

**2007 Yearly Report for AOARD-AFOSR Project
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**Hybrid Inorganic/Organic Photovoltaics: Translating Fundamental
Nanostructure Research to Enhanced Solar Conversion Efficiency**

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1. Overview

Polymer based solar panels and photovoltaic devices offer flexible lightweight, large area structures and radiation resistance which are basic requirements for military aircraft, space and other opto-electronic devices. However, the current research on purely organic or polymer-based photovoltaics is progressing at an undesirable phase in the efficiency of these devices due to the inefficient harvesting of the UV and IR-photons, as well as the limited carrier mobility in polymers. The purpose of our research is to develop key concepts that will enable new design criteria for plastic-based hybrid photovoltaics that will produce large enhancements in the efficiency. Specifically, we will utilize a polymer nanocomposite containing quantum dots for photosensitization, along with carbon nanotubes or pi-conjugated molecules for enhancing carrier separation as well as carrier mobility for subsequent charge collection.

2. Objectives

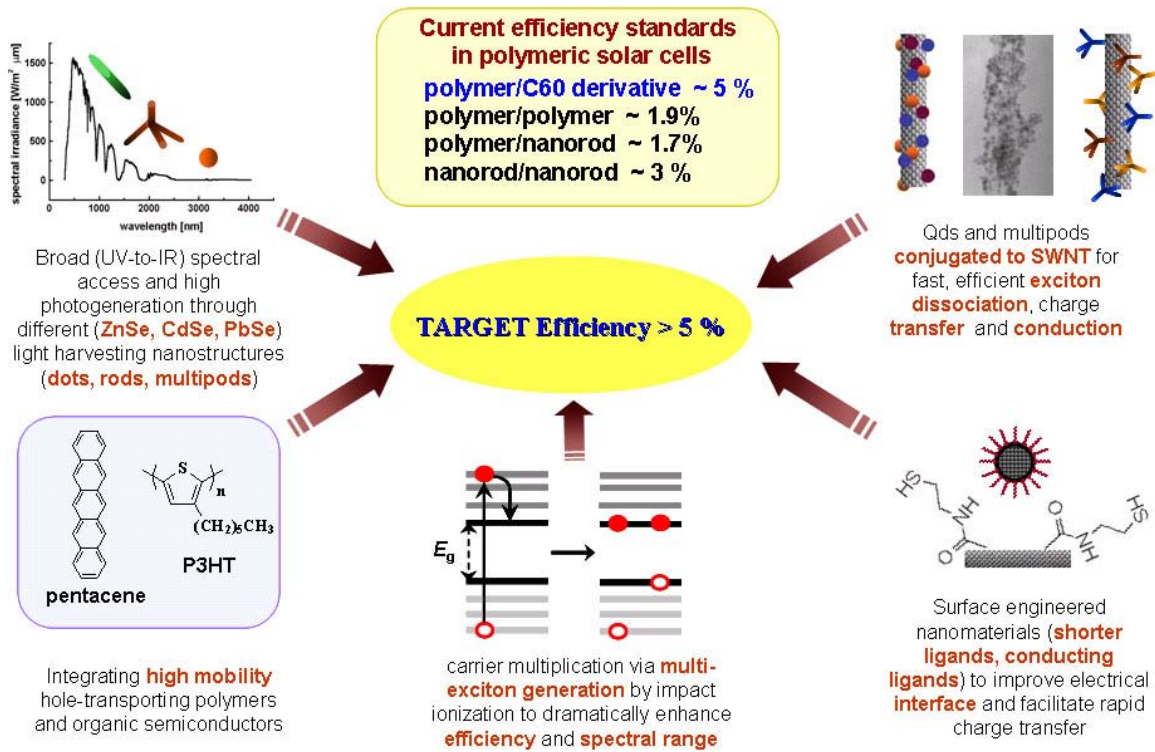
The objective of this research is to design and characterize conjugated oligomers/polymers and surface capping linkers for quantum dots, aimed towards facilitating the charge separation and enhancing the mobilities of carriers, which can lead to highly efficient quantum dot:carbon nanotubes: polymer nanocomposites based solar cells. These studies will significantly contribute to the understanding of efficient quantum-dot based solar cell architectures. The details are given below;

- Preparation of various quantum dots, conjugated oligomers and polymers.*
- Enhanced broadband energy harvesting using engineered and surface functionalized semiconductor nanocrystals (quantum dots) of various sizes, shapes and compositions.*
- Enhanced exciton dissociation and minimized recombination via bandgap-engineered multi-component hybrid nanocrystals through control of interfacial chemistry and linkage to other components.*
- Enhanced and balanced carrier mobility and efficient charge transfer through the incorporation of carbon nanotubes into organic matrices containing conjugated molecules.*
- Introduction of conjugated linker molecules for interconnection of inorganic nanocrystals and nanotubes for improved electron transfer between these nanoscale components.*

3. Approaches (Research Plan)

Semiconductor nanocrystals (quantum dots) of various sizes, shapes and material compositions offer an efficient way of harvesting of broadband energy (UV-to-IR). Carrier multiplication can be achieved by multiexciton generation processes in nanocrystals with optimized exciton dynamics. Increasing the exciton dissociation and minimizing the recombination via bandgap-engineered multi-component hybrid nanocrystals constituting pentacene or single wall carbon nanotube (SWCNT) as well as through control of interfacial chemistry and linkage to other components is also envisaged. Enhanced and balanced carrier mobility and efficient charge transfer through the incorporation of carbon nanotubes-quantum dot conjugates or pentacene-quantum dot composites into organic matrices significantly improved photoconductivity of polymer/nanocrystal hybrid materials. We have obtained a maximum external quantum efficiency of ~8%, which is a spectacular improvement over all earlier results with such hybrid composites. The carrier mobility will be enhanced by incorporating quantum dots (QDs) within a polymer matrix at nanocrystal concentrations well below the percolation limit. We are developing a variety of conjugated linker molecules for

interconnection of inorganic quantum dots and SWCNT for improved electron transfer between these nano-scale components.



4. 1st Year Results

1) QD Synthesis

Previously, in our group we have successfully mastered the size control of PbSe quantum dots by employing the conventional method. Now we are involved in the development of efficient size control of CdSe QDs using nanocrystal seeding technique (this technique represents the use of nanocrystal seeds during crystal growth, in this case CdSe nanocrystals are added to act as seeds on which crystal growth occurs in high boiling point solvent like n-octadecene) (Figure 1). We have investigated seeding effect for size controlling of CdSe QDs. As a result, we were able to synthesize size-enhanced QDs absorbing at longer wavelengths.

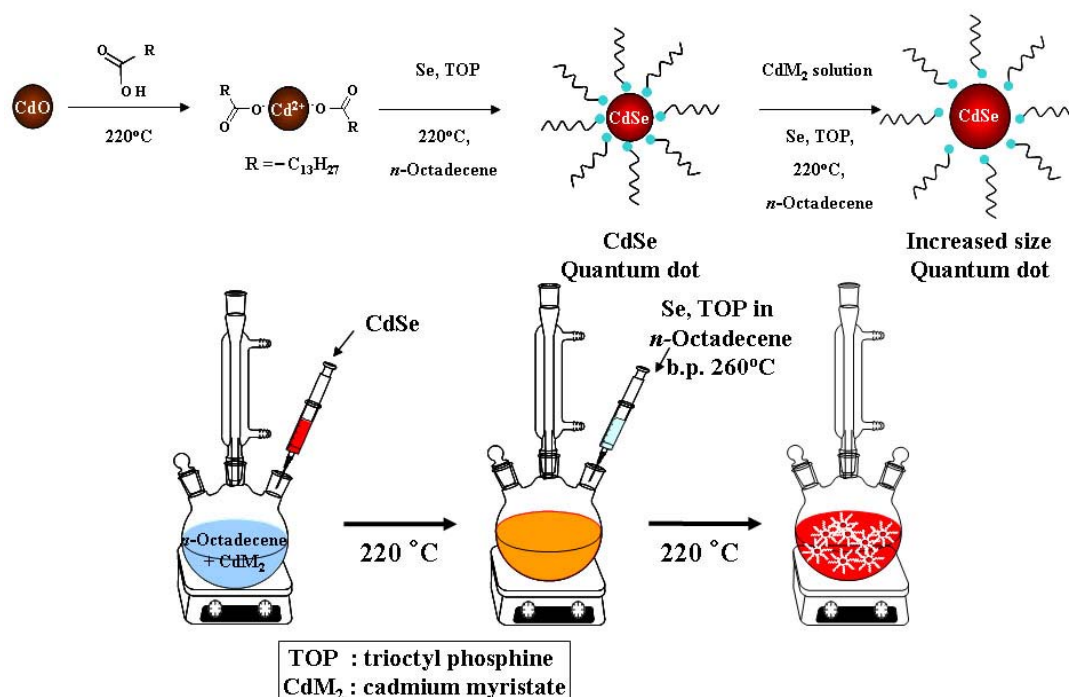


Figure 1. Synthetic route for size-enhanced QDs by the use of nanocrystal seeding technique

As shown in Figure 2, well-tuned CdSe QDs showing size dependent UV and PL characteristics were successfully synthesized. Nanocrystal seeding effect was demonstrated using absorption spectrum. The QDs size was measured by TEM. Maximum size of CdSe QDs is about 4 nm, which was achieved through a cost effective one pot synthesis (Figure 3). This method enables us to increase the size of QD which is approximately 3.4 nm using conventional process.

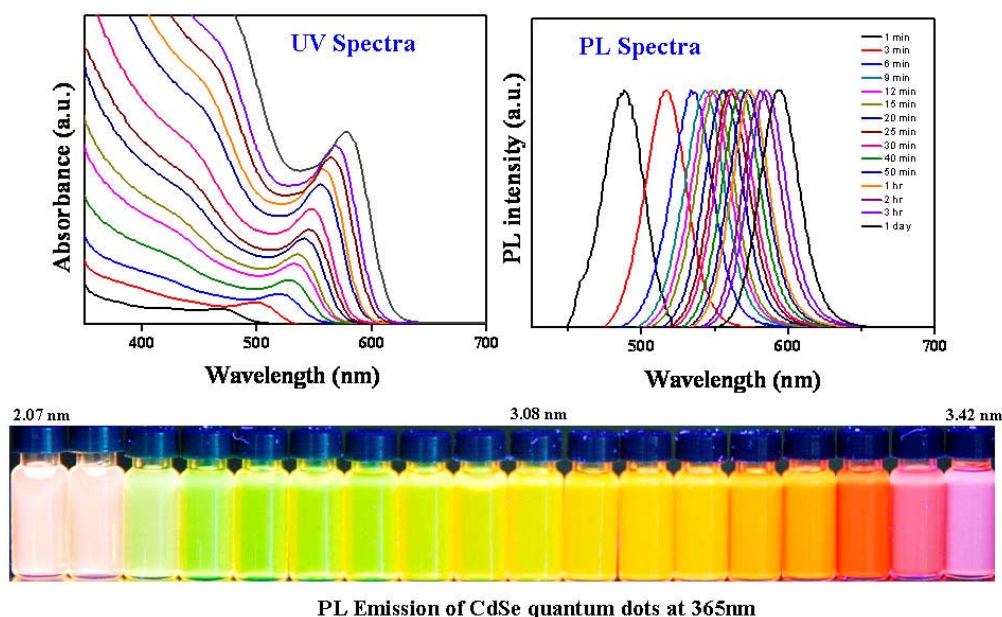


Figure 2. Tuning of UV and PL by changing the size of CdSe QDs

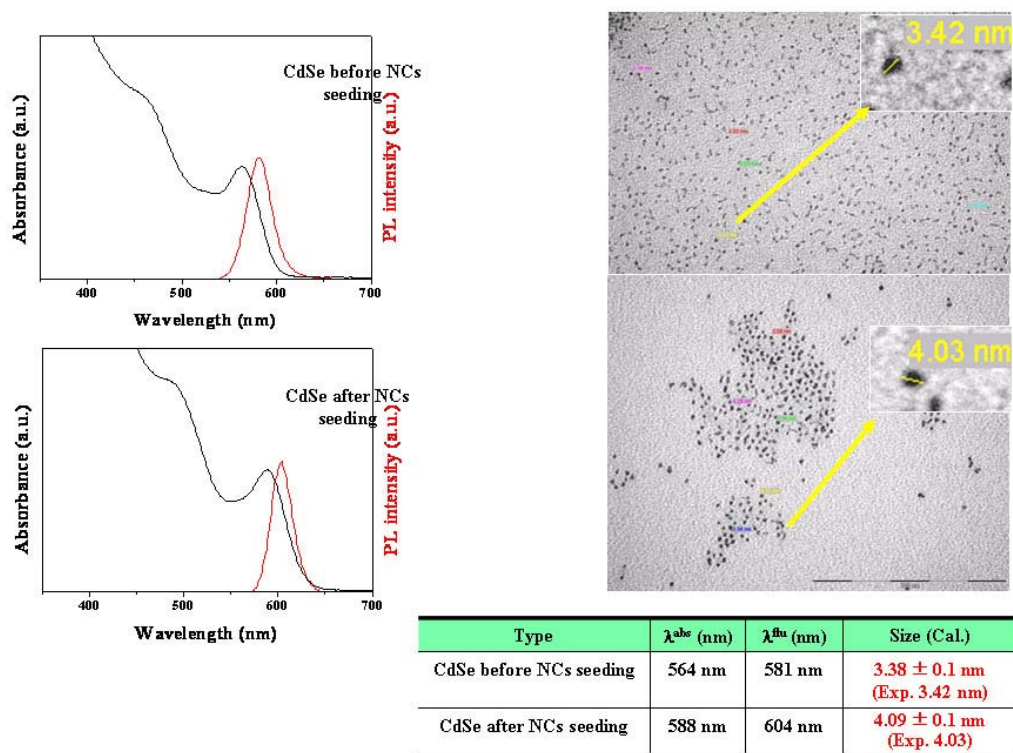


Figure 3. Increase in size of CdSe QD obtained by nanocrystal seeding technique.

As shown in Figure 4, we also prepared water-soluble and fluorescent quantum dots (CdSe, CdS, ZnS) by using a green method (less toxicity method). Distinguishable emission colors could be observed in the red rectangle area. The right image are the same solution on the left side when diluted 6 times with water. Figure 4b and 4c represent UV and PL spectra of CdSe, CdSe/CdS, and CdSe/CdS/ZnS systems.

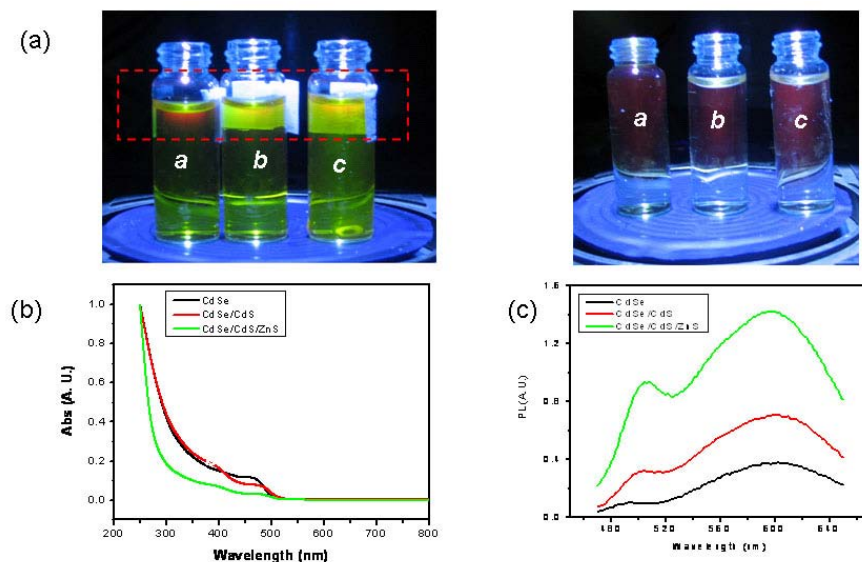


Figure 4: (a) Three water-soluble and fluorescent quantum dots fabricated in Prof. He's lab (a: CdSe, b: CdSe/CdS, c: CdSe/CdS/ZnS). The right image are the same solution on the left side when diluted 6 times with water. (b) The UV-visible absorption for Fig (a). (c): The corresponding PL spectra.

In our continuing studies with PbSe QDs we have tried varying the surfactant stabilizers used in the synthesis of QDs. It was found that dodecanethiol (DDT) functionalized QD shows a greater current generation when compared with those functionalized with shorter surfactant chains like butanethiol (BT) and oleic acid (OA) (Figure 5). This leads us to believe that the conductivity of a nanocomposite device composed of similar load of PbSe dots with different surface exchanged ligands will be different. Because all these ligands are aliphatic chains, only the chain length will determine the insulating sheath thickness and consequently the potential barrier height.

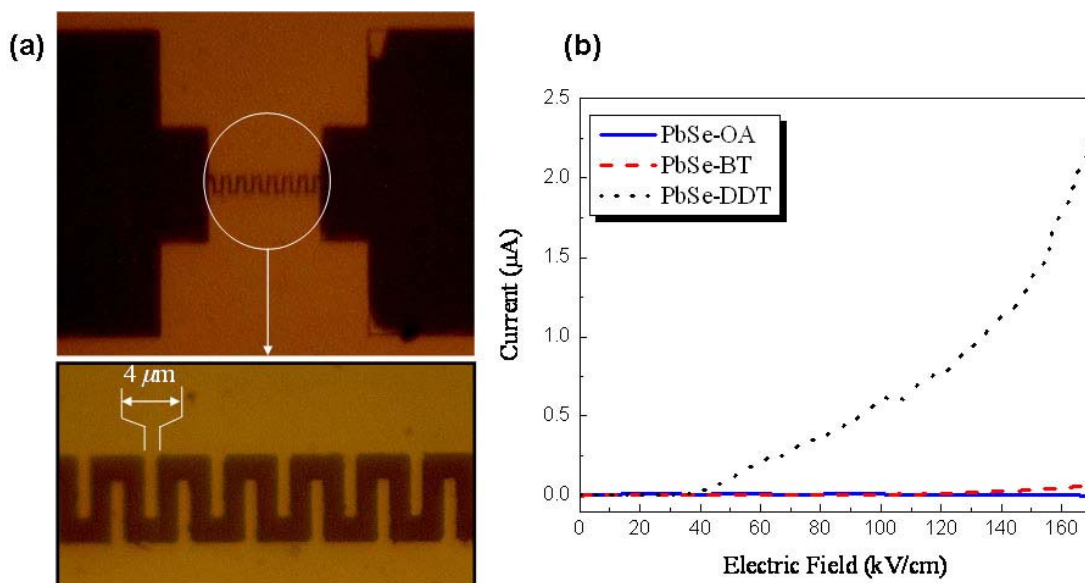


Figure 5. A device using planar interdigitate electrodes (Ti/Au:30nm/65nm) on the SiO₂ substrate was fabricated and each surface functionalized PbSe QD was drop casted for conductivity measurement. I-V scan shows PbSe-DDT has good conductivity. PbSe-BT is not good to make a good surface quality film (applied voltage to the 4 m gap is 0V~ 65V).

2) Synthesis of SWCNT-CdSe and PPyNT-PbSe

The procedure of attaching CdSe QDs onto SWCNT is given in Figure 6. First, the SWCNT surface was carboxylated by oxidation with a mixture of H₂SO₄/HNO₃. SWCNTs were stirred in H₂SO₄/HNO₃ (3:1) solution for 24 h at room temperature (RT). The reaction mixture was centrifuged and washed with water several times to remove the excess acid. *N*-(3-dimethylaminopropyl)-*N*-ethylcarbodiimide hydrochloride (EDAC) was added to the carboxylated SWNT (SWNT-COOH) in DMSO to activate the carboxyl group, followed by the addition of 2-aminoethanethiol (AET) and stirring for 12 h at room temperature. After the coupling reaction with AET, excess EDAC and AET were removed by centrifuging and washing with DMSO and acetone. The precipitate was sonicated in chloroform to obtain a stable dispersion. TEM images show that CdSe QDs bind to the terminal -SH group of the SWNT well in copious population (left). Right figure shows a zoom of a single SWNT-CdSe conjugate with the lattice fringes of CdSe.

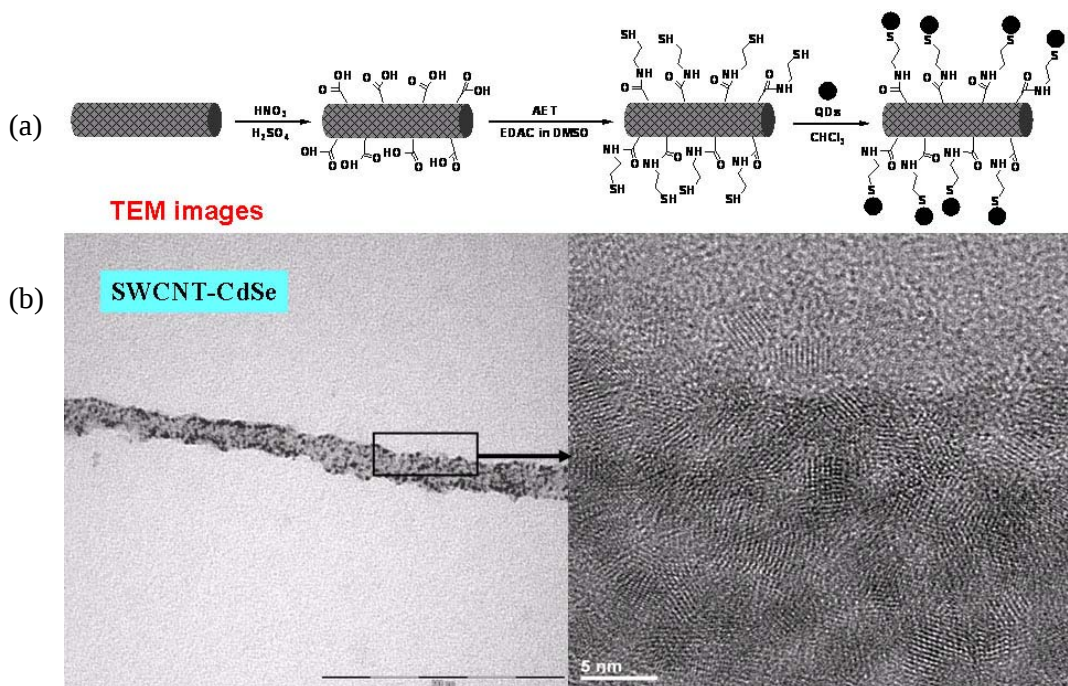


Figure 6. (a) Synthetic route and (b) TEM images for SWCNT-CdSe.

Moreover, thiol group functionalized conducting polypyrrole nanotubes were successfully synthesized by same procedure as in the case of SWNT-CdSe (Figure 7). PbSe QDs were incorporated on thiol functionalized polypyrrole nanotubes in chloroform solution then characterized by TEM. As shown in TEM images, high concentration of PbSe QDs were attached to the surface of polypyrrole nanotubes. This is an innovative approach because high contact area between QDs and nanotubes can produce a high density of polaron and bipolaron in conducting polymer main chain, which affect the conductivity of polypyrrole nanotubes in comparison with their conventional bulk composite materials.

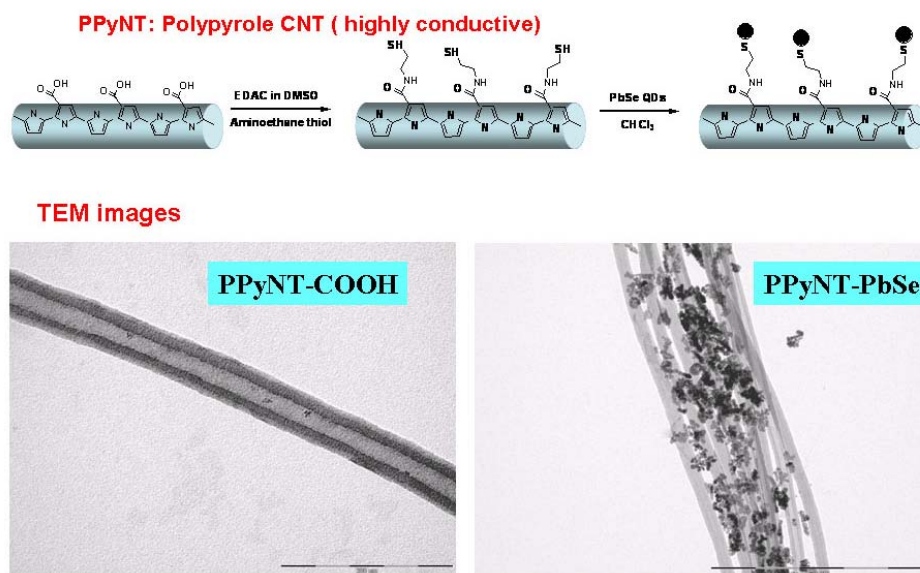


Figure 7. (a) Synthetic route and (b) TEM images of PPyNT-PbSe

3) Synthesis of Electron Donors and Acceptors for PV Applications.

The host material in which the QDs are dispersed in the device has to have good charge separation properties for fast conduction of the photo-generated carriers. Molecules including covalently bonded donor acceptor moieties are found to be efficient in bringing about effective charge separation in aftermath of photo-excitation. To investigate these effects we have designed both electron donating and electron accepting systems. When an acceptor type system is combined with a donor type system it is found that they show efficient photosensitization. Such a combination can then be used along with QDs acting as photosensitizers to produce efficient photocurrents.

To this end, we have synthesized various electron acceptor C₆₀ derivatives coupled with thiophene oligomers as acceptor systems which gives rise to an acceptor type molecule with effective charge separation on photoexcitation (Figure 8a). The hosts were characterized with MALDI-TOF. They show good solubility in toluene and chlorobenzene. The detailed electronic and optical properties are being studied.

Indolo[3,2-b]carbazole, 5,11-dihydro-5,11-dimethyl- copolymerized with propanedinitrile, 2-(4H-cyclopenta[2,1-b:3,4-b']dithien-4-ylidene)- or 2,1,3-benzothiadiazole are polymeric systems in which donor and acceptor moieties combine to give rise to a donor type polymeric system in which there is a fast charge separation dynamics. Both these polymers are in the final stage of synthesis and characterization (Figure 8b).

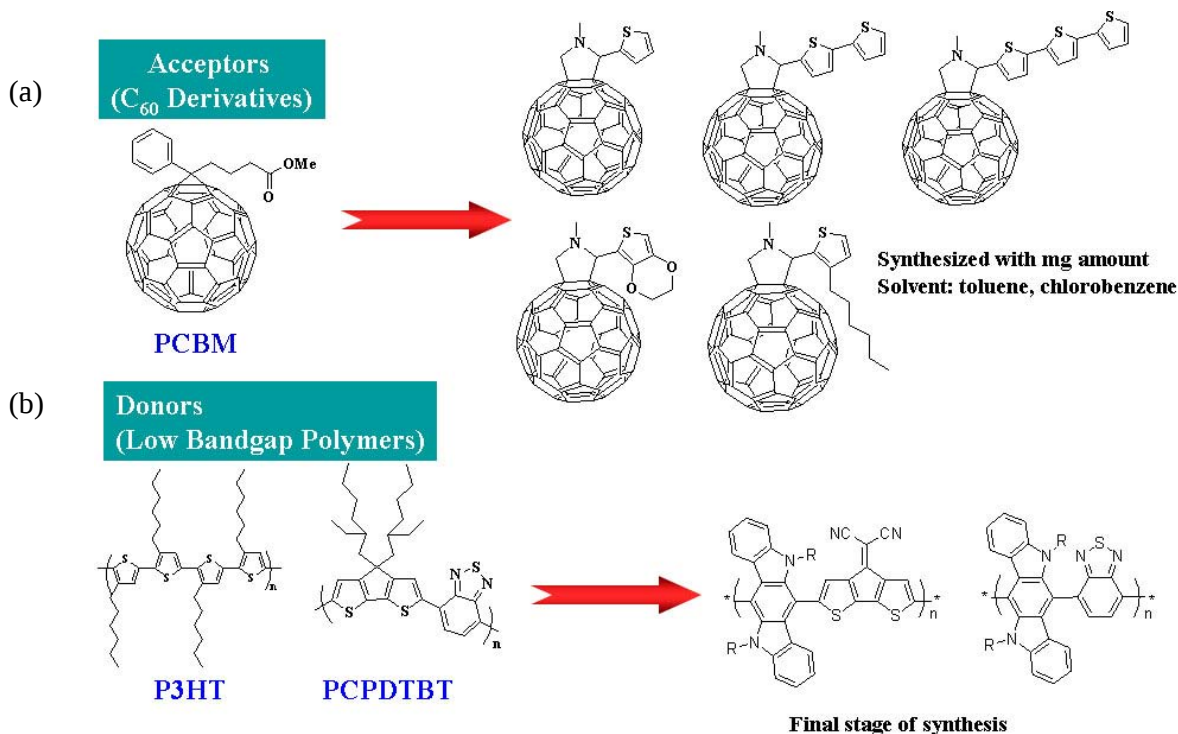


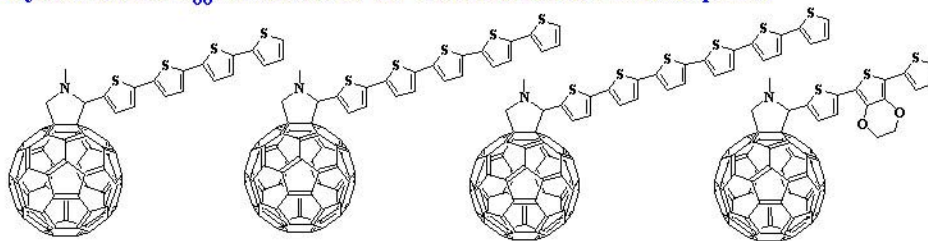
Figure 8. Chemical structures of synthesized electron donors (a) and Acceptors (b) for PV devices

5. Future Plan

As a next step to be carried out in the second year the materials and the basic theory of the conceptive hybrid photovoltaics developed during this project will be applied in the realization of effective photovoltaic devices. The improvements that could be brought about are manifold in

the material (low band gap materials suited for hosts) front including those in the design of new materials to suit the device architectures found to be efficient in the present studies. A understanding of the interaction between the QD-SWNT composites and the polymeric host systems including the charge transfer dynamics would bring to light the full potential of this promising devices which in turn would aid design in future. After the initial studies on the donor and acceptor host systems mentioned in Figure 8, the effect of increasing conjugation length and functionalization of fullerene derivatives on the charge separation dynamics of the hosts will be investigated. Furthermore, we will investigate new copolymeric systems involving different donor acceptor materials (Figure 9).

- **Evaluation of Optical and Electrical Properties for QDs, C60 and Conjugated Polymers**
- **Effective organic components of system identified**
- **Full evaluation of QD-SWCNT optical properties**
- **Understanding of synergistic effects in QD-SWCNT**
- **Synthesis of C₆₀ derivatives as efficient electron acceptors**



- **Synthesis of efficient electron donors; Low bandgap materials**

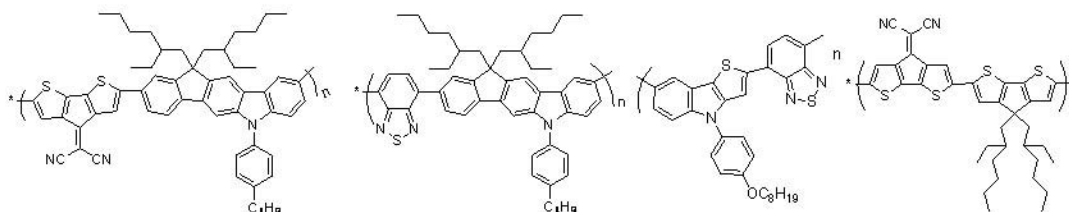


Figure 9. Future plan for hybrid inorganic/organic photovoltaics