoelectric scanner. Once the tip “feels” the structure on the surface, it will detect the vertical movement then the position of the reflective laser beam on the photo-detector would change. In order to maintain the constant force, the signal from the detector generates an electronic feedback through the machine that the scanner would lower or raise the stage to decrease or increase the distance between surface and tip. AFM can measure the interaction between the tip and the surface due to capillary, electrostatic, van der Waals and frictional forces, ranging from $10^{-12}$ to $10^{-6}$ N [68].
Figure 2.6. Schematic illustration of AFM: (a) General parts in an AFM; (b) when the tip moves along the sample surface, it bends because of the interaction between tip and the surface.

2.2.4 Transmission Electron Microscopy (TEM)

Besides observing the structure changes in real time from BAM at micron resolution, it is also crucial to understand the configuration formed by nanostructures, i.e. CdSe TPs. Therefore, TEM is one of the options that allow us to image those clusters.

In the early of twentieth century, scientists tried to utilize electrons as the light source to overcome the limitation of relative large wavelength from visible lights. A modified correlation of wavelength of electrons in TEM is [69]:

\[
\text{correlation of wavelength of electrons in TEM} = \frac{1}{\lambda} \quad \text{(in TEM)}
\]
\[ \lambda_e \approx \frac{h}{\sqrt{2m_0E(1 + \frac{E}{2m_0c^2})}} \]  

where \( h \) is Planck’s constant and \( m_0 \) is the rest mass of an electron. Figure 2.7a shows the main scheme illustration of TEM (adapted from Rose [70]). Generally the emission light source of TEM is a tungsten filament or a lanthanum hexaboride (LaB\(_6\)) source [71]. By applying high voltage of current through the filament connecting with the electron gun, the electron gun starts to emit electrons; then use electromagnets to manipulate the electron beam. By increasing or decreasing the intensity of magnetic field, one would be able to vary the focusing power. Normally there are three lenses in TEM for forming the images: condenser lenses, objective lenses and projector lenses. Condenser lenses are charge of primary beam formation, while objective lenses are used for focusing beam on the sample and projector lenses are responsible for expanding beam on imaging devices, respectively. We used JEOL 1230 High Contrast Transmission Electron Microscopy (HC-TEM) (JEOL, Tokyo, Japan) in this project, which has working voltages of 40-120 kV, as shown in Figure 2.7b.
2.2.5 Ultraviolet-Visible (UV-vis) Spectrophotometer

UV-vis spectrophotometer is widely used to determine the optical properties of materials [72-75] in analytical chemistry. The \( \pi \)-electrons or non-bonding electrons of the materials can absorb the incident light ranging from ultraviolet to visible light and get excited to higher energy molecular orbitals. The relationship between the absorbance and the solution concentration is the Beer-Lambert Law. In Chapter 4, UV-vis absorption
tests are performed to determine how the band gap of MEH-PPV was influenced by various solvent combinations. We used a Shimadzu UV-2450 (Shimadzu, Kyoto, Japan), as shown in Figure 2.8 to conduct the UV-vis absorption tests.

![Shimadzu UV-2450](image)

**Figure 2.8.** Picture of Shimadzu UV-2450.

### 2.2.6 Photoluminescence (PL) tests

On the other side, once the $\pi$-electron was excited to higher molecular orbital, eventually it will return from the excited state to certain vibrational levels of the ground state and emit energy in the form of light, known as the photoluminescence (PL) effect. Therefore, a spectrofluorometer is used to measurement the emitted fluorescence signals to determine the vibrational levels of the structure. In Chapter 4, we test how the
emission spectra changed with where we transferred the MEH-PPV thin film, i.e. surface pressure; in Chapter 5, this technique also helped us to determine the best ratio between CdSe TPs and MEH-PPV to obtain the best charge transfer. We conducted the PL tests by using SPEX FluoroLog-3 spectrofluorometer (Horiba Jobin Yvon Inc., Edison, NJ) as shown in Figure 2.9.

![SPEX FluoroLog-3 spectrofluorometer](image)

**Figure 2.9.** Picture of SPEX FluoroLog-3 spectrofluorometer.

### 2.3 Methodology

#### 2.3.1 Langmuir isotherms, Langmuir-Blodgett/Langmuir-Schaefer transfer
As mentioned earlier, CdSe TPs, POPC, and MEH-PPV were dispersed in CF or CB. The mixed systems, CdSe TPs/POPC, MEH-PPV in CF/CB, and CdSe TPs/MEH-PPV, were mixed immediately every experiment. A 100 μL syringe (Hamilton, Reno, NV) is used to spread out the desired amount of the mixture at the air/water interface of the trough. For pure sample experiments, we dilute the prepared bulk solution to the desired concentration then spread it out on the trough. After a desired amount of the sample was added to the interface, the solvent was allowed to evaporate for 20 minutes for CF, and 40 minutes for CB or CF/CB to ensure complete solvent removal from the interface in Chapter 4. Afterwards, the barriers were normally set to decrease the effective trough area at a rate of 1500 mm²/min. When the Langmuir trough was mounted on BAM, the compressing rate of the barriers was set even slower at 600 mm²/min in order to take undisturbed images. All the experiments were performed at 20 ± 0.1 °C, which was controlled by the thermal circulator, F25-Heating and Refrigerated Circulator (Julabo, Kutztown, PA).

When taking real time images of the monolayer using BAM, the Langmuir trough was mounted such that the focus of the laser beam was at the air/water interface, as shown in Figure 2.10. We further transferred the thin films onto carbon support grids for TEM imaging and silicon wafers from AFM analysis. Further details on the transfer experiments will be elaborated in the corresponding chapters.
When working with BAM, the compressing rate of the barrier of Langmuir trough was set at 600 mm²/min.

2.3.2 Fabrication of the hybrid solar cell

Figure 2.11a shows the basic structure of a solar cell. The anode, or called photoanode, is typically indium tin oxide (ITO) or fluorine-doped tin oxide (FTO); meanwhile, there have been a number of different metal cathodes such as Al, Ag, Au, Ca [34-36, 41]. Many researchers have focused on improving the PCE by applying different oxidized layers between the photoactive layer and cathode [76]. Depending on whether the solar cell assembly is conventional or inverted [76], either the ITO or FTO can be treated as cathode, vice versa. The structure of the solar cell – conventional or inverted – will affect the choice of the buffer layer, too. The buffer layer can be an electron collecting layer such as ZnO or TiO₂, while a mixture of poly(3,4-ethylenedioxythiophene) and poly(styrenesulfonate) (PEDOT:PSS) is the most common hole transparent layer used [76]. The buffer layer is used for smoothing the rough surface
of electrodes, improving the contact between them and the photoactive layer and reducing the contact resistance; meanwhile, it also helps to collect more holes/electrons and blocks the counter charges [34-36, 41]. In Figure 2.11b, we depict the structure of heterojunction hybrid solar cell in Chapter 5.

The patterned ITO substrates were purchased from Ossila (Sheffield, UK). These solid substrates were washed and ultrasonicated successively in solutions of acetone, water, and then isopropanol, followed by ozone-plasma cleaning for 10 minutes prior to use. Conventionally, PEDOT:PSS is widely used as the hole transparent. However, because the process we propose in Chapter 5 involves the water surface, water-soluble PEDOT:PSS layer will not be suitable [77]. Therefore, TiO$_2$ is chosen as the electron collecting layer to replace PEDOT:PSS, as well change the solar cell to an inverted type of hybrid solar cell [76, 78]. The ethanol-TiO$_2$ solution was made in the following procedure [78]: First, mix ethanol, deionized water and concentrated hydrochloric acid under the volume ratios of 100, 2.5 and 1, respectively. Then titanium tetraethoxide was mixed with the ethanol solution above with the volume ratio of 1 to 8. The mixture solution was stirred for 20 minutes and filtered through a 0.45 $\mu$m filter before use. We will reveal more specific fabrication details in Chapter 5.

Another issue that came up in this fabrication process is about the ligand exchange step. In papers reported by Greenham et al. in 1996 [42] and 1997 [79], they indicated that by replacing the ligand, trioctylphosphineoxide (TOPO), coated either on CdS or CdSe nanoparticles with pyridine, the charge separation between the inorganic nanocrystals and MEH-PPV significantly improved (Figure 2.12a). Since then, most of the ligand exchange steps that took place in the making of the organic/inorganic hybrid solar cell
have mainly followed this method [34-36, 41]. However, this ligand exchange step was accomplished before the nanocrystals were combined with the conjugated polymer, and consequently this step typically results in the formation of aggregated nanocrystals since the short ligand (pyridine) cannot prevent coagulation of the nanocrystals in a bulk solution, as shown in Figure 2.12b. We simply cannot deposit this type of irregular and polydisperse clusters onto the air/water interface. Therefore, a new method is needed to achieve the ligand exchange step.

**Figure 2.11.** Schematic illustration of (a) a conventional solar cell; (b) inverted type we utilized in Chapter 5.
Figure 2.12. Effect of replacing the ligand on the nanocrystals: (a) two nanoparticles, CdS and CdSe, were studied here; black dots present nanocrystals with TOPO ligands coated and hollow squares are nanocrystals treated with ligand exchange by pyridine. The PL intensity decreased with increasing weight percentage of nanocrystals, indicating better charge transfer between MEH-PPV and nanocrystals (adapted from Greenham et al. [42]); (b) TEM images of the CdSe sTPs used in the thesis being treated with ligand exchange of pyridine as well. We can clearly see that these TPs aggregated to a larger cluster instead of more well-distributed over the TEM grid, compared to Figure 2.1a.

The aggregation issue arisen from the ligand exchange step has drawn great attention to those that utilize nanoparticles for solar cells [34-36]. An alternative method is to conduct the ligand exchange step after the device is made. Seo et al. [80] used acetic acid as the short ligand to replace the long ligand, oleic acid, from the surface of PbS
nanocrystals as shown in Figure 2.13. The results from Fourier Transform Infrared (FTIR) spectroscopy (Figure 2.13a) shows that the peak at 1460 cm$^{-1}$ of $\nu$(CH$_2$) bending decreases while the peak at 1337 cm$^{-1}$ increases for $\nu$(CH$_3$) bending (the two dotted lines) [81]. This is the evidence that oleic acid (CH$_3$[CH$_2$]$_7$CH=CH[CH$_2$]$_7$COOH) was replaced by acetic acid (CH$_3$COOH) since acetic acid only has methyl group, while the signals for carboxylic group at 1537 and 1410 cm$^{-1}$, representing the anti-symmetric $\nu_{as}$(COO$^-$) and the symmetric $\nu_s$(COO$^-$) stretches of the oleate ligand bound to the nanocrystal, respectively, remain before and after the treatment [82].

We utilize this procedure to replace oleic acid ligands from CdSe TPs. This method is conducted as a post-treatment to avoid undesired aggregation of CdSe TPs during processing. In detail, the ligand exchange step was completed by submerging the device, before depositing silver layer, in an acetic acid/acetonitrile solution (the concentration of acetic acid was from 0.01M to 1M) under continuous stirring for 30 minutes [80]. The average thickness of the final photoactive layer was about 100 nm, measure by profilometry. The silver electrode then was thermally evaporated onto the photoactive layer with thickness of 80 nm. A post-annealing step was completed right after the silver electrode deposition at 150 °C for 30 minutes. The photoactive area of the device is 3.9 mm$^2$. The solar cells were tested by the light simulator and the I-V curve was recorded. A typical I-V curve is shown in Figure 2.14. The intercept point of the curve with V-axis is called open-circuit voltage ($V_{oc}$), while the one with I-axis is called short-circuit current ($I_{sc}$). $V_{oc}$ is determined by the combination of band gaps of materials in the photoactive layer. One can find the maximum power point ($P_{max}$) along the characteristic curve, and
the corresponding voltage and current is noted as $V_{\text{max}}$ and $I_{\text{max}}$, respectively. The PCE ($\eta$) can be calculated by the following relation:

$$
\eta = \frac{P_{\text{max}}}{P_{\text{in}}} = \frac{V_{\text{OC}} \times I_{\text{SC}} \times FF}{P_{\text{in}}}
$$

(2.5)

where $P_{\text{in}}$ is the incident light power. $FF$ is the fill factor, which is an indicator of the quality of the solar cell. $FF$ can be obtained by the relation below:

$$
FF = \frac{P_{\text{max}}}{V_{\text{OC}} \times I_{\text{SC}}} = \frac{V_{\text{max}} \times I_{\text{max}}}{V_{\text{OC}} \times I_{\text{SC}}}
$$

(2.6)

in Chapter 5, these four parameters were used to evaluate the performance of the hybrid solar cell.
Figure 2.13. (a) FTIR spectra for PbS nanocrystals treated with acetic acid/acetonitrile solution under different time; (b) schematic of fabrication steps for the solar cell (adapted from Seo et al. [80]).

Figure 2.14. Schematic of a I-V characteristic curve of a solar cell. One can notice that $FF$ is the ratio of the yellow-shaded area to the blue-shaded area. When two areas are closer to each other, it gives a higher $FF$ and PCE.
2.4 Summary

We use a Langmuir trough to perform the template strategy of ordering CdSe TPs at the air/water interface, either with POPC or MEH-PPV. By combing Langmuir trough with BAM, we are able to record real-time images of the morphology on the trough. Further characterization of the LB/LS thin films of pure materials and mixtures are completed by TEM and AFM. Other optical properties such as absorption and fluorescence emission tests were accomplished by UV-vis spectrophotometer and spectrofluorometer. The fabrication of the hybrid solar cells were made via the LB transfer and conventional spin-coating method. In the following three chapters, we will elaborate on more experimental details and the results from CdSe short TPs/POPC system (Chapter 3), MEH-PPV deposited from CF/CB onto the air/water interface (Chapter 4), and CdSe long TPs/MEH-PPV system and its application on the hybrid solar cell (Chapter 5).
3 Templating CdSe Tetrapods at the Air/Water Interface with POPC Lipids

Surfactants have been widely used as templating agents to pattern the orientation of nanoparticles of various conformations. In this chapter, we report the use of a lipid, 1-palmitoyl-2-oleoyl-sn-glycero-3-phosphocholine (POPC), as a template to order CdSe tetrapods (TPs) at the air/water interface using a Langmuir trough. The surface pressure versus area isotherms for CdSe TPs and CdSe TPs/POPC are examined and monitored by Brewster angle microscopy (BAM). The transferred thin films are further characterized by transmission electron microscopy (TEM) and atomic force microscopy (AFM). Initially disc-like structures containing randomly oriented TPs form during solvent evaporation. Upon decreasing surface area, these discs merge into larger continental structures. In a mixed CdSe TPs/POPC system, these discs organize into wire-like networks upon compression. We detail how lipid molecules can be used to direct the two-dimensional assembly of TPs.
3.1 Introduction

Controlling the aggregation of nanocrystals in the active layer has remained a challenge in the development of the organic/inorganic photovoltaic devices. The morphology within the active layer of the photovoltaic device is a crucial factor in a cell’s performance [41, 83]. It is thought that vertically aligned nanocrystals favor higher power conversion efficiencies (PCE) [38, 41, 84-86]. One of the advantages of tetrapod-shaped semiconducting nanocrystals is their tendency to orient normal to the substrate 4. The branched structure of semiconducting tetrapod nanocrystals, CdSe [37, 49, 87, 88], CdTe [89] and ZnO [90, 91], has also been shown to enhance the external quantum efficiency (EQE) of photovoltaic devices [38]. The most common current method used to assemble the active layer is based on spin coating a mixture of conjugated polymers and inorganic nanocrystals. This solution process is followed by solvent evaporation and an annealing step to make the active layer. Control of the aggregate morphology is exerted on a macroscopic scale by tuning the annealing temperature and time [43]. In this Chapter, we examine a new method to control nanocrystal aggregation using lipid molecules to create a well-controlled 2-D thin film of CdSe TP aggregates using a “bottom-up” method via 2-D templating using a Langmuir-Blodgett technique.

As we introduced in Chapter 1, several groups have shown the application of the template organization at the air/water interface, for example, amphiphilic polymers can be used to order gold nanoparticles into different structure such as network [26]. These soft templates oftentimes can organize into multiple configurations, leading to a multitude of templates to organize the nanoparticle. One particular example is that of templating gold nanoparticles with dipalmitoylphosphatidylcholine (DPPC) [25]. It is
thought that DPPC molecules form an interface between the nanoparticles and the water surface, causing the DPPC to control the assembly of the nanoparticles at the air/water interface. We will relate back to this report later again in the discussion section. Previous work has only used templating molecules with spherical particles. In this study, we utilize lipid molecules as soft templates to stabilize 2-D structures of tetrapod-shaped nanocrystals. Interestingly, the anisotropic shaped tetrapods have the ability to adopt a larger number of conformations compared to the spherical nanoparticles previously studied. Additionally, TPs have the ability to interdigitate with each other. We ask whether the lipid molecules, which have a much smaller area per molecule at the interface than the TPs, can lead to long-range ordered TPs.

Experimentally, the self-assembly of CdTe TPs at the air/water interface has been reported previously [15], however, there has not been investigations into the use of template-directed assembly to create well-ordered TP structures. Sinkovits and Luijten [92] recently used simulations to predict how the assembly of tip-functionalized TPs can be manipulated sterically by charged nanoparticles. Here, we use 1-palmitoyl-2-oleoyl-sn-glycero-3-phosphocholine (POPC, Figure 2.2a and 3.1a) as a soft template to control the assembly of oleic acid coated CdSe TPs (Figure 3.1b) at the air/water interface. Note that the TPs here are the short one we introduced in Chapter 2. POPC is stable at room temperature and the 2-D phase behavior has already been extensively studied [93, 94]. Concurrent microscopic visualization with changing surface pressures is achieved using Brewster angle microscopy (BAM). In general, we can monitor changes in the structure of the monolayer from a gas-like phase to a liquid phase until it reaches the limit of stability in 2-D and finally collapses into a 3-D structure. Further characterization of the
thin film using atomic force microscopy (AFM) and transmission electron microscopy (TEM) is accomplished by transferring the thin film from the air/water interface onto the desired substrate.

Figure 3.1. Components of TPs/lipid system: (a) the molecular structure of POPC; (b) TEM image of CdSe TPs. The scale bar in the inset represents 20 nm.

3.2 Materials and Methods

3.2.1 Materials

Coated with a layer of oleic acid, CdSe TPs are dispersed in chloroform with estimated concentration of 20 mg/mL (i.e. 7.86 μM). POPC is dissolved in chloroform at a concentration of 2 mg/mL (i.e. 2.63 mM) and stored in the refrigerator (-4 °C) until use. The water used in the Langmuir-Blodgett trough was pretreated with a Thermo Scientific
Barnstead Nanopure Diamond system (Thermo Fisher Scientific, Waltham, MA, USA) at resistivity of 18.2 mΩ-cm.

### 3.2.2 Langmuir Isotherms and Langmuir-Blodgett Depositions

The TP and lipid solutions are mixed at equal volumes prior to each experiment. After 100-150 µL of the sample is added to the interface, we wait at least 20 min to allow for chloroform evaporation before starting compression. The compression rate of the barriers is 5 mm/min (1500 mm²/min). All the experiments are performed at 20 ± 0.1 °C, controlled by the thermal circulator. All the transfer ratios of Langmuir-Blodgett depositions fall within the range of 1.0 ± 0.2.

### 3.2.3 Characterization

The thin film at the air/water interface was transferred vertically onto the TEM grids for TEM imaging and Si substrates for the AFM analysis. The 300 mesh carbon type A grids were obtained from Ted Pella, Inc. (Redding, CA, USA). Si substrates were cut from Si wafer, purchased from Silicon Sense, Inc. (Nashua, NH, USA), into area of 1 cm by 0.5 cm. Each Si substrate was washed by acetone, water, isopropanol and piranha solution (caution: strong oxidizing solution) right before the experiment [18]. The procedures of characterization on BAM, TEM, and AFM were following the protocol we detailed in Chapter 2.
3.3 Results and Discussion

The average arm length and diameter of the CdSe TPs here are, respectively, 11.0 nm and 4.5 nm. The oleic acid coating (nominally ~2 nm thick) imparts colloidal stability to the particles suspended in chloroform. These particles orient so that the three arms sit on the substrate while the fourth arm projects away from the surface, as shown by the black dot in the inset of Figure 3.1. The isotherms for POPC, CdSe TPs and CdSe TPs/POPC are shown in Figure 3.2 with corresponding BAM images indicating the film structuring at the air/water interface under various surface compressions.

**Figure 3.2.** Langmuir isotherms of CdSe TPs (-----), POPC (········) and CdSe TPs (0.29 mol %)/POPC (———). The insets: BAM images of POPC (a and b), CdSe TPs (c – e) and CdSe TPs/POPC (f and g). The scale bars in BAM images are all 100 µm. The long red dash line is the extrapolation line made at 15 mN/m, giving us the limiting area of 240 nm².
3.3.1 Pure POPC and CdSe TPs systems

In Figure 3.2a, we observe the typical gas-liquid-expanded coexistence phase for POPC where there are void spaces in the POPC monolayer. This phase, which is seen in amphiphilic molecules like pentadecanoic acid [95] and lipids [96], is known as a “Langmuir foam.” As the POPC film is compressed further it undergoes a phase change from the gas-liquid-expanded coexistence phase to the liquid-expanded phase. The surface becomes relatively smooth and the void spaces found in gas-liquid-expanded coexistence phase disappear, as shown in Fig. 3.2b. The liquid-expanded monolayer collapses close to 48 mN/m, consistent with that reported previously [93, 94]. This corresponds to a POPC cross-sectional area of 0.9 nm\(^2\).

The isotherm for pure CdSe TPs has three stages: a plateau at the beginning of the compression then an increasing surface pressure when the mean molecular area is compressed from 250 to 125 nm\(^2\); followed by a short plateau, where the monolayer collapses, and finally a step jump after 90 nm\(^2\), corresponding to the formation of a multilayer. The corresponding BAM images, shown in Figure 3.2c – e, follow the phases observed via the isotherm. Before compression is applied, large aggregates of TPs form at the interface, as shown in Figure 3.2c and corresponding low magnification TEM images in Figure 3.3. Upon compression, these aggregates form larger and more densely packed structures (Figure 3.2d), at which point the surface pressure keeps increasing. Finally, the complete coverage of the surface is achieved and the aggregates are compressed so that the monolayer collapses to form multilayers, as shown in Figure 3.2e.
**Figure 3.3.** Low magnification of TEM images of transferred CdSe TP aggregates at (a) 0 mN/m and (b) 5 mN/m. The large aggregates in (a) is size-comparable to those island structures we observed from BAM images (Figure 3.2c). And the surface coverage of CdSe TPs aggregates on the water surface increases with surface pressure. The scale bar corresponds to 5 μm.

TEM images (Figure 3.4) reveal more detail about the conformation formed by TPs. We can see from Figure 3.4a that initially TPs aggregate into disc-like structures with diameter around 100 nm at the water surface. This structure varies from the ribbon-like structure of CdTe TPs observed by Goodman and coworkers [15]. In their system, ribbon-like structures of aggregates formed and continued to grow with increasing surface pressure until it collapsed at 39 mN/m. Interestingly, instead of plateauing at a constant surface pressure after collapse, they observe a rapid rise in the surface pressure after collapse, similar to what we observe in Figure 3.2e. We suspect the main difference in this initial conformation is a result of the oleic acid coating of CdSe TPs and the size
difference between our CdSe TPs and the CdTe TPs (which had an arm length of 47 nm). The CdSe TPs are deposited with chloroform onto the air/water interface. Once the solvent evaporates, the TPs undergo a dewetting process [15, 97], where the hydrophobic ligand on the TPs causes the film to destabilize, resulting in disc structures. Gelbart et al. [98] observed that spherical nanoparticles assemble into discs at the air/water interface when the radius of metal core of the nanoparticle is larger than the thickness of coated surfactant. Various conformations, from discs to hexagonal closed-packed arrays were observed with spherical nanoparticles as the surface pressure increased. In our system, the oleic acid coating thickness is much smaller than the TPs, leading to the initial disc structures, which falls into the prediction from Gelbart’s. Upon further compression, these discs can be ordered as shown in Figure 3.3c; however, the TPs are unable to order within the discs. This is likely because of the anisotropic structure of the TPs, where multiple configurations and particle interdigitation are favorable.

The TP monolayer thickness is 14.7 nm estimated from its arm length. From AFM analysis at 0 mN/m, the average thickness of the thin film is 14.6 nm. Additionally, each TP occupies an area of 340 nm$^2$ at the onset point (also based on a 2-D area calculated from its arm length). A limiting area of 240 nm$^2$ is obtained by extrapolating the linearly increasing region from 8-15 mN/m, as shown in Figure 3.2. The ratio between the onset area and the limiting area is 1.4, indicating that there is some interdigitation of the TPs. Eventually the monolayer of TPs collapses, as shown in Figure 3.4d. At 20 mN/m, the average thickness of the film is 16.2 nm, while it increases to 26.2 nm at 35 mN/m. The TP aggregates remain the same size with increasing surface stress until collapse. This is in contrast to Goodman et al. [15] who showed that their larger CdTe TPs aggregates
formed ribbons which grew in width with surface pressure. In our case, the TPs aggregates are “locked” initially and further compression does not lead to aggregate growth. The difference in configurations may be attributed to the size difference: the larger CdTe TPs are better able to entangle with each other, leading to structures that are strongly dependent on surface pressure.

**Figure 3.4.** TEM images of CdSe TPs aggregates that were transferred at (a) 0 mN/m, (b) 5 mN/m, (c) 20 mN/m, and (d) 35 mN/m, respectively. From 5 mN/m (b) to 20 mN/m (c) the disc-like TPs aggregates begin to merge with each other and form larger aggregates, eventually stacking to irregular multilayer structure (35 mN/m, d). The scale bars in images represent 100 nm.
3.3.2 Mixed POPC and CdSe TPs system

The POPC and CdSe TPs are mixed together at a number ratio of 340:1. This ratio was chosen after several control experiments to ensure that POPC would act as a templating agent. When the mixture is placed at the air/water interface, we observe that the CdSe TP aggregates preferentially organize in the liquid-expanded regions, resulting in a pattern similar to that of the pure POPC, as shown by BAM images in Figure 3.2f, as opposed to the large irregular aggregation observed in the pure CdSe TPs case (Figure 3.2c). This is especially evident at low surface pressures. Further compression packs the TP aggregates closer together (Figure 3.2g). From the isotherm of the mixture, we also found that once POPC is added to the system, the available area for CdSe TPs decreases, as we can see that the surface pressure of POPC/CdSe TPs climbs up much earlier than the limiting area (240 nm$^2$) for pure CdSe TPs.

The mixture of CdSe TPs/POPC illustrates a distinctly different assembly from that of the pure CdSe TPs case. Figure 3.5a–d depict the morphological change of TPs aggregates in POPC from 0 mN/m to 35 mN/m. Similar to that observed in the pure TP case, the TPs assemble into disc-like aggregates, as shown in Figure 3.5a. With additional compression, the disc structures start to touch and after 20 mN/m the discs begin to merge together, forming a pearl necklace-like structure. Finally, at a surface pressure of 35 mN/m, the necklace-like structure undergoes further coalescence to form wire-like structures. These aggregated TP wires are microns in length with a width that is similar to that of the original discs. This is unlike the pure TP case, where the aggregated islands become isotropically larger under compression. This is very similar to that found by Zhang et al. [99] using simulations: in 2-D system, adding larger particles into a
homogeneous system leads to clusters of small particles organized by a network of larger particles. POPC provides the function of confining and preventing large-scale aggregation of the CdSe TPs thus forcing the TPs to form a different morphology, as shown in Figure 3.5a – d. Figure 3.5e and 3.5f are the higher magnification images at 5 mN/m and 35 mN/m, illustrating the interdigitation of the TPs in either the discs or wire-like format. Also, notice that the wire structures are more densely packed with some multilayer organization.
Figure 3.5. TEM images of CdSe TPs (0.29 mol%)/POPC transferred at 0 mN/m (a), 5 mN/m (b), 20 mN/m (c) and 35 mN/m (d), respectively. Higher magnification images of 5 mN/m (e) and 35 mN/m (f). The scale bars in (a) – (d) represent 100 nm.

The AFM thickness analysis on the pure CdSe TPs and CdSe TPs/POPC thin films are summed up in Figure 3.6. As mentioned earlier, in the pure CdSe TPs case (black hollow square in Figure 3.6a), the thin film of CdSe TPs remain at 14.7 nm until the monolayer collapse and continue to form multilayer. The thickness records at 20 mN/m and 35 mN/m are 16.2 nm and 26.2 nm, respectively. We can also clearly see that the large and irregular-shaped continental structures observed in the BAM image (Figure
3.2c) are composed of numbers of discs formed by TPs, shown in Figure 3.6b. At the onset of collapse, large cracks begin to appear within the aggregates, as shown in Figure 3.6c. In the CdSe TPs/POPC case (red dot in Figure 3.6a), the disc structures do not merge until relatively high surface pressure (35 mN/m). The film remains a monolayer of CdSe TPs at 0 mN/m, 5 mN/m and 20 mN/m that are with a thickness around 15 nm (13.8 nm, 15.4 nm and 14.9 nm, respectively). After 35 mN/m, collapse occurs where the discs, excluded by the POPC molecules, merge together to form wire-like networks (Figure 3.6e) and eventually forming multilayer structures with average thickness of 21.9 nm.
Figure 3.6. (a) Thickness analysis from AFM data (black hollow square: pure CdSe TPs; red dot: TPs/POPC); the two insets are the representative profile analysis of TPs/POPC film transferred at two different surface pressure. The error bars represent one standard deviation. AFM representative images of transferred CdSe TPs thin films at (b) 0 mN/m and (c) 35 mN/m; transferred TPs/POPC thin films at (d) 0 mN/m and (e) 35 mN/m. The scale bar in each AFM image represents 2 μm and the z-range is 100 nm. We can tell that in the TPs/POPC system the morphology changed from connected discs to wire-like networks through the compression.

The Langmuir isotherms of POPC and CdSe TPs/POPC share similar features, such as the collapse point; the only distinguishable difference is the slope of the isotherm at
the increasing part of the curve, where POPC molecules move from the gas-liquid-expanded coexistence phase to the liquid-expanded phase. The slope of the Langmuir isotherm is representative of the elastic modulus of the film, $Cs^{-1}$ [100-102]:

$$Cs^{-1} = -A \left( \frac{d\pi}{dA} \right)$$

Where $\pi$ is the surface pressure and $A$ is the mean molecular area. Generally, a steeper isotherm slope indicates a more rigid film that is more difficult to compress. Adding CdSe TPs to POPC slightly increases the compressibility of the whole system. Hassenkam and coworkers [25] showed that the lipid molecules (DPPC) provided a barrier between gold nanoparticles and the water surface. The gold spherical particles simply floated on the lipid molecules. To test whether the TPs also float on POPC, we perform a simple experiment as shown in Figure 3.7 in which we utilize fluorescent lipids to monitor the lipid organization. We mixed 1-palmitoyl-2-{12-[(7-nitro-2-1,3-benzoazadiazol-4-yl)amino]dodecanoyl}-sn-glycero-3-phosphocholine (NBD-PC), the indicator of the distribution of POPC, with POPC at 1 mol %, and repeated the same experiments described before. Uniform fluorescence can be observed in the pure POPC case (Figure 3.7a). In the mixed case, the TP pattern is darker than that of the pure POPC (due to strong absorbance by CdSe), but not completely black, indicating the presence of a lipid layer beneath the TPs acting as a mobile layer by which the TP aggregates are organized. Hence, a similar mechanism can be used to describe the TPs/POPC system: TP aggregates orient along the pattern established by the underlying POPC monolayer,
instead of forming irregular continental structures. As mentioned previously, from the BAM experiments (Figure 3.2f) the TP aggregates pack along with the liquid-expanded phase of POPC instead of the void space, meaning POPC molecules direct the placement of TP aggregates at the air/water interface. Therefore, the TPs/POPC assembly can be described as follows: at low surface pressures, the hydrophobic tails of POPC have room to orient randomly at the water surface and the TP aggregates (discs) organize on top of the POPC, to minimize water contact. At higher surface pressures, the POPC are forced to orient eventually reaching a condensed phase where the POPC become close packed with their hydrophobic tails normal to the water surface. An illustration depicting this proposed mechanism is provided in Figure 3.8. This condensing process excludes and forces the TP aggregates to join together as found in [99], eventually leading to wire networks, e.g. at 35 mN/m, of interdigitated and multilayer TPs, as shown in both AFM and TEM images.
Figure 3.7. Fluorescent microscopic images of (a) POPC/NBD-PC and (b) CdSe TP aggregates/POPC/NBD-PC transferred at 15 mN/m. Images are both taken at the edge of the thin film. We found that in (a) POPC and NBD-PC mixed very well. In the TP aggregates/POPC/NBD-PC case, the darker part represents the TP aggregates; we can tell the TPs aggregates sit on the top of POPC/NBD-PC thin film.
**Figure 3.8.** The schematic illustration of assembly mechanism of CdSe TPs/POPC. At lower surface pressure stage (i), the TP aggregates (discs) randomly disperse above POPC thin film, where some of the hydrophobic tails of POPC still lay on the water surface; (ii) when entering higher surface pressure stage, the POPC molecules come closer and the hydrophobic tails stand up. The condensing process of POPC excludes and forces the TP aggregates to link together, eventually make the multilayer wire-like networks, e.g. at 35 mN/m, as we saw from the AFM and TEM images. In this cartoon, the TPs and the POPC molecules are drawn proportionally; the coating, oleic acid, on the TPs surface is not included.
3.4 Conclusions

The 2-D assembly of nanoparticles at the air/water interface using Langmuir-Blodgett technique has been widely utilized [10-15, 103] to control nanoparticle spatial organization. More recently, template organization has been added to better stabilize and increase the possible configurations for spherical nanoparticles [25-28, 104-106]. In this chapter, we have shown how a highly anisotropic nanocrystal, CdSe TPs that have the ability to interdigitate, can self-organize with a POPC lipid template into disc-shaped aggregates upon chloroform evaporation at the water/air interface. We have shown that disc-like TP aggregates can be manipulated into wire-like structures by tuning the surface pressure of CdSe TPs/POPC thin films at the air/water interface. The resulting disc-shaped aggregates are different from that observed by Goodman et al. on the 2-D assembly of CdTe TPs at the air/water interface, where they found more ribbon-like structures [15]. The width of the ribbon-like structures formed by CdTe TPs grows with the surface pressure [15]. While for our system, disc-shaped CdSe TPs/POPC aggregates do not change in size, but are directed into wire-like structures. By utilizing POPC as a templating agent, wire-like structures of CdSe TPs were always found at high surface pressures. The justification for this work is the need to create TPs structures that are able to be organized into wire-like structures for possible photovoltaic applications. CdSe TPs have been approved as a promising material used in the organic/inorganic hybrid solar cell [38, 39, 107], but the uncontrolled aggregation of TPs has limited their use as an effective electron pathway in the active material [41]. By utilizing a templating method to organize the TPs into wire-like structures, our method offers a novel way to create well-organized TP structures, a potential benefit to creating functional active materials for
photovoltaic devices. In Chapter 5, we will show how this technique actually helps to build up the heterojunction hybrid solar cell and improve the PCE. In the next chapter, we will show how different solvent combinations affect the morphology of the conjugated polymer at the air/water interface.
4 Evaporative Assembly of MEH-PPV Rings Using Mixed Solvents at the Air/Water Interface

Controlling the morphology of conjugated polymers has recently attracted considerable attention because of their applications in photovoltaic (PV) devices and organic light-emitting diodes (OLEDs). In this chapter, we describe the self-assembly of a common conjugated polymer, poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV), into ring-like structures via solvent evaporation on an air/water interface. The films are monitored using Brewster angle microscopy (BAM) and transferred onto a solid substrate by either the Langmuir-Blodgett (LB) or the Langmuir-Schaefer (LS) method and further characterized by atomic force microscopy (AFM). The morphology of the MEH-PPV thin film at the air/water interface can be controlled by the spreading solvent. By mixing solvents of varying spreading coefficients and evaporation rates, such as chloroform and chlorobenzene, MEH-PPV can be assembled into micron-sized ring structures. The optical properties of these MEH-PPV ring structures are also characterized. Lastly, MEH-PPV can be used as a soft template to organize microscale structures of nanoparticles.
4.1 Introduction

Conjugated polymers hold great promise in applications such as organic light-emitting diodes (OLEDs) [50-54], photovoltaic devices (PVs) [33, 55-59], and field effect transistors (FETs) [108-110] because of their electrical, mechanical, and optical properties. The fabrication of these devices often uses a solution process, such as spin-casting the polymer solution on the solid substrate, making a thin film. Parameters such as the dispersed solvent, spin rate, film thickness and annealing temperature will strongly influence the polymer chain packing and the morphology of the thin film [111-113] and thus affect the physical characteristics of the thin film, for example, the optical properties. Studies have shown that the film morphology is a crucial factor for the performance of photovoltaic devices and one of the most difficult to control [43, 114].

Poly(p-phenylene vinylene) (PPV) and its derivatives are one example of a conjugated polymer that has found applications in various optoelectronic applications [115, 116]. To improve processability, side chains are attached to the PPV backbone, forming a “hairy rod” structure. One such derivative is poly(2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene) (MEH-PPV). Evaporation-induced self-assembly has been used to produce well-ordered 2-D patterns of MEH-PPV. In this method, the polymer moves to the contact line during evaporation, and the polymer template forms as the contact line undergoes a repeated stick-slip motion [117]. More recently, concentric rings of MEH-PPV have been formed by controlling the evaporation using a confined geometry [118, 119]. The limitation is controlling the contact line effectively.
Here, we report a novel method to produce rings of MEH-PPV based on the evaporation of mixed solvents at an air/water interface without the use of a contact line, typical of many evaporation-assisted assembly methods. One of the most familiar is the “coffee ring” deposition in which Marangoni flows, driven by surface tension gradients, replenishes liquid to the pinned contact line of a drying drop resulting in entrained solutes being transported to drop edge [120-122]. Our method dissolves MEH-PPV in a mixed chloroform and chlorobenzene solvent and deposits it onto an air/water interface using a Langmuir trough. The effectiveness is attributed to the differences in the solvent evaporation rates and spreading coefficients between chloroform and chlorobenzene. The formation of these MEH-PPV rings is limited to a specific blend ratio of chloroform to chlorobenzene. We use Brewster angle microscopy (BAM) to monitor the polymer morphology at the air/water interface. Additionally, we transfer the polymer films to a solid substrate using either a Langmuir-Blodgett (LB) [3] or Langmuir-Schaefer (LS) [9] technique and further characterize them using an atomic force microscope (AFM). One advantage of LB or LS is that it can be used to manufacture large-scale thin films 30 31. To the best of our knowledge, no similar results have been previously reported regarding the LB/LS films of PPV derivatives forming these ring structures [123-131]. The optical properties of these ring structures are also characterized.

### 4.2 Materials and Methods

#### 4.2.1 Materials

MEH-PPV was dispersed in either solvent at a concentration of 2.5 mg/mL. For the
hybrid solvent case, the chloroform and the chlorobenzene solution were mixed immediately before the experiment. Silicon wafers were purchased from Silicon Sense, Inc. (Nashua, NH, USA) and cut into 2 × 1 cm substrates using a diamond cutter. Glass substrates were obtained from Thermo Fisher Scientific (Waltham, MA, USA). These slides were also cut to the proper size for further characterization. The solid substrates were washed and ultrasonicated successively in solutions of acetone, water, and then isopropanol, followed by ozone-plasma cleaning for 5 minutes prior to use.

4.2.2 MEH-PPV Deposition onto a Langmuir Trough

All surface pressure isotherms and Langmuir-Blodgett/Langmuir-Schaefer transfer experiments were performed using a KSV 2000. The specification of this trough has been detailed in the previous chapters. The Langmuir trough and barriers were washed with water and ethanol before and after each use. After 30-35 μL of the sample was added to the interface, the solvent was allowed to evaporate for 20 minutes for CF and 40 minutes for CB or CF/CB to ensure complete solvent removal from the interface. Afterwards, the barriers were set to decrease the effective trough area at a rate of 1500 mm²/min. All the experiments were performed at 20 ± 0.1 °C controlled by the thermal circulator. The trough again was combined with a BAM to monitor the changes in polymer morphology at the air/water interface in real time.

4.2.3 Transfer of the MEH-PPV film to a substrate

The polymer films at the air/water interface were transferred either vertically via LB
or horizontally via LS onto either glass or silicon substrates. All the transfer ratios of Langmuir-Blodgett depositions fell within a range of $1.0 \pm 0.2$, regardless of the substrate used. The majority of films reported were transferred via LB. LS transfer was performed for experiments that examined the initial ring formation. AFM thickness measurements were recorded for a single layer on a silicon substrate with a Nanoscope IIIA atomic force microscope (Digital Instruments, Plainview, NY). The optical properties of the films were characterized using UV-visible absorbance tests performed using a Shimadzu UV-2450 (Shimadzu, Kyoto, Japan) on films with 4 layers thick. The 4-layer film was transferred consecutively via LB from the air/water interface onto a glass slide while keeping the surface pressure constant. Birefringence measurements for a single layer on a glass substrate were also conducted using a Zeiss Axioplan 2 polarized optical microscope (Zeiss, Thornwood, NY, USA). Images of the film were taken with the polarizer/analyzer at a $0°/+90°$ configuration and a $-45°/+45°$ configuration.

### 4.3 Results and discussion

#### 4.3.1 MEH-PPV ring structures and corresponding surface pressure isotherms

Figure 4.1 shows characteristic BAM images of MEH-PPV at the air/water interface for various solvent mixtures at low surface pressure. In the pure solvents, either chloroform or chlorobenzene, the polymer is distributed over the trough area fairly uniformly, but each has a particular morphology. As shown in Figure 4.1a and 4.1b, when deposited from chloroform (CF), the MEH-PPV forms a network-like morphology
versus a close-packed island-like structure from chlorobenzene (CB). MEH-PPV ring structures appear when the polymer is deposited from a blended CF/CB solvent at ratios of 2:1 or 5:1, respectively. These rings have a diameter ranging from 1.5 \( \mu \text{m} \) to 100 \( \mu \text{m} \). A larger distribution in the size of the rings and higher packing density is characteristic of the higher CF blended solvent (shown in Figure 4.1d and Figure 4.2c). As the solvent ratio of CF/CB is increased to 10:1, the ring structure disappears. We conducted tests on reversed mixed solvent ratios, such as 1:2 and 1:5, and could not find ring structures (data not shown) at the air/water interface.

Figure 4.1. BAM images of MEH-PPV film deposited from (a) chloroform (CF), (b) chlorobenzene (CB), and hybrid solvent combinations of (c) CF/CB = 2:1, (d) CF/CB = 5:1, (e) CF/CB = 10:1. Scale bars: 100 \( \mu \text{m} \).

As shown in Figures 4.2a and 4.2b, AFM analysis of a representative MEH-PPV ring formed using a CF/CB solvent ratio of 2:1 shows uniform radial symmetry of the ring. The ring thickness measurements are shown in Figure 4.2c. Interestingly, for rings formed at a CF/CB solvent ratio of 5:1, the average ring thickness is approximately 26 nm, regardless of the ring size. For a CF/CB solvent ratio of 2:1, the average ring
thickness is closer to 38 nm, but there is a larger standard deviation for this ratio (11.8 nm). Additionally, the average diameter for rings formed at a CF/CB solvent ratio of 5:1 is 10.3 μm, while for a CF/CB solvent ratio of 2:1, it is 15.1 μm. We run another control experiment with CF/CB = 2:1 for different volumes as shown in Figure 4.3. We found that the added amount of polymer solution onto the air/water interface is not a critical factor to either ring thickness or ring diameter. The average ring thickness and size from adding 60 μL is 34.6 nm and 16.0 μm, respectively, while it is 32.9 nm and 12.8 μm from adding 15 μL. We did see that there are a few larger ring structures found in the 60-μL case but mostly ring diameter falls under 30 μm. Increasing the volume of the polymer solution added to the air/water interface did not change the average thickness of the film. Therefore, having a higher-CF blended solvent combination deposited on the water surface yields smaller and thinner MEH-PPV ring structures.
Figure 4.2. Representative (a) height and (b) cross-sectional AFM images (deposited from CF/CB = 2:1, transferred at a surface pressure of 10 mN/m) of the ring structure. The images are 20 μm × 20 μm. (c) AFM height analysis of MEH-PPV film deposited from CF/CB = 2:1 (black dots) and CF/CB = 5:1 (red squares).
Figure 4.3. The control experiment about the added volume effect: AFM thickness analysis of MEH-PPV film deposited from CF/CB = 2:1 with added volume of 15 µL (green triangle) and 60 µL (purple circle).

The isotherms of the surface pressure versus trough area for MEH-PPV deposited from different solvent ratios are shown in Figure 4.4. These four isotherms are similar in that they exhibit a liquid-expanded phase and collapse at a surface pressure of approximately 15 mN/m. The main difference is the onset point of entering the liquid-expanded phase. For the CF case, this onset occurs at a smaller trough area than for the CB case, indicating that MEH-PPV occupies a larger surface area when deposited from CB. This observation is consistent with the simulation result indicating that there is a higher degree of π-π stacking along the MEH-PPV chain in CB after solvent evaporation [132]. In the hybrid solvent cases, we found that at the volume ratio of CF/CB = 2:1, the
onset point of the trough area is larger. This observation can be explained based on the BAM images (Figure 4.1c and 4.1d). We observed that in the case of CF/CB = 2:1, the packing density of the ring structures is not as high as in the case of CF/CB = 5:1. Additionally, the average ring diameter in the case of CF/CB = 5:1 is smaller, and therefore, the onset point requires a smaller trough area before the rings contact each other.

**Figure 4.4.** Surface pressure versus trough area of MEH-PPV deposited from different solvent combinations of CF (green), CB (blue), CF/CB = 2:1 (yellow) and CF/CB = 5:1 (red).
4.3.2 Optical properties of MEH-PPV rings

To determine whether the MEH-PPV rings possess new properties, various optical measurements were performed. The UV-visible absorption spectra for MEH-PPV thin films deposited onto glass slides under different solvents at a surface pressure of 10 mN/m are shown in Figure 4.5. The spectra for films of MEH-PPV rings are red-shifted compared to the films formed in the pure solvents. Table 4.1 shows the wavelength where maximum absorbance is observed for MEH-PPV films at different surface pressures and solvent ratios. For the pure solvent cases, the absorption peak is a function of the surface pressure and undergoes a blue shift with increasing surface pressure. For the hybrid solvent cases where MEH-PPV rings are observed, the absorbance peak is independent of the surface pressure. Additionally, the band gap of the MEH-PPV film was estimated with Tauc’s relation [133-135] under various solvent conditions, as shown in Table 4.2. The band gap is slightly lower for the mixed solvent case where MEH-PPV rings are observed. This lower band gap behavior implicitly indicates a high degree of π-π stacking between the polymer chains [136]. Band gap of a material refers to the energy different between the highest occupied molecular orbital and the lowest molecular orbital. The band gap of a conjugated polymer could be adjusted by adding substituted group on the benzene ring or side chain [33], which requires new synthetic methods normally. Here we provided an easier way to fine-tune the band gap of MEH-PPV. Even though the difference of band gaps between solvent combinations are not significant, we have not seen this behavior reported in the literature to the best of our knowledge, among the MEH-PPV thin film at the air/water interface [124, 127, 129].
Figure 4.5. UV-visible absorption spectra of MEH-PPV thin films transferred at a surface pressure of 10 mN/m.

Table 4.1. UV-visible absorption measurements of the wavelength at maximum absorbance for MEH-PPV films formed under varying solvent combinations at different surface pressures.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$\lambda_{\text{max}}$ (nm) $\pm 10\text{ mN/m}$</th>
<th>$\lambda_{\text{max}}$ (nm) $\pm 14\text{ mN/m}$</th>
<th>$\lambda_{\text{max}}$ (nm) $\pm 18\text{ mN/m}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CF</td>
<td>473</td>
<td>449</td>
<td>439</td>
</tr>
<tr>
<td>CB</td>
<td>480</td>
<td>478</td>
<td>456</td>
</tr>
<tr>
<td>CF/CB=5:1</td>
<td>517</td>
<td>517</td>
<td>514</td>
</tr>
<tr>
<td>CF/CB=2:1</td>
<td>500</td>
<td>500</td>
<td>500</td>
</tr>
</tbody>
</table>
Table 4.2. Band gap calculations and maximum absorbance peaks of MEH-PPV films deposited under different solvent combinations at a surface pressure of 10 mN/m.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$\lambda_{\text{max}}$ (nm)</th>
<th>Band gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CF</td>
<td>473</td>
<td>2.19</td>
</tr>
<tr>
<td>CB</td>
<td>480</td>
<td>2.25</td>
</tr>
<tr>
<td>CF/CB=5:1</td>
<td>517</td>
<td>2.16</td>
</tr>
<tr>
<td>CF/CB=2:1</td>
<td>500</td>
<td>2.15</td>
</tr>
</tbody>
</table>

Previous reports have shown that MEH-PPV films formed by spin-casting exhibit birefringence behavior that is dependent on the molecular weight of the MEH-PPV [137, 138]. Koynov and coworkers showed that thin films of high molecular weight MEH-PPV (Mn = 1.05 × 10^5 g/mol) formed by spin-coating in toluene exhibited large birefringence due to their highly oriented PPV chain segments compared to low molecular weight MEH-PPV (Mn = 6.4 × 10^3 g/mol), which had randomly oriented chain segments. For MEH-PPV rings formed under a CF/CB = 2:1 ratio, large birefringence is also observed, indicating highly ordered PPV chain segments, as shown in Figure 4.6. Interestingly, although we are using a high molecular weight MEH-PPV, films formed using a pure solvent (CF or CB) do not exhibit birefringence, indicative of isotropic orientation of chain segments. In addition to molecular weight, the solvent plays a critical role in controlling the polymer morphology.
Figure 4.6. Birefringence images from the case of CF/CB = 2:1. (a) Bright field image; (b) polarizer set at 0° and analyzer at +90°, orthogonally; (c) polarizer set at -45° and analyzer at +45°. The scale bar represents 20 µm.

4.3.3 Proposed Mechanism for Ring Formation

The spreading coefficient describes the difference between the work of adhesion and the work of cohesion of a liquid spreading on a surface [139]. The spreading coefficient of a solvent onto a water surface can be calculated as follows: 

\[ S = \gamma_{\text{water}} - \gamma_{\text{solvent}} - \gamma_{\text{solvent-water}} \]

where \( \gamma_{\text{water}} \), \( \gamma_{\text{solvent}} \) and \( \gamma_{\text{solvent-water}} \) are the surface tension of water, the surface tension of the solvent and the interfacial tension between the two liquids, respectively. When the spreading coefficient is positive, the spreading process is spontaneous. The spreading coefficients for chloroform and chlorobenzene are 13.04 mN/m and 2.31 mN/m, respectively [140], at 20°C. The smaller spreading coefficient of chlorobenzene indicates that it spreads less easily on the water surface than chloroform. The MEH-PPV morphology is controlled by the dewetting of the solvent at the air/water interface during solvent spreading and evaporation. One common theory is that as the
solvent evaporates, the polymer film thins until it reaches a critical thickness where it ruptures [141, 142]. In the case of the hybrid CF/CB solvent cases, there is a competition between the spreading of the two solvents. Figure 4.6 shows a MEH-PPV ring in a solvent ratio of 2:1 captured via LS transfer immediately after deposition onto the air/water interface. Notice that holes have nucleated within the polymer film, as shown in Figure 4.7a. A closer examination of the MEH-PPV film in Figure 4.7b shows that the polymer films appear to thin radially, dewetting from the surface, and form a ring structure.

![Image](image_url)

**Figure 4.7.** Transferred ring structure immediately via LS transfer after deposition of polymer solution (CF/CB = 2:1) at the air/water interface: (a) the image is 20 μm × 20 μm, and the red square represents the location of image (b); (b) we can see the residual thin polymer film still slightly attached to the rim.

Molecular simulations of MEH-PPV under various solvent conditions offer insight into why microscale ring structures are observed. Simulations by Shi and coworkers...
showed that in an aromatic solvent, such as chlorobenzene, the ethyl-hexyloxy side chains of MEH-PPV tend to point towards the chain backbone to minimize the enthalpy of mixing, leading to a spiral cylinder morphology. In a non-aromatic solvent, such as chloroform, the polymer chain adopts a twisted conformation to gain more configuration entropy [112]. Lee and coworkers have also simulated the structure of MEH-PPV in various solvent combinations [132]. Their results show a higher degree of $\pi$-$\pi$ stacking along the MEH-PPV chain in CB/CF compared to CF/toluene after solvent evaporation, resulting in a larger occupied surface area. They also showed that in the hybrid solvent case (CF/CB = 2:1), MEH-PPV retains the largest mean radius of gyration in solution and forms a higher degree of ordered $\pi$-$\pi$ stacking after solvent evaporation. It is likely that the competition between minimizing the enthalpy of side chain mixing and gaining configuration entropy leads to the formations of these microscale ring structures. As we found from the UV-vis results for different solvent combinations, the mixed solvent cases show a lower band gap, indicating higher $\pi$-$\pi$ stacking in the mixed solvent case (TABLE 4.2). One should note that the window for the formation of stable ring structures is limited. As we demonstrate in Figure 4.1e, the ring structures disappear when the ratio of CF/CB exceeds 10:1.

4.3.4 Templating Rings of Nanoparticles

As we introduced earlier, polymer templates have been widely used to direct nanoparticle assembly over large areas [26, 143]. We used MEH-PPV to template micron sized rings of nanoparticles. CdSe nanoparticles were dissolved in CF with a volume fraction of $8.6 \times 10^{-4}$ and mixed with MEH-PPV dissolved in CB in a 2:1 weight ratio
and placed on the air/water interface. As previously described, the films were transferred onto grids for transmission electron microscopy (TEM) and imaged using TEM. As shown in Figure 4.8, rings of nanoparticles are readily formed, illustrating the potential of this method for nanolithography.

![Figure 4.8. Representative TEM images of CdSe NPs/MEH-PPV.](image)

### 4.4 Conclusion

In this paper, we illustrate the formation of MEH-PPV rings via a novel evaporative assembly method that utilizes hybrid CF/CB solvent deposition onto an air/water interface. The size of the ring structures can be manipulated by changing the CF/CB ratio within a limited range. The ring formation results from the different solvent spreading coefficients, evaporation rates and polymer molecular orientations. These ring structures
possess interesting optical compared to MEH-PPV thin films deposited from either chloroform or chlorobenzene. The MEH-PPV rings exhibit a high degree of \( \pi-\pi \) stacking along the backbone. Further applications involve exploiting the birefringence properties of these rings or utilizing MEH-PPV as templates to order nanoparticles. In the next chapter, we finally mixed MEH-PPV and CdSe TPs together to fabricate the hybrid solar cell. We will see how the template technique works on the structure inside the active layer and the final PCE.
5 Interfacial Assembly of Nanocomposites for Heterojunction Hybrid Solar Cells

Hybrid solar cells that combined organic conjugated polymers with inorganic nanoparticles into low-cost nanocomposites offer great potential as the third generation of thin film photovoltaics. The major limitations of these materials have been the aggregations of the nanoparticles within the polymer matrix, which limits charge transfer and high power conversion efficiencies (PCE). In this chapter, we demonstrate an interfacial assembly method to control the morphology of the nanocomposite. First CdSe tetrapods (TPs) are organized into a percolating network morphology with poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) at the air/water interface. Then, the film of MEH-PPV/CdSe TPs is transferred to a substrate using the Langmuir-Blodgett method. This process in repeated in a layer-by-layer assembly method until the desired thickness for the photoactive layer is achieved. The photoactive layer is characterized by the transmission electronic microscopy (TEM), UV-visible (UV-vis) absorption and photoluminescence (PL) emission tests. Two different sizes of CdSe TPs were mixed with MEH-PPV and tested in this paper. Our results show that a
photoactive layer formed using this interfacial assembly method results in higher PCE compared to the conventional spin-coating method. It is likely that the higher PCE is a result of the controlled morphology. This study highlights the importance of controlling the structure of the inorganic material within the organic matrix for hybrid solar cells.

5.1 Introduction

Bulk heterojunction hybrid solar cells are based on the photoactive layer composed of organic conjugated polymers [34, 35, 41, 42, 83], which serve as electron donor and transports photogenerated holes, with inorganic semiconducting nanoparticles, which accepts and transports electrons [38, 39, 42, 107, 144-147] blended together. As mentioned in Chapter 1, one difficulty has been the aggregation of ligand-capped nanoparticles in the conductive matrix. This has led to poor charge transport to the electrode and inefficient exciton dissociation at the donor/acceptor interface. It is thought that creating bicontinuous percolating networks will lead to effective charge transport [41, 148]. Therefore, the morphology of the nanocomposite plays an important role in the performance of the photovoltaic. Several groups have made progress in controlling the morphology of the photoactive layer by tuning the shape of the nanoparticle [147] or controlling processes, such as post-annealing temperature and time [43-45]. Directed assembly methods are also being utilized to orient the direction of charge transport [46-48].

Here, we demonstrate an interfacial assembly method that utilizes the air/water interface to control the morphology of the nanoparticles within a conductive polymer
matrix. This method is based on a soft-templating approach in which amphiphilic molecules [25-27, 104] are utilized to organize the nanoparticles at the air/water interface. The nanoparticles used are CdSe tetrapods (TPs), whose arm length can be tuned by modifying synthesis procedures [49]. The TPs are mixed with poly[2- methoxy-5-(2′-ethylhexyloxy)-p-phenylene vinylene] (MEH-PPV), a conjugated polymer. MEH-PPV serves a duel role of the organic component of the active layer as well as the templating agent for the TPs. The 2-D phase behavior of MEH-PPV at the air/water interface has been studied [124, 127] and devices such as light-emitting diodes based on MEH-PPV have been fabricated [149] previously. Therefore, MEH-PPV is chosen over other common conjugated polymers, such as poly(3-hexylthiophene-2,5-diyl) (P3HT) due to its stability at the air/water interface. By controlling the surface pressure of the system, CdSe TPs can be assembled into a percolating network structure on the air/water interface using MEH-PPV. The film can be transferred onto a solid substrate using Langmuir-Blodgett or Langmuir-Schaefer methods. Multilayers of MEH-PPV/CdSe TPs were built up by repeated film transfers to form a nanocomposite active layer for hybrid photovoltaics. We report the performance of these films using metrics such as PCE, fill factor (FF), open-circuit voltage ($V_{oc}$) and short-circuit current density ($J_{sc}$), and compare them with those obtained from films formed using conventional spin-coating.

5.2 Materials and Methods

5.2.1 Materials

Two sizes of CdSe TPs were synthesized by following the method previously
reported [49], as shown in Figure 2.1. CdSe TPs and MEH-PPV were both dispersed in chloroform. A MEH-PPV solution of 2.5-3.0 mg/mL was made, stirred for at least one day and filtered through a 0.45 μm filter before use. The concentration of CdSe TP solution was 2.5-25 mg/mL. The MEH-PPV and CdSe TPs solutions were mixed and immediately used. The ratio between MEH-PPV and CdSe TPs were adjusted by weight.

5.2.2 **Langmuir-Blodgett transfer and characterization of MEH-PPV/CdSe TPs thin films**

The procedure of using a Langmuir trough and related cleaning steps has been introduced previously. After 10-30 μL of a sample of MEH-PPV/CdSe TPs was deposited onto the air/water interface, the solvent was allowed to evaporate for 20 minutes. Afterwards, the barriers were set to decrease the effective trough area at a rate of 1500 mm²/min. The MEH-PPV/CdSe TPs organize into a network morphology at a particular surface pressure. At the desired surface pressure, the MEH-PPV/CdSe TPs film was transferred to a glass substrate using a vertical LB transfer. All the experiments were conducted with a water subphase temperature of 20 ± 0.1 °C controlled by thermal circulator. The optical properties of the films were characterized using UV-visible absorption measurements (Shimadzu UV-2450, Shimadzu, Kyoto, Japan) and photoluminescence tests (SPEX FluoroLog-3 Spectrofluorometer, Horiba Jobin Yvon Inc., Edison, NJ). Transmission electron microscopy (TEM) images of the active layer were also captured (JEOL 1230 high contrast transmission electron microscope, JEOL Ltd., Tokyo, Japan).
5.2.3 Fabrication of photovoltaic devices

For our inverted heterojunction hybrid solar cells, the patterned ITO substrate serves as the cathode and a TiO\(_2\) layer is deposited as a cathode buffer layer that enables efficient electron extraction. A filtered ethanol-TiO\(_2\) solution (procedure was detailed in Chapter 2, section 2.3.2) was spin-coated onto the patterned ITO substrate at 3000 rpm. The average thickness of the final TiO\(_2\) film is about 80-90 nm, as determined by profilometry. The interfacial assembled MEH-PPV/CdSe TPs is transferred to the TiO\(_2\) coated ITO substrate using a Langmuir-Blodgett method. This process is repeated in a layer-by-layer assembly method until the desired thickness for the photoactive layer is achieved. Because the transferred films are not uniform, gaps in the active layer are back-filled by spin-coating either a MEH-PPV or a mixed MEH-PPV/CdSe TPs solution. Passivating ligands, oleic acid, on the CdSe TPs are exchanged to short ligands by submerging the substrates in an acetic acid/acetonitrile solution (the concentration of acetic acid in acetonitrile was 0.01-1M) under continuous stirring for 30 minutes [80]. The average thickness of the photoactive layer is 100 nm, as measured by profilometry. Silver was thermally evaporated to a thickness of 80 nm to form the anode. A post-annealing step was completed immediately after silver electrode deposition in which the device is baked at 150 °C for 30 minutes. The photoactive area of the device is 3.9 mm\(^2\). The schematic of this photovoltaic has been shown in Figure 2.11b.

Conventional bulk heterojunction hybrid solar cells are also prepared as described above, except that the photoactive layer is prepared by spin-coating the MEH-PPV/CdSe TPs blend onto the TiO\(_2\) layer to form a film that is about 100 nm thick. The two devices
were compared by testing using a light simulator under AM 1.5G and recording current density-voltage (I-V) characteristics.

5.3 Results and Discussions

5.3.1 MEH-PPV with Short CdSe TPs

The surface pressure versus molecular area isotherms of the MEH-PPV/CdSe TP films provides information about the phase behavior of the molecules at the air/water interface. First, the results with the shorter 11nm arm CdSe TPs are examined. In order to determine the optimal mixture of MEH-PPV to CdSe TPs, two different ratios were considered. Figure 5.1 shows isotherms for MEH-PPV, a 1:1 mixture of MEH-PPV/CdSe TPs, and a 1:3 mixture of MEH-PPV/CdSe TPs. The three curves show a monotonic increase in the surface pressure with decreasing surface area, characteristic of a liquid-expanded phase, until the monolayer collapsed at 18-20 mN/m. Extrapolation of the isotherms to zero pressure leads to a mean molecular area of 0.42 nm$^2$ for MEH-PPV, 0.52 nm$^2$ for the 1:1 mixture ratio, and 0.72 nm$^2$ for the 1:3 mixture ratio. This indicates that the presence of TPs significantly inhibits the close-packing of the MEH-PPV. The slopes of the three isotherms significantly vary, indicating different compressibility moduli for the three systems. In general, a larger slope indicates a more rigid film, as we introduced in Chapter 3. Therefore, having more short TPs in the thin film increases the compressibility of it.

The morphology of the films can be obtained from TEM images of the LB transferred films. Transfer ratios close to 1 could be obtained using a TEM grid. Figure 5.2a shows
that when the 1:1 mixture films are transferred at lower surface pressures (7 mN/m), the CdSe TPs organize into a loose network structure. The zoomed-in inset in Figure 5.2a shows that the TPs are not continuously connected. At higher surface pressures (17 mN/m), a percolating network structure is formed, as shown in Figure 5.2b. Finally, at 20 mN/m, the film collapses and the TPs organize into aggregates, as shown in Figure 5.2c.

**Figure 5.1.** Langmuir isotherms for MEH-PPV/short TPs (briefed as sTP in the figure).
Figure 5.2. TEM images of MEH-PPV/short TPs (1:1) thin film at different surface pressure: (a) 7 mN/m; (b) 17 mN/m; (c) after collapse; (d) MEH-PPV/short TPs (1:3) thin film transferred from 10 mN/m. The scale bar in the inset image of (a) is 50 nm.

Increasing the MEH-PPV/CdSe TPs mixture ratio to 1:3 results in a percolating network of TPs at a lower surface pressure (10 mN/m), as shown in Figure 5.2d. This higher ratio and surface pressure was chosen to form the photoactive layer for the hybrid photovoltaic. Multiple transfers were performed to build up the active layer. Specifically, the 1:3 mixture is transferred at 10 mN/m for a total of five times onto a TiO₂ coated ITO substrate. Initial results showed that the photocurrent density of this device was lower than 0.1 mA/cm², because the transferred films were not close-packed. Higher surface pressure transfers resulted in films that no longer had a percolating network morphology. Therefore MEH-PPV was spin-coated onto the active layer to back fill the gaps. This was followed by the addition of five more layers of CdSe TPs/MEH-PPV deposited by LB at 10 mN/m to generate a photoactive layer of approximately 100nm. The additional five-layer was also for increasing the vertical segregation over the photoactive layer [86]. This combined Langmuir-Blodgett and spin-coating (LB-SC) resulted in a better electrical performance compared to a photoactive layer formed by simply spin-coating a 1:3 MEH-
PPV/CdSe TP mixture onto a TiO$_2$ coated ITO substrate. Typical current-voltage (I-V) characteristics of these films are shown in Figure 5.3. The current density and PCE of the LB-SC active layer was enhanced dramatically compared to the spin-coated active layer. We continued applying this method to fabricate more devices with longer TPs, as previous reports have shown better performance using longer TPs [150]. In the next section, we have a full set of tests with different ratios of long TPs with MEH-PPV.

**Figure 5.3.** I-V characteristic curves of hybrid solar cells from the conventional method (spin-coating, SC) and the LB-SC method with MEH-PPV: short TP = 1:3. The inset TEM image shows the multilayers of network structures via LB before spin-coating.
5.3.2 MEH-PPV with Longer CdSe TPs

Though the combine LB/SC methods resulted in higher electrical performance compared with traditional spin coating, the PCE results were still below that reported previously. For this reason, the use of TPs with longer arm lengths (30-40nm) was examined. Isotherms for interfacial assembled films of MEH-PPV with longer TPs at various ratios are shown in Figure 5.4. In addition to the 1:1 and 1:3 ratio that was studied with the shorter TPs, a 1:5 and 1:10 ratio was also examined to maximize the TP content. One can compare the onset points of these four isotherms with the ones of Figure 2. We can identify that the onset points here (0.62 nm$^2$ for the 1:1 ratio, 1.05 nm$^2$ for the 1:3 ratio, 1.22 nm$^2$ for the 1:5 ratio, and 2.10 nm$^2$ for the 1:10 ratio) are much larger than the ones shown in Figure 5.1 since the long TPs occupy more space at the air/water interface. For a given ratio, the mean molecular area is larger than observed with the shorter TPs due to the TPs occupying more interfacial area. The morphologies of these mixtures were monitored using TEM, as shown in Figure 5.5. As with the shorter TPs, a sparsely connected structure was observed at a 1:1 ratio at a surface pressure of 15 mN/m while a percolating network structure was observed for both 1:3 and 1:5 ratios at 10 mN/m. However, at the 1:10 ratio, significant TP aggregation was observed, indicating that the MEH-PPV is not able to adequately function as a soft-template for high nanoparticle content.
Figure 5.4. Langmuir isotherms for MEH-PPV/long TPs.

Figure 5.5. Representative TEM images of transferred thin film of MEH-PPV: long TP = 1:3 at 15 mN/m in (a) and (b); and MEH-PPV: long TP = 1:5 at 10 mN/m: (c) lower magnification image; (d) zoom-in image.

5.3.3 Optical and electrical properties of the MEH-PPV/long TPs films

Absorption spectra of the photoactive layers are shown in Figure 5.6. As shown in Figure 5.6a, the absorption peak for MEH-PPV film is 507 nm and for the longer TPs is 539 nm. Increasing the TP content results in the UV absorption peak to red-shift from
507 nm to 511, as shown in Figure 5.6b. As shown in Figure 5.6c, photoluminescence tests show that increasing the CdSe TPs improved charge transfer, likely due to increased contact area between the donor and receptor [151].

Figure 5.6. Optical properties of MEH-PPV, CdSe long TPs and the thin film of mixtures: (a) UV-vis absorption spectra of MEH-PPV and long TPs; (b) UV-vis absorption spectra of different ratios of MEH-PPV:TP; (c) corresponding PL spectra from different ratios of MEH-PPV:TP.

Another comparison between using our interfacial assembly method and spin-coating to form the active layer is through the current-voltage curves obtained by simulated light emission. Heterojunction solar cells were assembled in a similar manner to that describe for the short TPs. Initially, five layers of MEH-PPV/long TPs at a 1:3 ratio and 10 mN/m surface pressure are transferred using LB, followed by back-filling the structure with MEH-PPV via spin coating, and finally transferring an additional five percolating layers using LB. Figure 5.7a shows that the interface assembly method has a more current
density for any given voltage, indicating a higher performance. We hypothesized that more photocurrent would be produced by increasing the TP content. Therefore we performed the back-filling with a mixed MEH-PPV/long TPs solution, labeled as “LB-SCmix” in Figure 5.7b, One notices that the I-V results from the LB-SCmix led to higher fill factor and PCE compared to spin-coating methods. Back-filling long TPs after LB transfer removes the voids in the network structure, which enhances the fill factor of the device and also increases the current density.

**Figure 5.7.** I-V characteristic curves of hybrid solar cells via the conventional method (spin-coating, SC) and the LB-SCmix method with (a) MEH-PPV: long TP = 1:3. For the LB-SCmix method here, we spin-coated the MEH-PPV/long TPs solution instead of MEH-PPV solution after LB transfer; (b) comparison between different ratios. Compared to (a), the main difference is that the concentration of MEH-PPV increased from 2.5 mg/mL to 3 mg/mL (the concentration of long TPs increased proportionally, too).
Finally, we further increased the concentration of the MEH-PPV solution from 2.5 mg/mL to 3 mg/mL in order to harvest more photocurrent, while keeping the final thickness of the photoactive layer at 100 nm. The performance testing results were summarized in Figure 5.7b. The current density increased with increasing TPs content in the mixture. This is consistent with what was determined from the PL test (Figure 7c): more long TPs result in better contact between MEH-PPV and long TPs which promotes better charge transfer. Compared to Figure 5.7a, the current densities and PCEs in Figure 5.7b are enhanced due to higher concentration of MEH-PPV (under the ratio of 1:3). Among all the devices in Figure 5.7b the one via LB-SCmix (red line) holds the best fill factor number and PCE. Figure 5.8 shows the highest PCE we had from MEH-PPV: long TP = 1:3, via LB-SCmix method. This is also the best PCE and current density ever reported under the combination of MEH-PPV and CdSe TPs [34, 41, 107].
Figure 5.8. I-V characteristic curve of the hybrid solar cell via LB-SCmix method with MEH-PPV: long TP = 1:3.

From Figure 5.7b, it is apparent that the amount of TPs in the mixture plays a big role but is not absolutely dominated. With the help of the network structure present in the active layer, electrons followed this percolating pathway through the photoactive layer to the cathode more easily, instead of a random route that will likely lead to recombination [41]. We clearly see how $J_{sc}$, FF and PCE benefited from this controllable structure in Figure 5.7. We could also clearly see that the PCEs from the devices with long TPs are consistently better than the ones with short TPs, as expected with the previous study by Lee et al. regarding the TP size effect on PCE when there were more contact areas between the long TPs and MEH-PPV[150].

However, what we cannot deny here is that when deploying the long TPs in the device, the differences of PCE/$J_{sc}$ between LB-SCmix process and the conventional
method decreased. We consider that this behavior is due to the standing height of long TPs (~ 40 nm) being comparable to the photoactive layer thickness (100 nm) then, while short TPs is around 20 nm. If one long TP sits right on top of another one, the pathway between the cathode and anode now is built with less chance of recombination; therefore, the network structure provides less impact effect. We found that the devices made from MEH-PPV: long TP = 1:5 via LB-SCmix method, the PCEs were not always higher than the conventional ones. This LB fabrication process does have limits and the optimal ratio of MEH-PPV to TPs and deposition concentration is required. As mentioned earlier, the templating function provided by MEH-PPV decreases resulting in increased aggregation of TPs in the thin film when the ratio of MEH-PPV: long TPs was increased to 1:10. The ratio MEH-PPV:TP = 1:3 showed the highest PCE and fill factor. These experiments highlight the importance in controlling the packing of TPs within the MEH-PPV matrix since it greatly influences the performance of the hybrid solar cell.

5.4 Conclusions

We have demonstrated that with the presence of MEH-PPV, CdSe TPs assembles into a percolating network-like structure at the air/water interface. By using LB transfer, a multi-layer structure of MEH-PPV/CdSe TPs is assembled as the photoactive layer. Two different sized CdSe TPs were studied and the PCE was higher for solar cells assembled using the LB method. The results also show that long TPs outperformed the shorter TPs, consistent with previous findings. This work has highlighted the importance of
controlling the nanocrystals packing inside the photoactive layer of the heterojunction hybrid solar cell.
6 Conclusions and Future Directions

6.1 Summary

The Langmuir-Blodgett technique has attracted much attention in probing the 2-D phase behavior of amphiphilic molecules such as surfactants, lipids, and polymers at the air/water interface. More recently, it has been applied to the assembly of nanoparticles and polymers on a 2-D interface. This system has benefited research on developing new superlattice structures, sensors and photovoltaic devices. A template organization strategy has developed along the way with this interfacial technique in order to add additional control on the assembly of the nanoparticles. Besides observing phase transitions or packing density changes at the air/water interface, one can transfer the monolayer or thin film from the water surface via Langmuir-Blodgett or Langmuir-Schaefer techniques onto a solid substrate, such as a glass slide or a TEM grid, to be further characterized on the optical properties or the morphology of the thin film. In this thesis, AFM and TEM were utilized to visualize the thickness and morphology of the thin film at the nanoscale, while BAM allows us to monitor the thin film in real time on the length scale of sub-millimeter to a few micrometers. UV-vis and photoluminescence tests were performed to characterize the optical-related properties of the thin film.
In Chapter 3, template organization was introduced as a method to control the arrangement of CdSe TPs at the air/water interface. POPC was used as the templating agent to manipulate the morphology of the TPs at the air/water interface. Without the presence of POPC, CdSe TPs aggregated to disc-like structures upon chloroform evaporation in order to minimize the surface energy due to the hydrophobic ligand, oleic acid, coated on the surface of TP. The packing of the nanoparticles is random inside the disc-like aggregates because the anisotropic structure of TP leads to interdigitation with neighboring particles. Under compression the disc-like structures collided and merged into larger continental-like structures. Further compression resulted in the collapse of the layer of CdSe TPs and a multilayer structured was observed. In the CdSe TPs/POPC system, the POPC layer acted as a buffer between the water surface and CdSe TPs. We found smaller disc-like structures at the beginning; however, under compression the size of the discs did not grow or merge to larger continental ones. Instead, the smaller discs merged into wire-like structures. And even after the collapse point, the wire-like structures remained intact while the thickness increased. With the POPC templating agent, we were able to transfer onto substrates structures made of TPs from discs to wires with the additional capability of tuning the thickness of the network.

The biggest application of CdSe TPs is their use in photovoltaic devices. We considered mixing CdSe TPs with a conjugated polymer, MEH-PPV, because of its stability on the water surface. In Chapter 4, we reported that MEH-PPV chains aggregated into ring-like structures, when depositing from a mixed solvent combination at the air/water interface. CF and CB, under certain ratios, ordered MEH-PPV into forming network or continental structures. The behavior was mainly driven by the
mismatch of the spreading coefficients and evaporation rates between CF and CB, as well as the polymer molecular orientations. We discovered under CF/CB = 2:1 and 5:1, the ring structures were stable. When the CF amount was increases significantly, beyond 10:1, we could only see stripes and broken rings. The ring structures showed red-shifted absorption peak compared to the pure solvent cases, and revealed the possibility of fine-tuning the band gap of MEH-PPV by simply changing the dispersing solvent. When mixing MEH-PPV and CdSe nanoparticles were mixed with a hybrid solvent solution and deposited at the air/water interface, it was observed that CdSe nanoparticles also formed ring structures, templated by the MEH-PPV polymer chains.

Since MEH-PPV was such an effective template for CdSe nanoparticles and it is frequently used in organic photovoltaic devices as an electron donor, a combined CdSe TP/MEH-PPV could be used to construct a heterojunction hybrid solar cell. As shown in Chapter 5, short CdSe TPs formed network-like structures, as well as long TPs, in a MEH-PPV matrix system at the air/water interface. We utilized the LB technique to construct the active layer of the photovoltaic device by transferring monolayers of CdSe TPs/MEH-PPV from the air/water interface onto a TiO$_2$ coated ITO substrate several times. These devices made via LB method were compared with the conventional devices made by spin-coating the mixed solution of MEH-PPV and TPs. We found that the PCEs from devices via LB technique were improved, due to the presence of the network structure inside the active layer. This percolating path provided by the network structure aided the electron transportation from produced site to the cathode. And the devices made from long TPs reveled better PCEs thanks to the higher contact between TPs and MEH-PPV. The best PCE was 1.51\% from the LB-aided device, as known as the best PCE
reported under the combination of MEH-PPV and CdSe TPs. Besides being able to achieve a new record for PCE, this chapter indicated the possibility of controlling the packing of TPs and further influenced the final performance. With these three steps of learning the assembly behavior of CdSe TPs and MEH-PPV at the air/water interface, we explored and extended the application of LB technique to actual application on the photovoltaic devices.

6.2 Future work

One of the remaining challenges for template organization is determining what other materials can be used. As shown in Chapter 1, amphiphilic block copolymers resulted in tunable patterns at the air/water interface. Perepichka et al. in 2010 [152] reported that by utilizing a polystyrene-\(b\)-poly(4-vinyl pyridine) diblock copolymer of 12 mol % VP content mixed with 3-n-pentadecylphenol (PDP) (PS-P4VP/PDP), they were able to produce well-ordered nanostrands at the air/water interface over large areas. Depositing this diblock copolymer from 1,1,2,2 tetrachloroethane (C\(_2\)H\(_2\)Cl\(_4\)), a less-versatile solvent than chloroform (CHCl\(_3\)), onto the subphase at lower temperature of 8-9 °C, more dense-aligned nanostrand was observed (Figure 6.1). We would like to explore more conjugated polymer candidates that have controllable patterns. Newly-developed conjugated polymers such as poly(\(\{4,8\text{-bis[(2-ethylhexyl)oxy]benzo[1,2-b:4,5-b’]dithiophene-2,6-diyl}\}\{3\text{-fluoro-2-[(2-ethylhexyl)carbonyl]thieno[3,4-b]thiophenediyl}\})\) (PTB7) and poly[N-9’-heptadecanyl-2,7-carbazole-alt-5,5-(4’,7’-di-2-thienyl-2’,1’,3’-}
benzothiadiazole)] (PCDTBT) are potential candidates as well because of their promising performance.

**Figure 6.1.** Top: schematic of the structure of PS-P4VP/PDP and its arrangement at the air/water interface. Bottom: AFM height images of PS-P4VP/PDP (1.0:1.3) monolayers deposited from different solvents at 8 °C with a copolymer solution concentration of 1.85 mg/mL, and transferred to mica at \( \pi = 5 \) mN/m. Scan size: (a) 8 \( \times \) 8 \( \mu \text{m} \)^2; (b) 8 \( \times \) 8 \( \mu \text{m} \)^2; (c) 10 \( \times \) 10 \( \mu \text{m} \)^2 (zoom-in image: 3 \( \times \) 3 \( \mu \text{m} \)^2) (adapted from Perepichka et al. [152]).
Also for MEH-PPV rings at the air/water interface, we cannot ignore the parallels of this system with the famous “coffee ring” effect. The coffee ring effect describes flows driven by surface tension gradients, when the contact line of a drying droplet is pinned, the liquid evaporates from the edge is replenished by the liquid from the interior, so the outward flow carries entrained solutes to the drop periphery, yielding a dense, ring-like deposits. In our case, we only observe rings for the mixed solvent case (CF/CB) and not the pure solvents case, though all case shown generate surface tension gradients as the solvent evaporates. Additionally, when the MEH-PPV in CF/CB solvent is spin-coated onto a silicon wafer, we did not observe the ring structures, even though this system should have a strong pinning effect. Though we cannot say that Maragoni flows are not present, we do think it is likely that the mixed solvent evaporates in such a way to nucleate sites for ring formation. We tried to utilize the CdSe nanoparticles as tracers by dispersing them in CF/CB = 2:1 and depositing them at the air/water interface. We could not find any ring structures but irregular aggregates formed by CdSe NPs. It could be that nanoparticles are “trapped” at the solvent/water interface, before the solvents evaporate. One future direction would be to better identify the mechanism and flow of the polymer chains after deposition.

On continuing to improve the PCE of the photovoltaics, effort on optimizing the experimental conditions and desired morphologies is needed. We showed the network structure of CdSe TPs inside the active layer is crucial to the performance, but it is still not the ultimate answer. A better morphology to the final PCE will be found when we acquire the ability to control the pattern formed by the templating agent/conjugated polymer. Another idea could come from the example we mentioned in Chapter 5, about
directing the electron transportation by building the nanowire/pillar structures in the photoactive layer. New structure designs with soft templating could greatly improve performance.


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