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“Hybrid Inorganic/Organic Photovoltaics: Translating Fundamental Nanostructure Research to Enhanced Solar Conversion Efficiency”

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Key Researcher (PI):

Prof. Kwang-Sup Lee
Department of Advanced Materials, Hannam University
461-6 Jeonmin-Dong, Yuseong-Gu, Daejeon 305-811, South Korea
Phone: +82-42-629-8857, FAX: +82-42-629-8854
E-mail address: kslee@hnu.kr

Joint Researchers

Prof. Alex N. Cartwright, Institute for Laser, Photonics and Biophotonics,
University at Buffalo, SUNY, Buffalo, NY 14260, USA
Phone: +1-716-645-2422 (Ext.1205), Fax: +1-716-645-3656
E-mail: anc@buffalo.edu

Prof. Paras N. Prasad, Institute for Laser, Photonics and Biophotonics,
University at Buffalo, SUNY, Buffalo, NY 14260, USA
E-mail: pnprasad@buffalo.edu

Prof. Sailing He
Dept. of Optical Engineering, Zhejiang Univ., Yu-Quan, China
E-mail: sailing@zju.edu.cn

**AOARD Program Manager
AFOSR Program Manager**

Dr. Thomas Erstfeld & Dr. Jim Chang
Dr. Charles Lee

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1. Abstract

Studies on organic and polymeric photovoltaic (PV) cells have been extensively pursued to enhance power conversion efficiency through increased charge carrier mobility and efficient harvesting of longer wavelengths of the solar spectrum by designing new materials. The purpose of our research is to develop key concepts that will enable new design criteria for organic PV cells based on polymeric nanocomposites, which are expected to produce large enhancement in power conversion efficiency. Here we report the results of our efforts at improving the structure of bulk heterojunction hybrid organic-inorganic solar cells by developing patternable materials to form bulk heterojunctions as well as improvement of the device structure by introducing a hole blocking layer to achieve efficient charge separation. In current phase as in the previous phase we have continued the design, synthesis and study devices involving lowband gap polymers and fullerene derivatives. The improved design of the polymeric materials have resulted in achieving broad spectrum active polymers, fullerene derivatives were also found to show improved properties with one of them showing very high value for electron mobility in an injected device.

2. Introduction

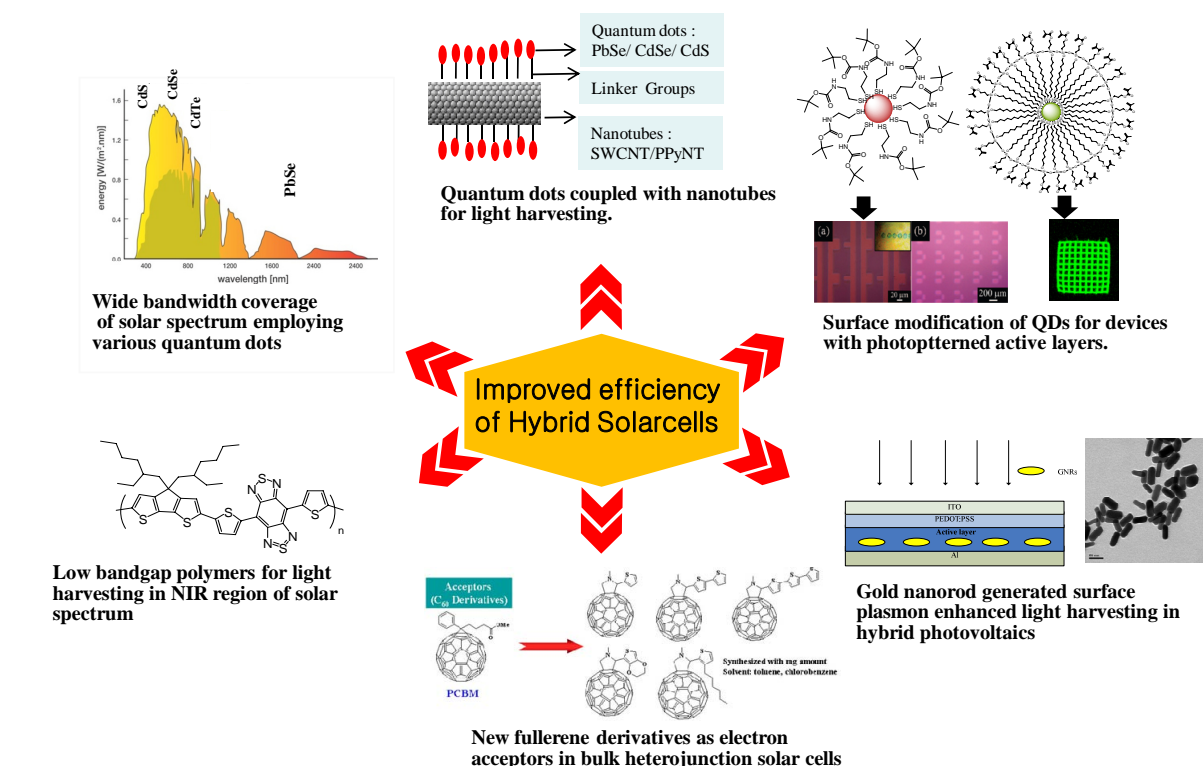
The features of polymer based photovoltaic devices such as flexibility, light-weight, radiation resistance and ease of use for large area structural applications suit them enormously for applications in military aircraft, aerospace applications and optoelectronic devices. However the current pace at purely organic or polymer-based photovoltaics is progressing would only lead to incremental increase in the efficiencies of these devices due to the inefficient harvesting of the UV and IR-photons, as well as the limited carrier mobility in polymers. Our research involve the hybrid approach in which inorganic materials like quantum dot (QD), carbon nanotubes (CNTs) and fullerene derivatives are combined with organic components to achieve efficient bulk heterojunction solar cells. We look at the materials, their interfaces and the resultant transport mechanisms in the devices to understand and improve our design of devices as well materials.

In this project we propose new approaches for highly efficient organic solar cells by applying a unique combination of our expertise in (i) synthesis of inorganic nanostructures, (ii) integration of polymeric nanocomposites with CNTs or polypyrrole nanotubes (PPyNTs) functionalized with UV-, Vis-, IR-active QDs by chemical modification, (iii) surface modification of QDs for efficient patterning of multilayer PV devices, (iv) synthesis of various C₆₀ derivatives coupled with thiophene oligomers, (v) synthesis of low band gap polymeric materials.

The focus of the second year of the AOARD project (Oct. 12, 2008- Oct. 11, 2009) can be broadly classified into two areas namely interface engineering in solar cells and the development of novel materials for applications in bulk heterojunction organic-inorganic solar cells. Achieving efficient charge separation and transport is an important criterion for achieving highly efficient bulk heterojunction solar cells. Our team has innovated on developing patternable interfaces for hybrid solar cells involving quantum dots. In the reported phase of the project we have successfully developed patternable semiconductor nanocrystals (quantum dots) and demonstrated their applications in devices. We have also observed some previously unreported trends in the optical activities of the quantum dots which hold a lot of promise for future photonic devices. Another study on the devices demonstrated the improvement of solar cell structure and hence efficiency by the introduction of a hole-blocking layer of PEDOT-PSS in In₂S₃/CuInSSe nanocrystal-based solar cells. During this phase of the project we have successfully designed, synthesized and tested new materials including lowband gap polymers for broad spectrum photovoltaic activity as well electron acceptor C₆₀ derivatives for polymer-fullerene hybrid solar cells. We have been able to develop very low bandgap polymers with

band gaps as low as 1.00 eV which are active in a wide region of the solar spectrum spanning 1000 nm (300-1300 nm). The devices involving these polymers are being studied. One of the fullerene derivatives showed values higher than those reported earlier for electron mobility with systems employing inkjet printing. The approaches that we have adopted in the current phase are summarized in the scheme below.

<Scheme: Research Approaches>



3. Results and Discussion

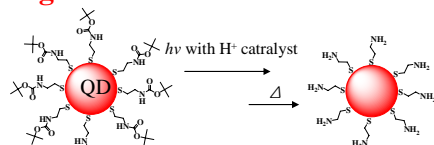
1) Photopatternable quantum dots (QDs)

Improving the interfacial interaction of the donor and acceptor groups in bulk heterojunction solar cells is a proven approach towards improving the efficiency of the solar cells. We have been exploring the scope of patternable QDs (nanocrystals) to create patterned interfaces. The exciton diffusion length in organic and hybrid organic solar cells is in the range of 10-20 nm; the development of patternable QDs would allow us to fabricate patterned bulk heterojunction interfaces of comparable dimensions. We have demonstrated the possibility of such patternable nanocrystals by ligating the QDs with a photoacid cleavable *tertiary*-butoxy carbonyl (*t*-BOC) unit. Spin coated films of *t*-BOC protected multiploid QDs of CdTe could be photopatterned successfully. Photocurrents were measured for both the unpatterned and patterned films and it was found that the latter showed more than an order of magnitude increase in photocurrent properties. The increase in photocurrents can be attributed to the cleavage of *t*-BOC units and the subsequent hydrogen bonding interaction between the photo-generated amino groups. This leads to a close packing of the quantum dots and hence increase the conductivity giving rise to and increase in photocurrent. Results in graphics are given below (Figure 1).

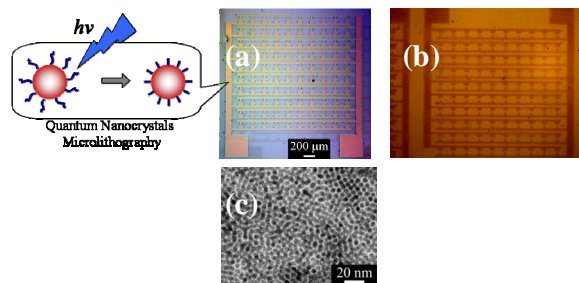
<Figure 1>

Surface Functionalization for Photo-Patternable QDs

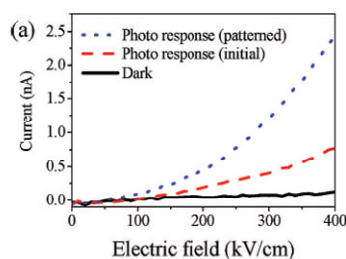
Photocleavage of *t*-BOC containing ligands



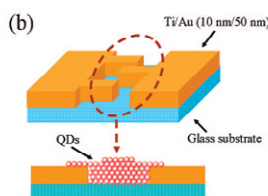
CdSe, CdTe, and PbSe ligands were functionalized with ligands containing terminal photo-acid cleavable *t*-BOC groups. The photocleaving of the *t*-BOC group is utilized to make patterned nanocrystals.



The *t*-BOC units in the ligand attached to the nanocrystals give amino groups on irradiation followed by heating. Figures (a) and (b) are 2-D patterns fabricated by photocuring 30 mg/ml films of photo-functionalized nanocrystals. The TEM image (c) shows the nanocrystals in photocured films.



Nano Lett., 8, 3262(2008)



Photocurrent Measurements of the nanocrystals were carried out before and after photocuring current-voltage curves (a) in the dark or with white light (100 mW/cm²) illumination for a film of *t*-BOC protected and deprotected CdTe nanocrystals (measured at the voltage scan rate of 1 V/s). The channel length is 4 μ m. Metal semiconductor metal (MSM) device structure (b) for photoconductivity measurement.

2) Photovoltaic Device Fabricated by Patternable QDs

Solar cell devices were fabricated from *t*-BOC functionalized nanocrystals as shown Figure 2. This devices involved a thermal cleaving of *t*-BOC unit. We demonstrate a relative improvement in power conversion efficiency of polymer nanocomposite photovoltaic cells consisting of poly(3-hexylthiophene) (P3HT) functionalized CdSe nanocrystals. Thermal deprotection processing of the *tert*-butoxycarbonyl moiety in the carbamate ligand surrounding the surface of CdSe nanocrystal significantly shortened the length of the ligand between nanocrystals and between the nanocrystal and the polymer matrix. The resulting device performance was investigated as a function of the composition ratio of P3HT/CdSe and the heating temperature. This simple and straightforward ligand deprotection strategy resulted in a significant increase in current density due to improvement of charge transport between the constituent materials. It was observed that the photovoltaic cell efficiency (PCE, solar cell efficiency) increased with increased thermal curing because of greater cleavage of *t*-BOC units. But its values over 260°C decreased due to thermal fluctuation (Table 1). As this processing could endow totally different solubility of nanocrystals before and after the chemical structural change of the ligand on their surface, this thermal deprotection technique of *t*BOC moiety in semiconducting nanocrystals can lead to a facile multilayered device fabrication for further photovoltaic device applications.

<Figure 2>

I-V Characteristics of PV Devices P3HT: CdSe

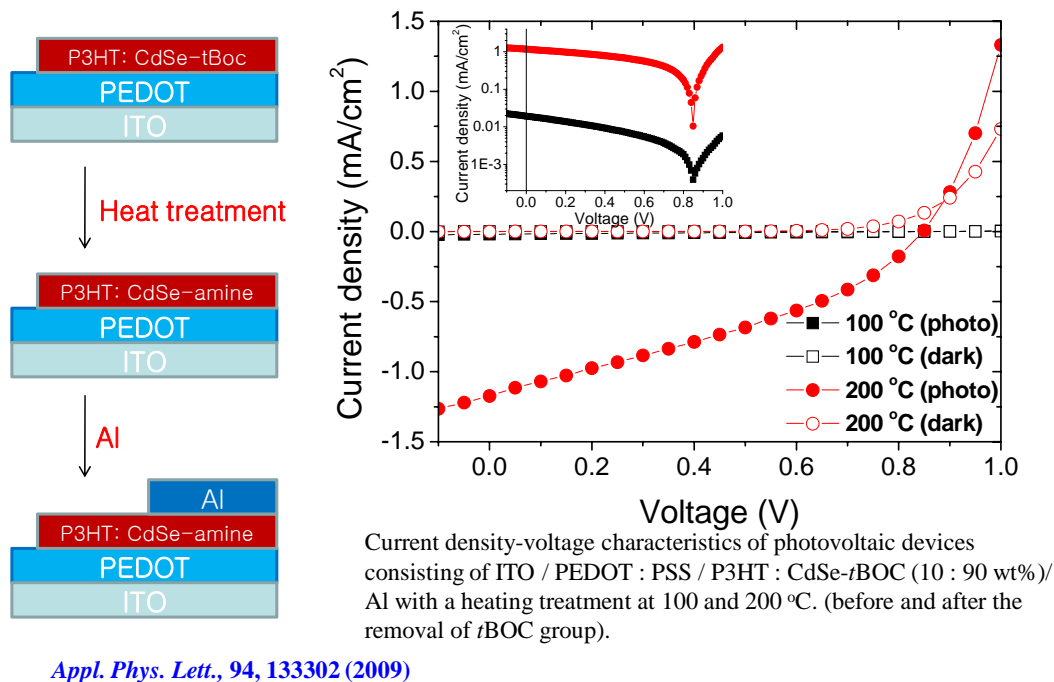


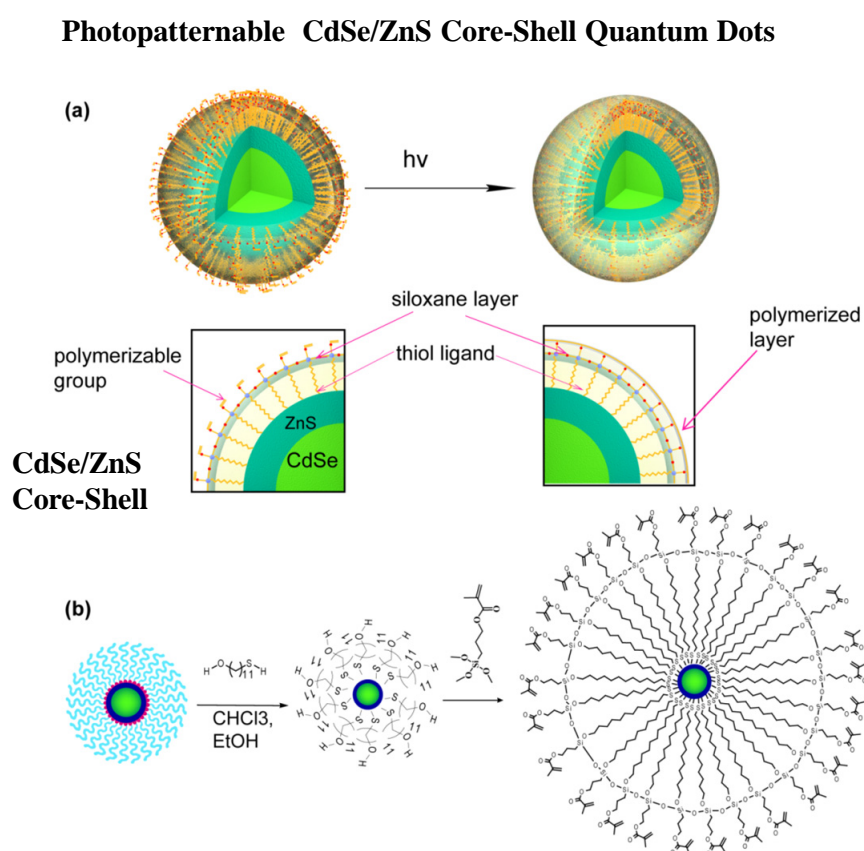
Table 1. Summary of device performance in P3HT: CdSe-*t*Boc wt %) (10:90 blend film with different heating temperatures for *t*BOC deprotection

Temperature (°C)	V_{oc} (V)	J_{sc} (mA/cm ²)	FF	PCE (%)
150	0.89	0.75	0.29	0.21
175	0.87	0.82	0.31	0.25
200	0.85	1.17	0.35	0.38
220	0.82	1.16	0.37	0.39
240	0.76	1.43	0.37	0.44
260	0.73	1.53	0.33	0.42
300	0.50	1.31	0.29	0.21

3) 3-D Patternable Core-Shell Type QDs

The controlled fabrication of two- or three-dimensional micro- and nanoscale structures containing nanoparticles is of great scientific importance for the development of efficient optoelectronic devices. We have designed and synthesized green functionalized quantum dots composed of a photopolymerizable outer corona constituting methacrylate and an inner siloxane layer, with a view making them photo-responsive and increasing their stability (Figure 3). Silanes are capable of forming dense films on nanoparticles. These dense films could act as a passivating layer, and also play a role in reducing the toxicity of the QDs. Also, the resulting photopatternable QDs are highly solution-processable and capable of forming photo-ordered films with considerable long range order resulting in an enhancement of optical properties.

<Figure 3>

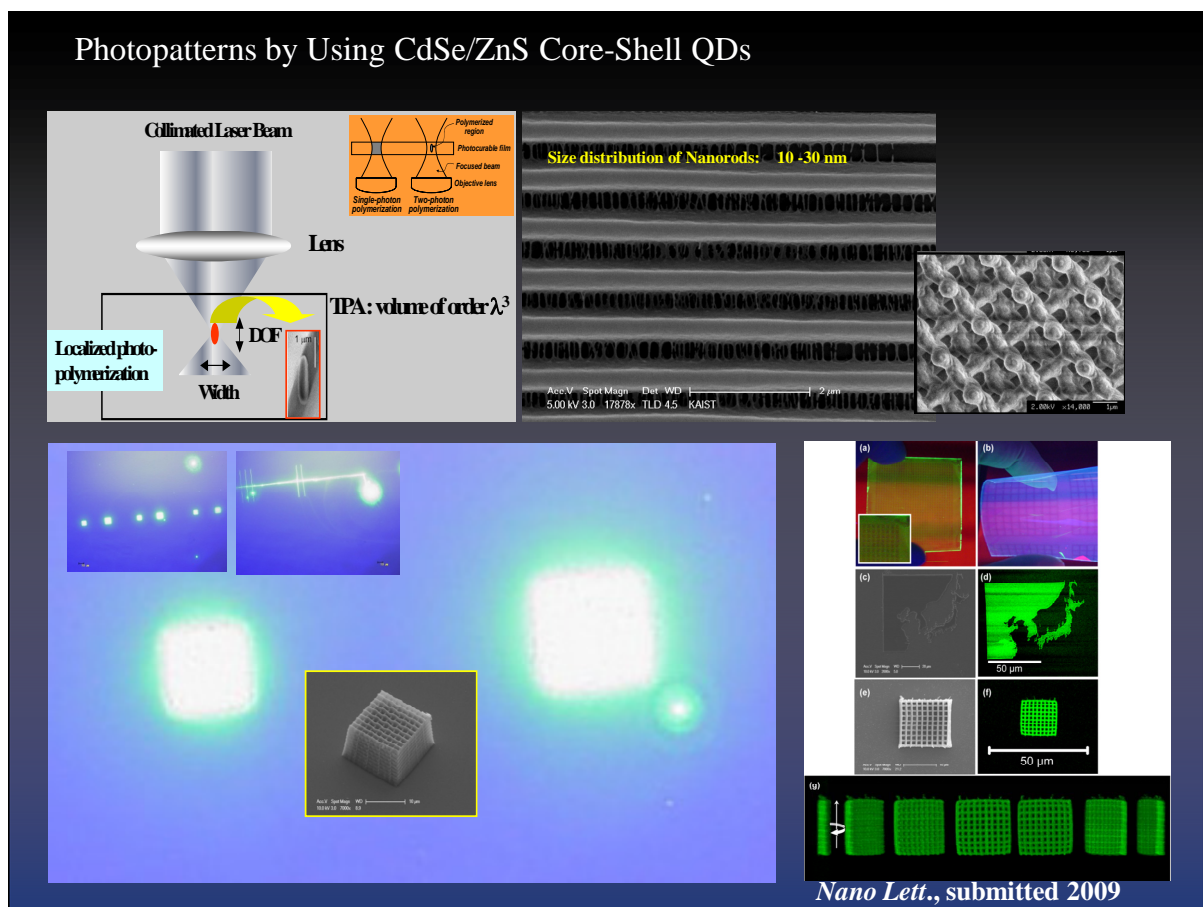


Two-photon polymerization is a promising tool for making 3D nano/micro devices. Very small line structures as well as array structures can be fabricated by two-photon lithography, which are demonstrated in Figure 4 (left from the top), we have achieved very small structures in the orders of tens of nanometers through a long irradiation technique. These structures are in the range of excitonic diffusion length and if we can replicate these structures with quantum dot structures it would give rise to very efficient light harvesting. We could dope the acrylate functionalized core-shell quantum dots in large quantities into photopatternable resins to create 3D nanostructures.

The inherent properties of photopolymerizable QDs such as their stability, PL, and ease of solution processability, make them suitable materials for the active layers of electroluminescent devices. The first example of a QD-based light-emitting diode (QD LED) was a device based on

an indium-tin-oxide (ITO) supported hole-transporting polyphenylenevinylene (PPV) film interfaced to a capped CdSe-nanoparticle film with Mg top electrode. To evaluate the potential of the photopatternable QDs, we fabricated electroluminescent devices in which the active layer was a spin-cast film of photofunctionalized QDs. We have been able to demonstrate the influence of photopatternable functionalization on the optical properties of QD films after photocuring. Photopatternable QD films were found to form dense quasi-ordered arrays post exposure. Photo-polymerization driven shrinkage of patternable QD films resulted in an increase of particle density in the photocured films, as well as a large enhancement in photoluminescence. The phenomenon of photodriven ordering in functionalized QDs is previously unreported to the best of our knowledge and provides a new method to control the microstructure of the quantum dot films. An exposed active layer in an electroluminescent device was found to show greater electroluminescence efficiency when compared to devices with un-exposed QD active layers.

<Figure 4>

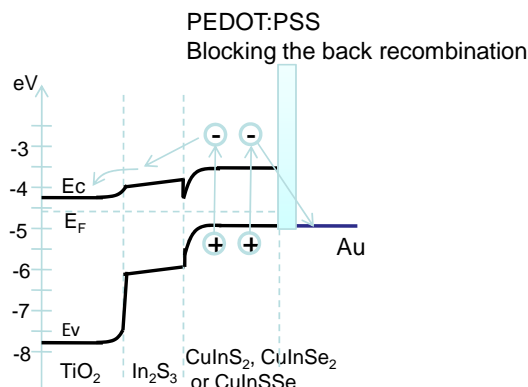
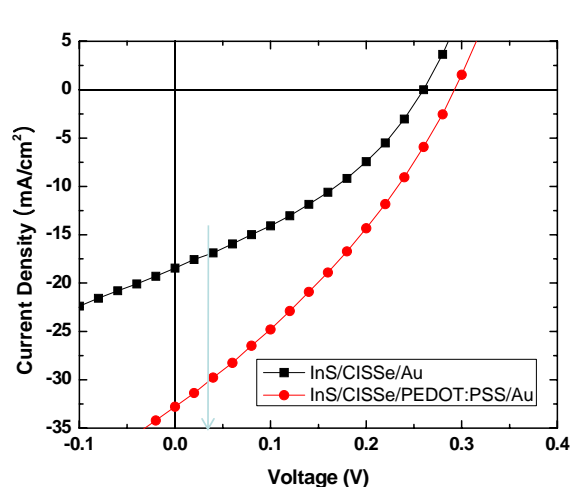


4) In₂S₃/CuInSSe Solar Cells

A part of our team is also focusing on the improvement of the structure of hybrid solar cell devices by looking at their structure and trying to improve the role and interaction of various layers constituting the solar cell. Recently we introduced a hole blocking PEDOT-PSS layer common in organic semiconductor devices in a solar cell constituting In₂S₃/CuInSSe and found that it improved the performance (1.69 → 3.16%). This could be seen as a result of effective charge separation in presence of the hole blocking layer (Figure 5).

<Figure 5>

Polymer Blocking Layer Effect on In₂S₃/CuInSSe Solar Cell



V_{oc} is similar
J_{sc} shows significant increase
FF is decreased
PCE increases due to the J_{sc} increment

	V _{oc} (V)	J _{sc} (mA/cm ²)	FF(%)	PCE(%)
w/o PEDOT:PSS	~0.26	18.4	35.3	1.69
with PEDOT:PSS	~0.29	33.5	31.9	3.16

→ PEDOT:PSS effectively blocks electrons & transports holes

5) Low Bandgap Polymers

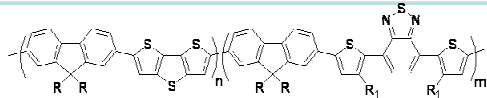
Solar cells based on polymeric materials are important in terms of their ease of processability, and optical properties. In order to access and harvest the NIR region of the solar spectrum we need low band gap polymeric materials which are suitable for absorbing radiation in this region. At the beginning of this project we envisaged to evolve criterion and structural motifs aiding this goal. The results are from devices performance of two polymers PFTB and PCTB in comparison with P3HT-PCBM bulk heterojunctions. Those polymers showed higher solar efficiency compared to P3HT based devices which is well known material in polymer-fullerene derivatives based solar cells (Figure 6). But, these polymers would not strictly fit into the criterion of low-band gap polymers. We followed a design paradigm in which the number of repeating groups were varied to observe the effect on the optical properties of the polymers PFTB and PCTB.

We have been able to develop very low band-gap polymers with band gaps as low as 1.00 eV. These polymers have a wide band width absorption spanning more than 1,000 nm (300-1,300 nm) in the solar spectrum. The photovoltaic devices involving these materials are being studied now. In Figure 7 the absorbance of various low bandgap polymers and their blends with PCBM are compared to outstanding materials from elsewhere. Please note that PCPDTBBT shows a larger bandwidth absorption in the NIR region than other polymers (eg., PCPDTBT reported by A. Heeger). This polymer blended with PCBM showed an absorption spanning a broad bandwidth spanning 750 nm-1450 nm with a peak at 1100 nm.

<Figure 6>

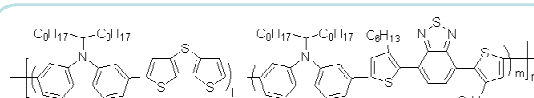
Low Bandgap Conjugated Copolymers: PFTB & PCTB

PFTB



$R = C_8H_{17}$; $R_1 = C_6H_{13}$ $n=0.1$, $m=0.9$

PCTB



$R = C_8H_{17}$; $R_1 = C_6H_{13}$ $m=0.9$, $n=0.1$

Abs: λ_{max}

521 nm

519 nm (with PCBM 1:4)

PL: λ_{max}

642 nm

642 nm (with PCBM 1:4)

Abs: λ_{max}

521 nm

519 nm (with PCBM 1:4)

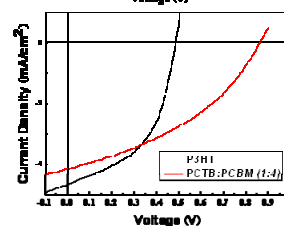
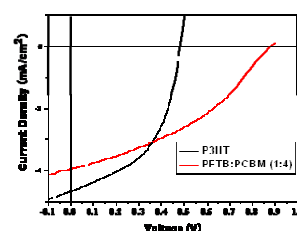
PL: λ_{max}

642 nm

643 nm (with PCBM 1:4)

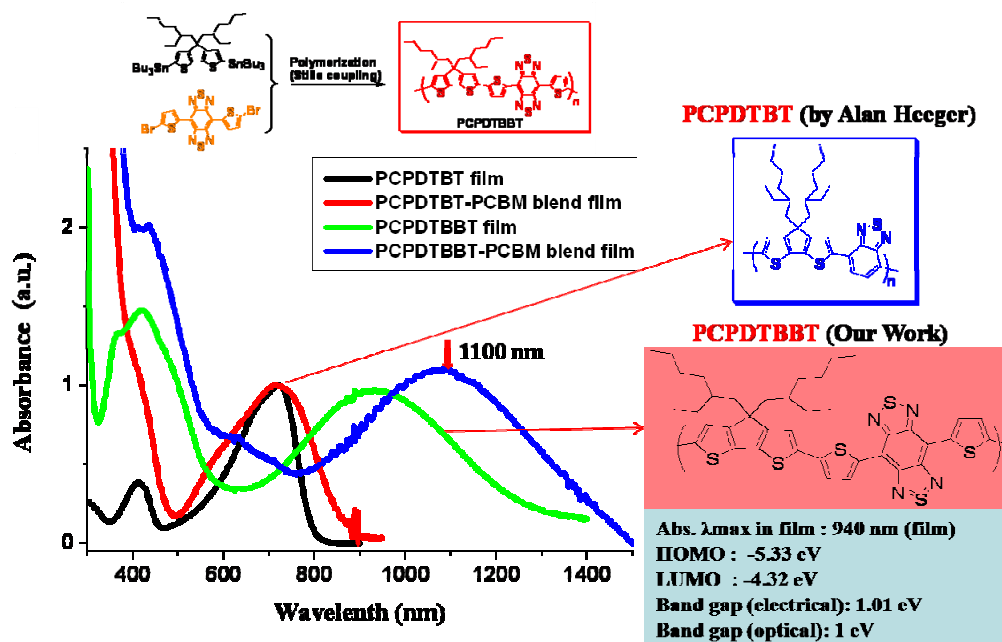
I-V Characteristics and Solar Cell Efficiency

Device	J_{sc} (mA/cm^2)	V_{oc} (V)	FF (%)	Solar Efficiency (%)
P3HT/PCBM (1:0.8)	4.234	0.485	49.68	1.02
PFTB/PCBM (1:4)	3.596	0.881	37.64	1.19
PCTB/PCBM (1:4)	3.782	0.862	38.74	1.26



<Figure 7>

Comparison of UV-vis Absorption of Low Bandgap Polymers



UV-vis absorption spectra of the PCPDTBT and PCPDTBBT polymer films and the polymer-PCBM blend films

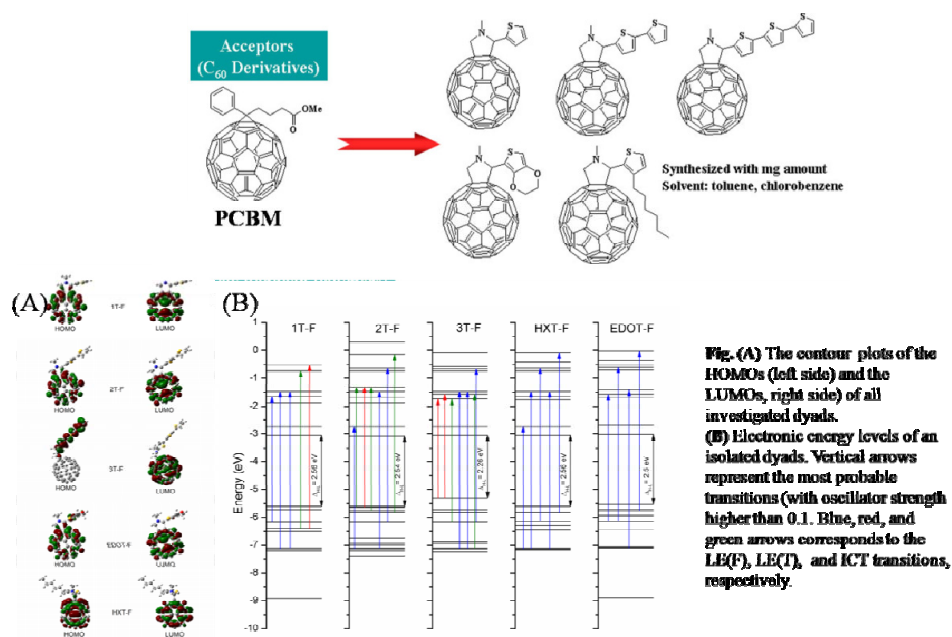
6) Synthesis and Physical Properties of Fullerene Derivatives

Composite materials of π -conjugated organic oligomers or chromophores with side chains appear to be very promising candidates for the construction of artificial photosynthetic system and optoelectronic devices. Efficient photoinduced electron transfer from an organic chromophore (electron donor) to an electron acceptor has been found application in plastic solar cells. To optimize this process the contact between the donor and acceptor must be very close. The best way of optimizing the electron transfer between both moieties of the system is to covalently bond the chromophore acting as the donor to the fullerene. Fullerenes are very often used as electron acceptors because they have small reorganization energies in electron-transfer reactions, therefore leading to slow charge recombination. On the other hand their unique physical and chemical properties make them an attractive component to be incorporated in functional molecular assemblies and supramolecular arrays. The reactive site in the fullerene is, in most cases, the C=C bond bridging pentagons in a pyracylene unit. Recently, as promising electron donor molecules we used selected oligothiophenes. Thiophenes are important compounds that are used as building blocks in many chemical synthesis. The thiophene oligomers and thiophene-based molecules have been widely studied experimentally and theoretically. Thiophene oligomers are interesting because of their properties such as ready accessibility, structural modifications, high π -conjugation, low oxidation potential, and environmental stability.

According to our best knowledge, our investigations of the vibrational properties of the oligothiophene-fullerene dyads were one of the first in literature. The goal in our research was synthesis of various oligothiophene-fullerene dyads and the analysis of vibrational properties of by infrared absorption and Raman scattering methods. Spectral investigations were supported by quantum chemical simulations of the molecular structure and normal mode vibrations of the dyads. The effect of the presence of C_{60} acceptor on the vibrational properties of the donors was also studied. It was shown that vibrational spectroscopy could be successfully used for characterization of such complex molecular systems as oligothiophene-fullerene dyads.

<Figure 8>

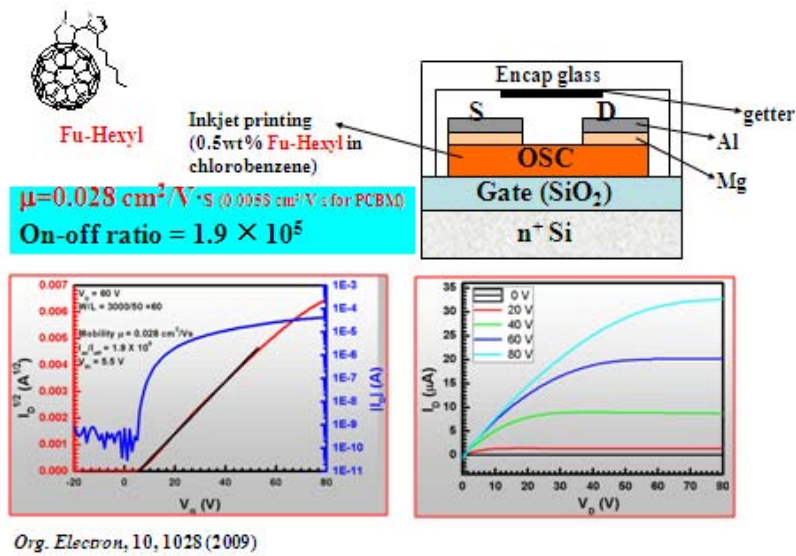
C_{60} Derivatives as Acceptors in Hybrid Bulk Heterojunction Solar Cells



One of the fullerene derivatives **Fu-Hexyl** showed very high value of electron mobility with inkjet printing (electron mobility $\mu=0.028 \text{ cm}^2/\text{V}\cdot\text{s}$; observed value for PCBM under the same conditions $\mu=0.0058 \text{ cm}^2/\text{V}\cdot\text{s}$). Figure 9 summarizes the structures of the material, the structure of the device used for testing the materials as well as a the dark current I_D Vs gate voltage (I_D Vs V_G) and dark current Vs dark voltage (I_D Vs V_D) for the devices. Figure 10 shows the current density Vs voltage graphs of **Fu-Hexyl**, and also summarizes the performance of the inkjet printed device of the same when compared to P3HT-PCBM. The efficiency of the Fu-Hexyl device is 2.44% when compared to 2.39% of P3HT-PCBM devices. Now we working on for observing optimized efficiency of solar cells based on Fu-Hexyl.

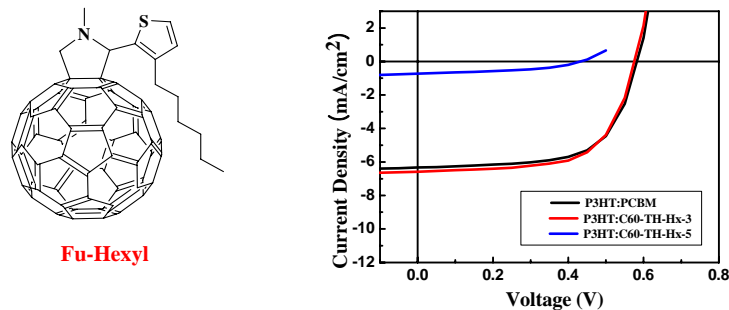
<Figure 9>

Electron Mobility of New n-Type C60 Derivative (Fu-Hexyl)



<Figure 10>

Efficiency of ITO/PEDOT:PSS/P3HT:C60 Derivative/TiOx/Al Solar Cells



Compounds	J_{sc} (mA/cm ²)	V_{oc} (V)	FF	E_{ff} (%)
P3HT:PCBM	6.32	0.582	0.65	2.39
P3HT:C60-TH-Hx-3	6.58	0.575	0.64	2.44

4. List of Publications

- 1) J. Seo, W. J. Kim, S. J. Kim, K.-S. Lee, A. N. Cartwright, and P. N. Prasad, *Appl. Phys. Lett.*, **94**, 133302 (2009).
“*Nanocomposite photovoltaics utilizing CdSe nanocrystals capped with a thermally cleavable Solubilizing ligand*”
- 2) W. J. Kim, S. J. Kim, K.-S. Lee, M. Samoc, A. N. Cartwright, and P. N. Prasad, *Nano Lett.*, **8(10)**, 3262-3265 (2008).
“*Robust Microstructures Using UV Photopatternable Semiconductor Nanocrystals*”
- 3) J. S. Kim, W. J. Kim, N. Cho, S. Shukla, H. Yoon, J. Jang, P. N. Prasad, T.-D. Kim, and K.-S Lee, *J. Nanosci. Nanotech.*, **9**, 6957-6961 (2009).
“*Synthesis and properties of Quantum Dot-Polypyrrole Nanotube Composites for Photovoltaic Application*”
- 4) E. Y. Park, J. S. Park, T.-D. Kim, K.-S. Lee, H. S. Lim, J. S. Lim, and C. Lee, *Org. Electron.*, **10**, 1028-1031 (2009)
“*High-performanace n-Type Organic Field-Effect Transistors Fabricated by Ink-Jet Printing using a C60 Derivative*”
- 5) B. Barszcz, B. Laskowska, A. Graja, E. Y. Park, T.-D. Kim, and Lee, *Chem. Phys. Lett.*, **479**, 224-228 (2009)
“*Vibrational spectroscopy as a tool for characterization of oligothiophene-fullerene linked Dyads*”
- 6) I. B. Barszcz, B. Laskowska, A. Graja, E. Y. Park, T.-D. Kim, K.-S. Lee, *Synth. Met.*, **159**, 2539-2543 (2009)
“*Vibrational Properties of Two Fullerene-Thiophene-Based Dyads*”
- 7) W. J. Kim, S. J. Kim, J. Seo, Y. Sahoo, A.N. Cartwright, K.-S. Lee, P. N. Prasad, *Mater. Res. Soc. Symp. Proc.*, **113**, F03-09 (2009)
“*Binding characteristics of surface ligands on PbSe QDs and Impact on Electrical Conductivity*”
- 8) Y. Cui, S. He, *Opt. Lett.*, **34(1)**, 16-18 (2009)
“*Enhancing extraordinary transmission of light through a metallic nanoslit with a nanocavity antenna*”