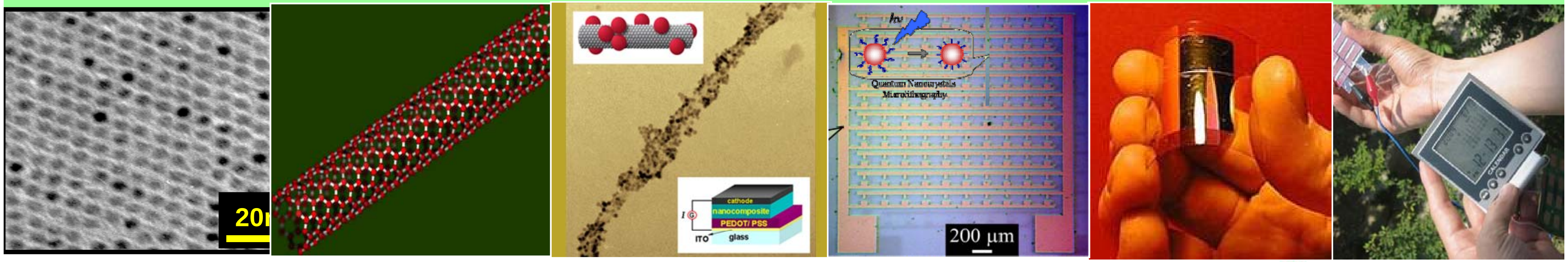
Organic-Inorganic Hybrid Materials for IR-Photodetection and Photovoltaics



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Hannam University

Kwang-Sup Lee

Department of Advanced Materials,
Hannam University, Daejeon 305-811, Korea

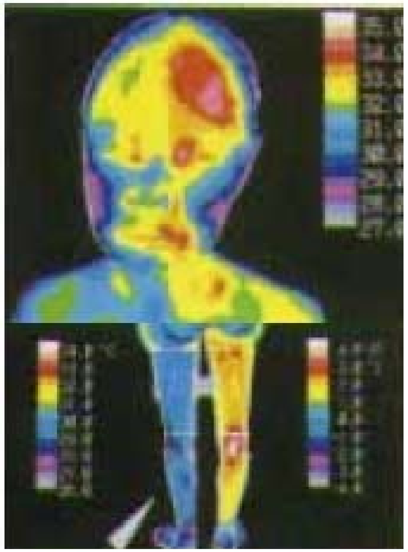
Contents

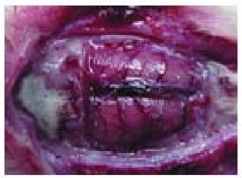
IR Photodetection

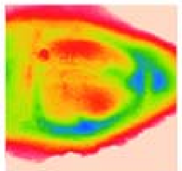
Increase detectivity → Increase number of applications

Military

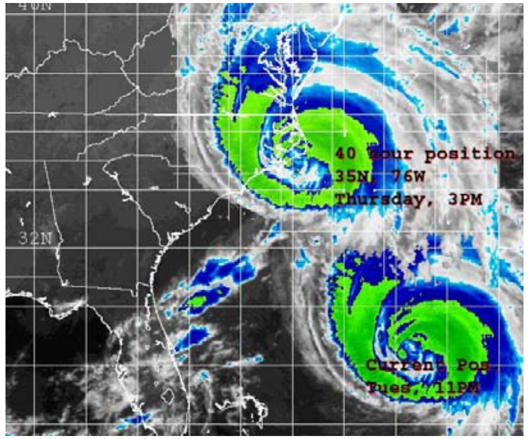
Medical
(Thermal Imaging)



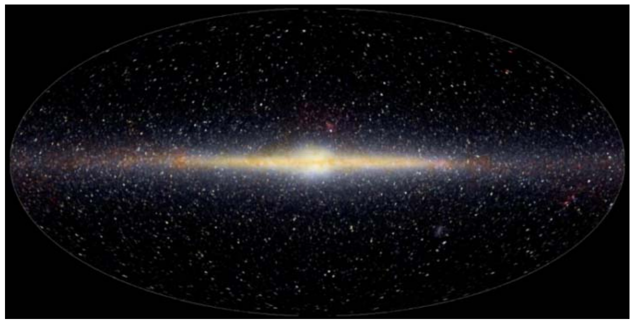




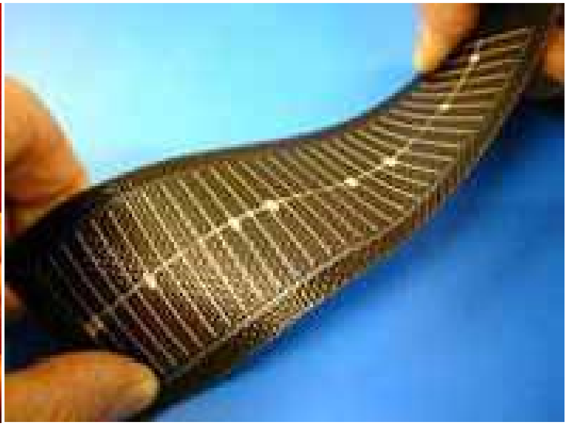
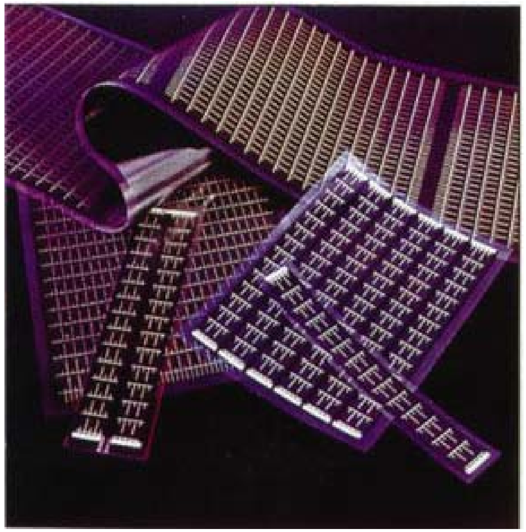
Weather



Astronomy:
Infrared Image of
the Milky Way

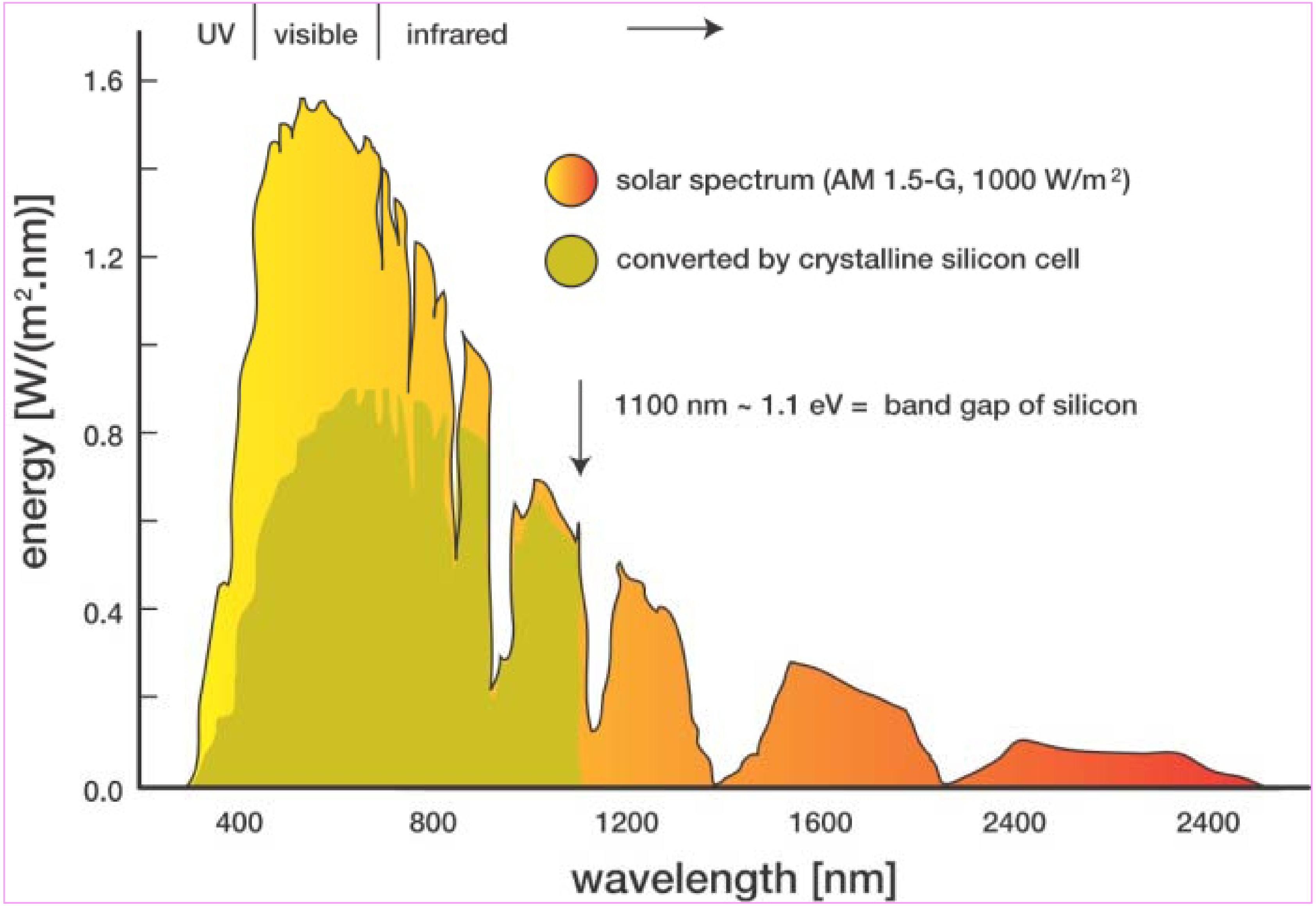




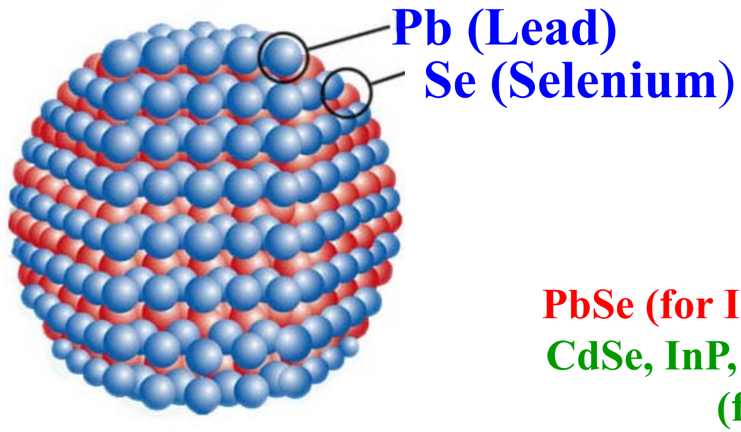




HOT SHOTS!
Back of SCOTTEVEST
Battery Charge Pack


Solar Spectrum



(Nanocrystal Quantum Dots)



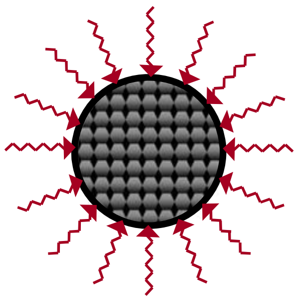
PbSe (for IR)

CdSe, InP, InP-CdS core-shell (for visible)

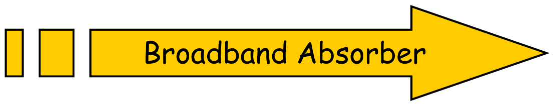
ZnSe, CdS (for UV)

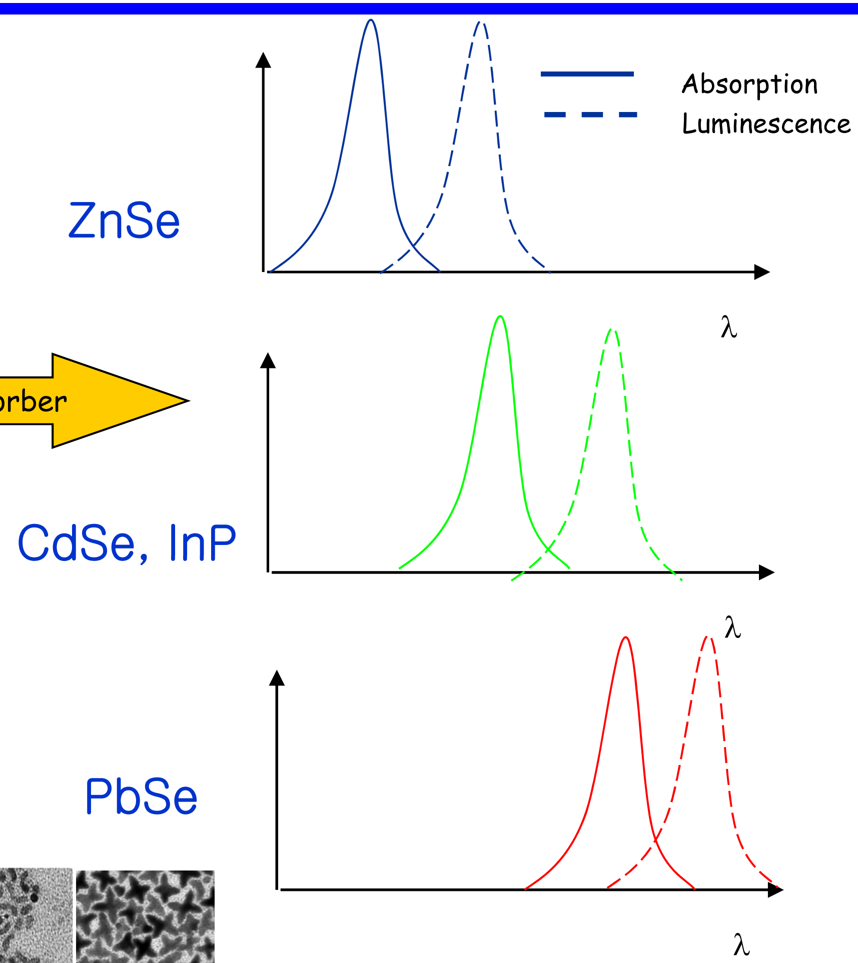
- **Semiconducting characteristics**
- **Excellent quantum size effects**
- **Efficient excitonic generation**
- **Tunable absorption and emission in the UV to IR**

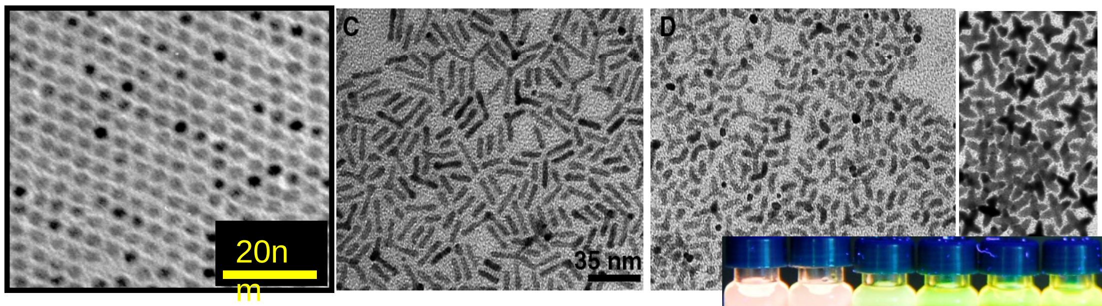
Tuning of Spectral Response by Choosing Quantum Dots



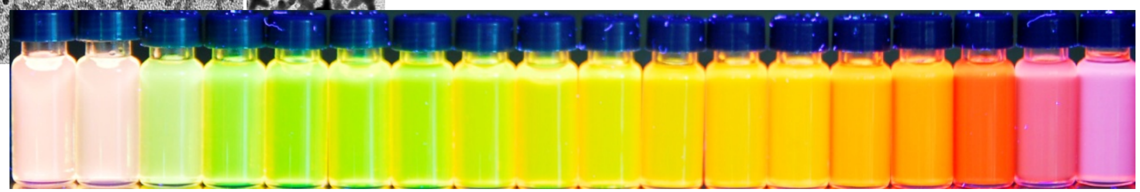
Quantum Dots



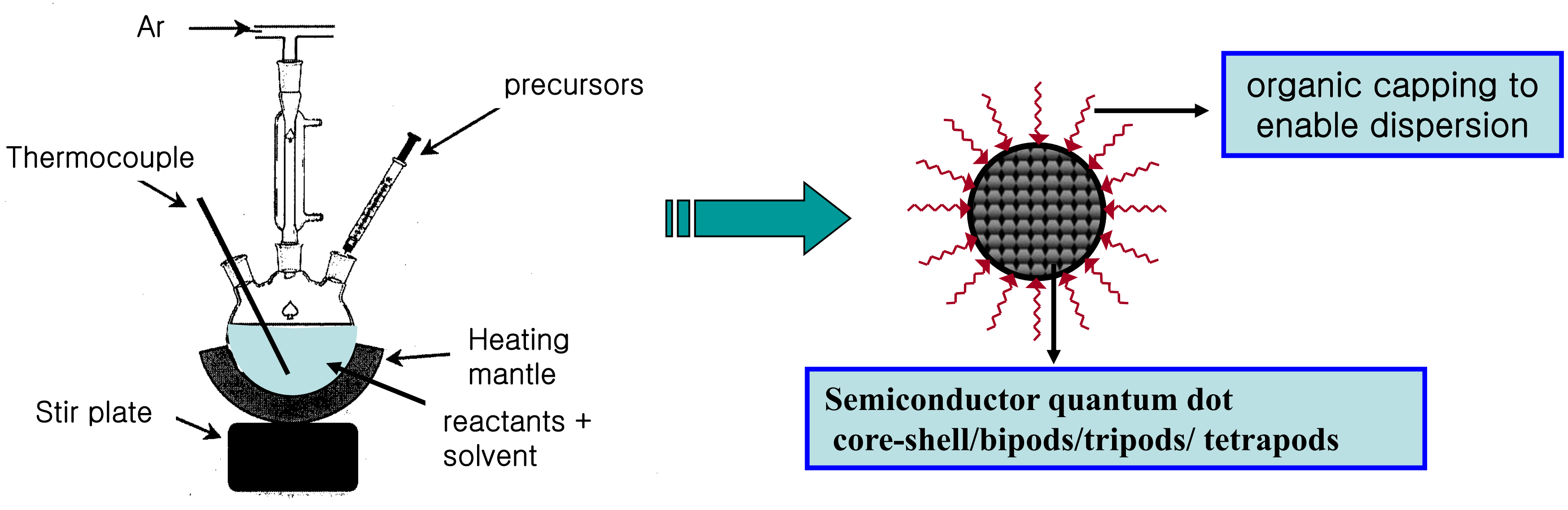




CdSe QD



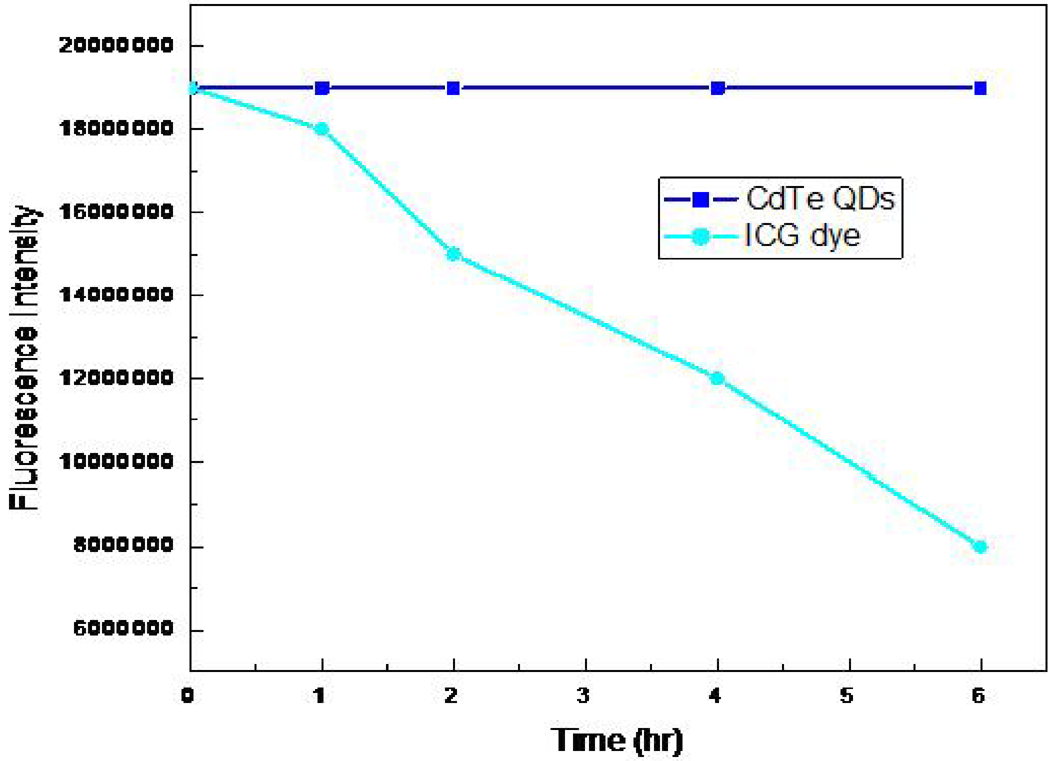
Preparation of PbSe Nanocrystals



(PbO + Oleic acid in tri-*n*-octylamine solvent)+ TOP-Se or TBP-Se

Comments: Size and shape control + Surface functionalization of the particles are very important steps.

Comparative Environmental Stabilities of IR QDs and IR Organic Dyes

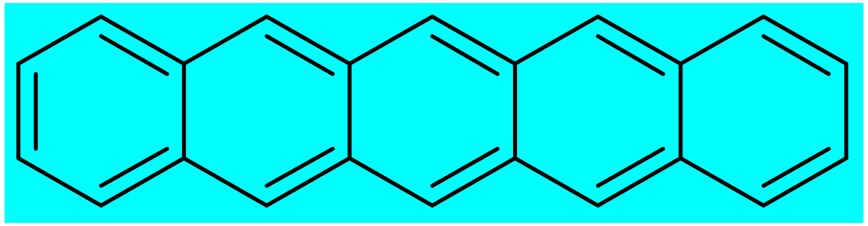


Excitation - 720 nm
Emission - 830 nm.

Normal laboratory environmental storage conditions.

Hybrid Materials for IR Photodetection

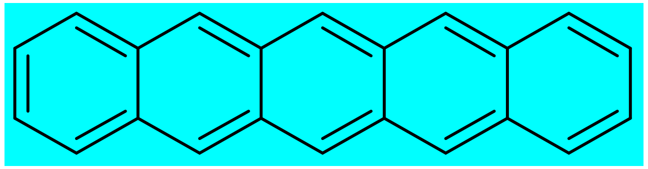
QD / Pentacene / PVK
Polymeric Nanocomposite



Pentacene

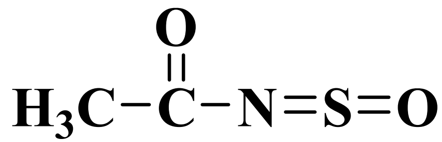
Synthetic Route for Pentacene Precursor

Ali Afzali, et.al, *J. Am. Chem. Soc.* **2002**, *124*, 8812.



Pentacene

+

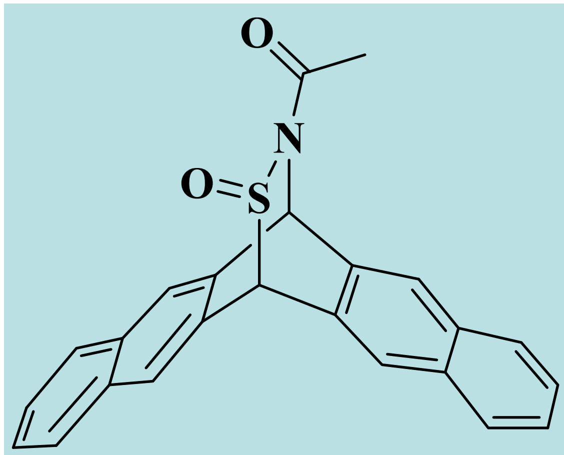


***N*-sulfinylacetamide**

CH_3ReO_3

→

$CHCl_3$

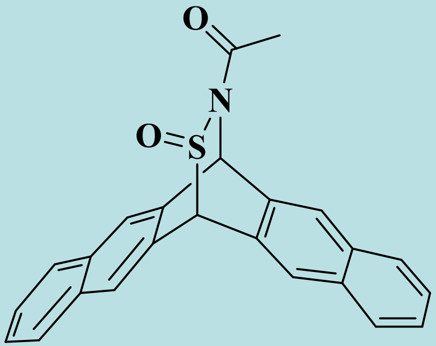


Pentacene precursor

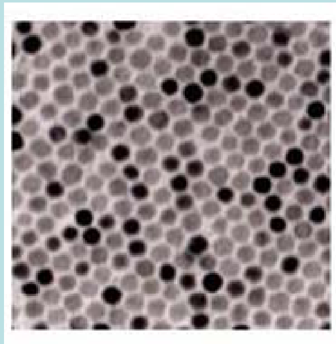
"Soluble in $CHCl_3$, CH_2Cl_2"

Prepared by the Diels-Alder reaction between pentacene & N-sulfinylamide in the presence of a catalytic amount of methyltrioxorhenium,

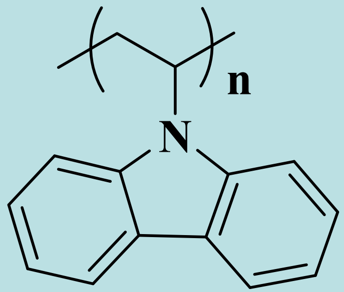
Device Processing for IR Photodetector



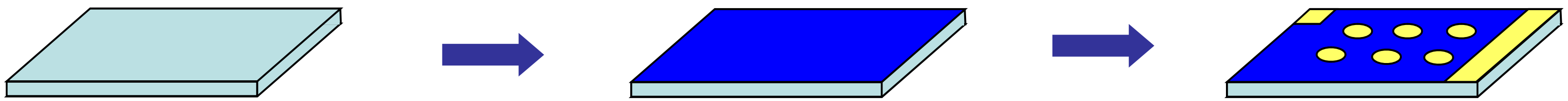
Pentacene precursor



PbSe nanoparticle



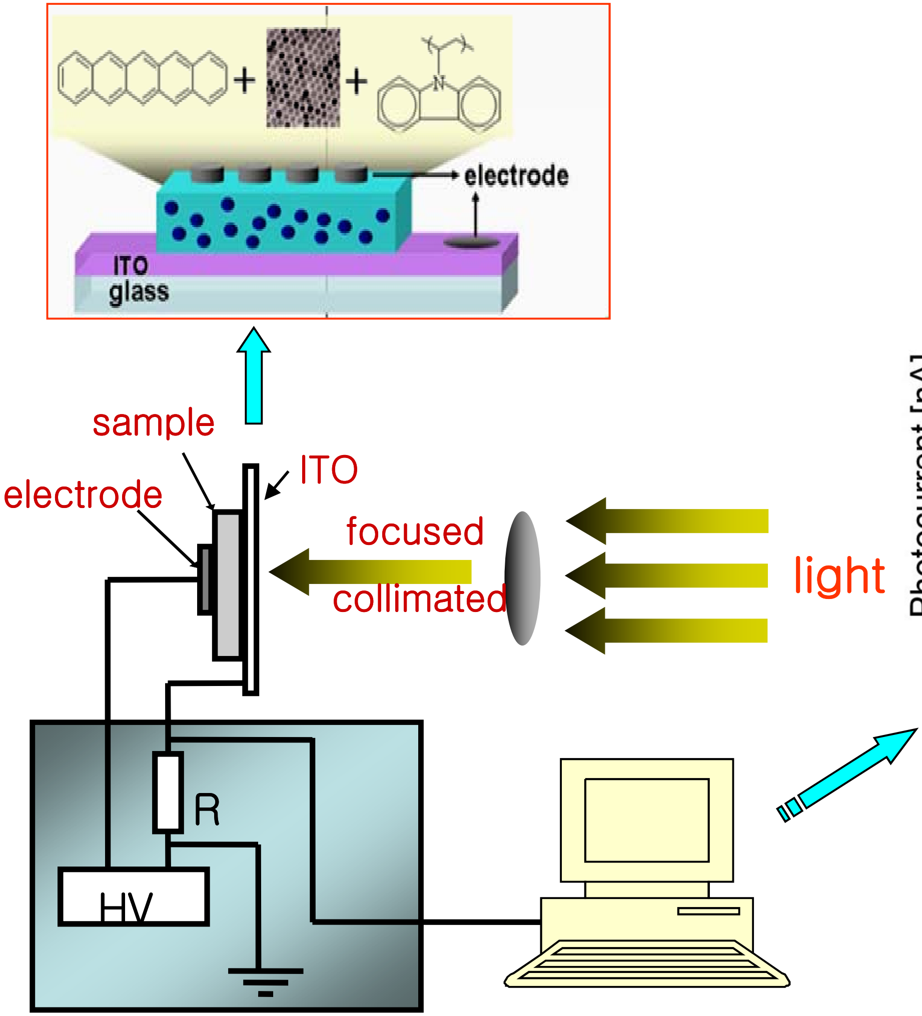
PVK



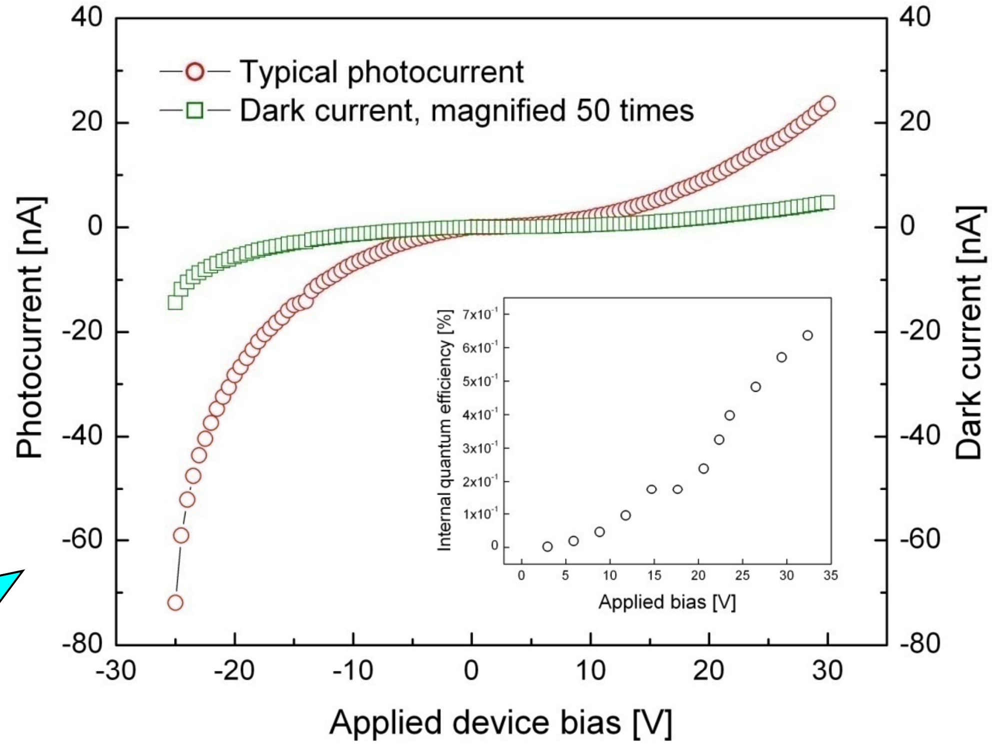
PVK–Pentacene precursor–PbSe Film → Baked in vacuum oven at 240 °C → Measured Photoconductivity

Film Composition: PVK 30 wt%, Pentacene precursor 30 wt%, PbSe 40 wt%

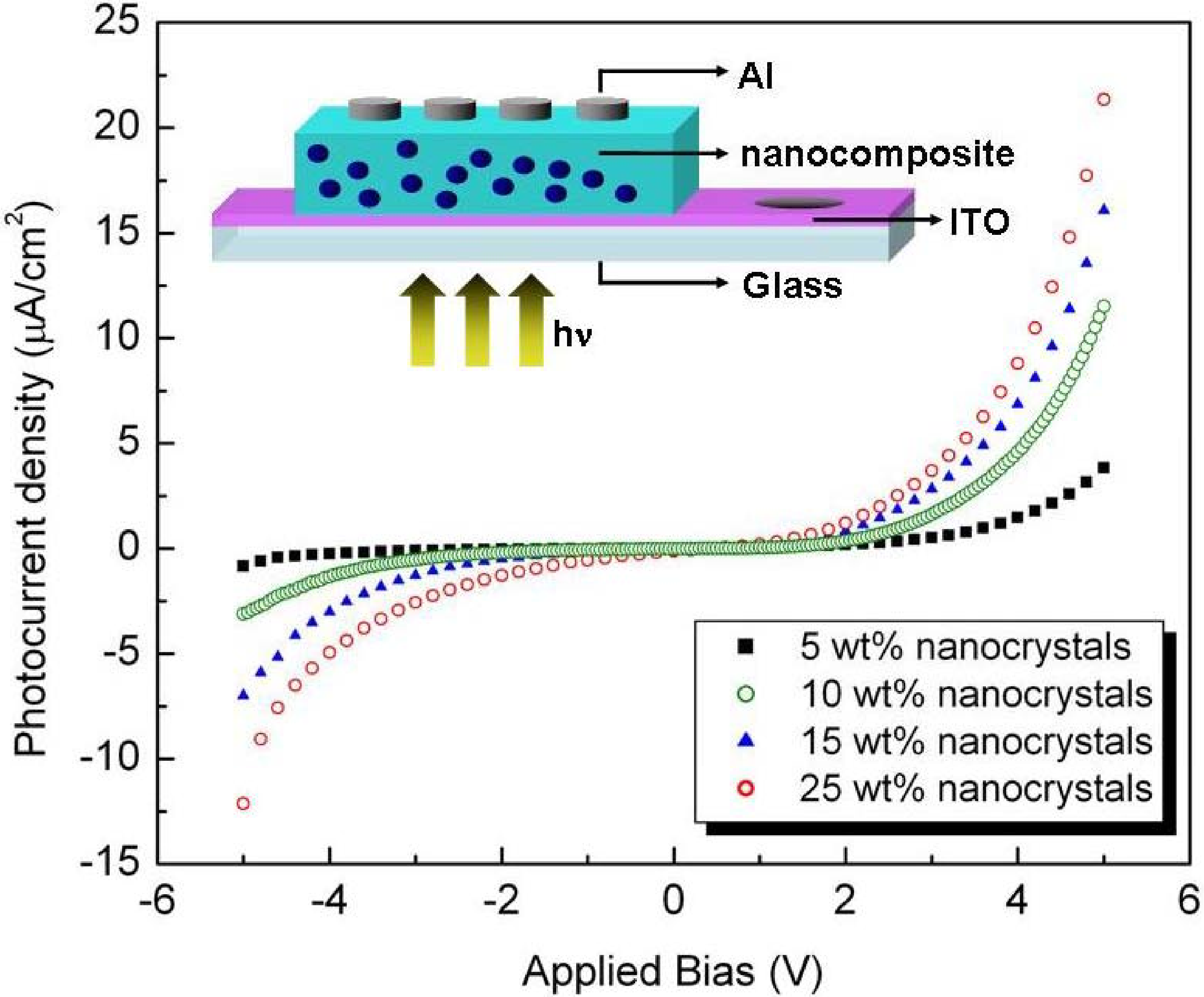
Evaluation of Photoconductivity



Keithley source meter



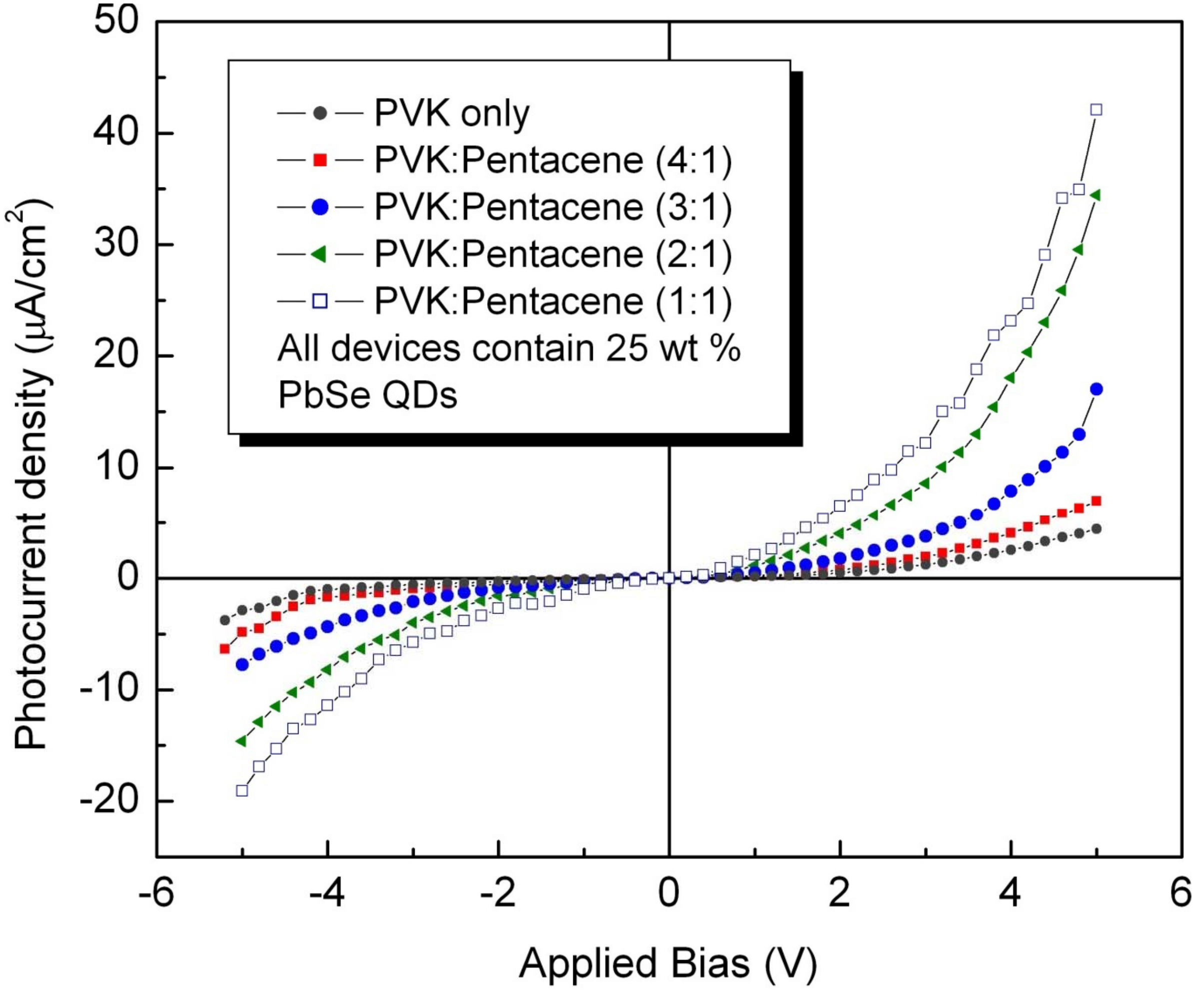
Typical I-V Curve



Photocurrent density as a function of applied voltage in devices with the same proportion of PVK: pentacene (3:1) but various amounts of PbSe nanocrystals as indicated in the legend.

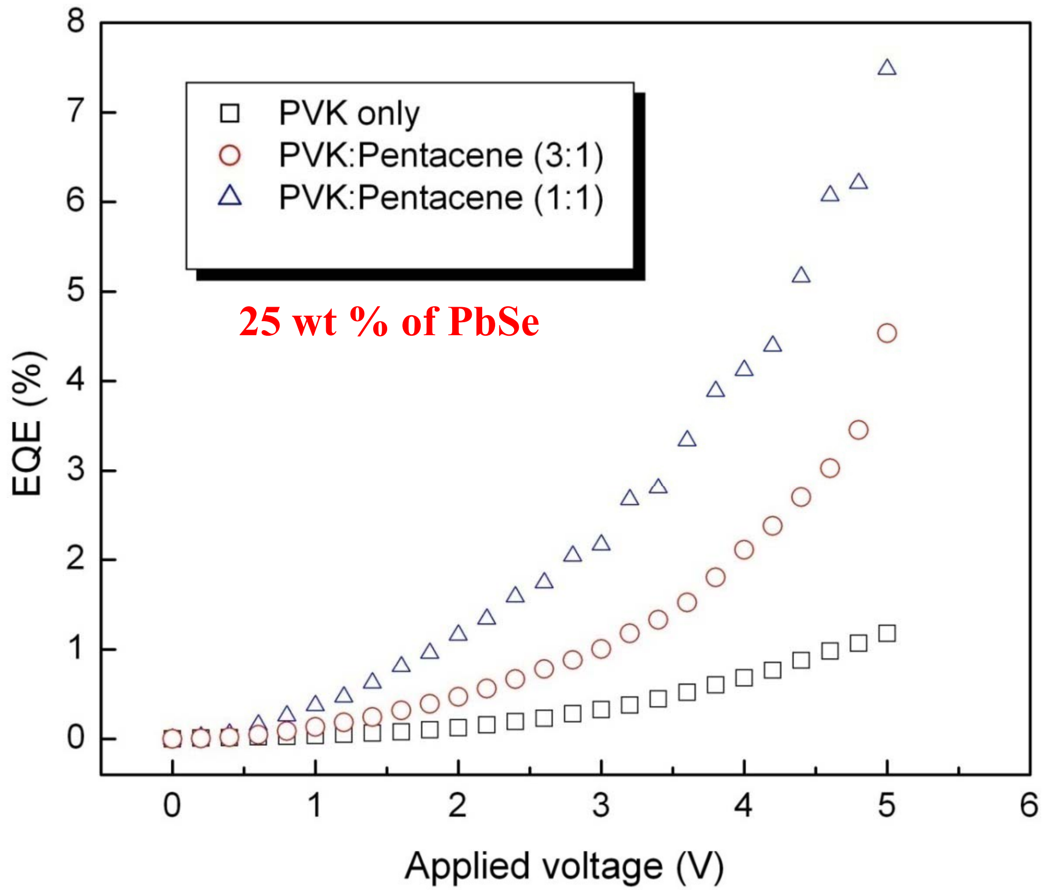
Appl. Phys. Lett., 87, 051109 (2006) / US Patent 0128021 A1, 2008

Photocurrent density as a function of applied bias (1340 nm) in different devices with varying proportions of PVK and pentacene



The photocurrent increases significantly as the amount of pentacene in the composite increases. The best performance was extracted in devices with equal amounts of PVK and pentacene (having 25 wt % of PbSe QDs). The enhancement in photocurrent, compared to a PVK-PbSe film, is over 8 times.

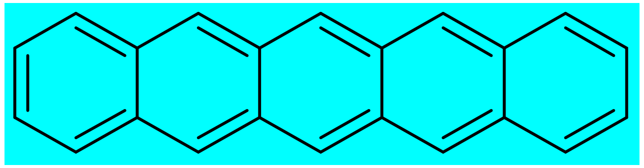
Comparison of the external quantum efficiency of the composite devices

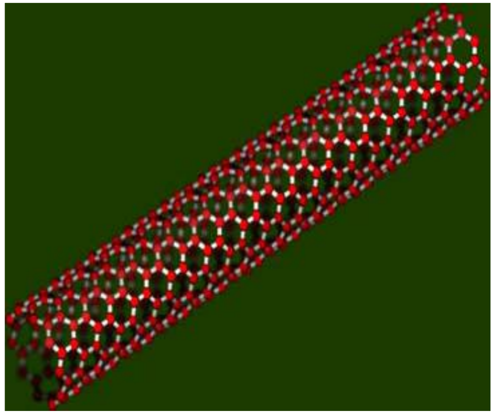


Max EQE:
~ 8% in the IR

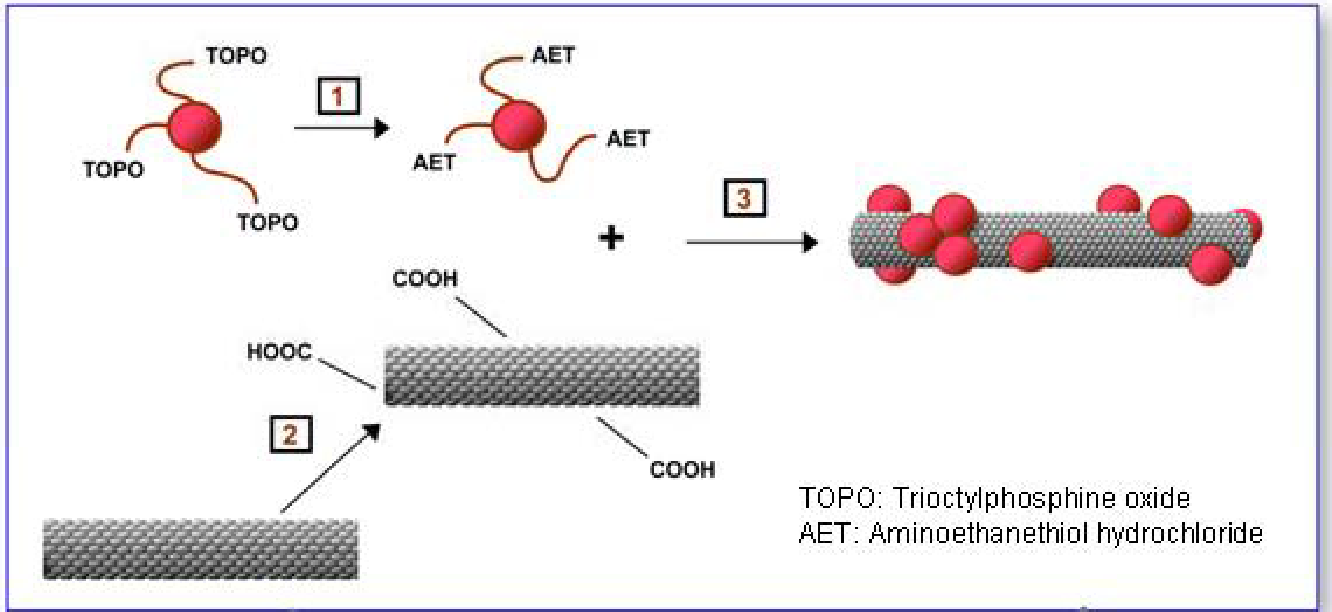
A maximum external quantum efficiency (EQE) of ~8% at an applied device bias of 5 V is achieved in the composite having equal amounts of PVK and pentacene. This is an improvement of eight times over the PVK:PbSe devices under similar experimental conditions.

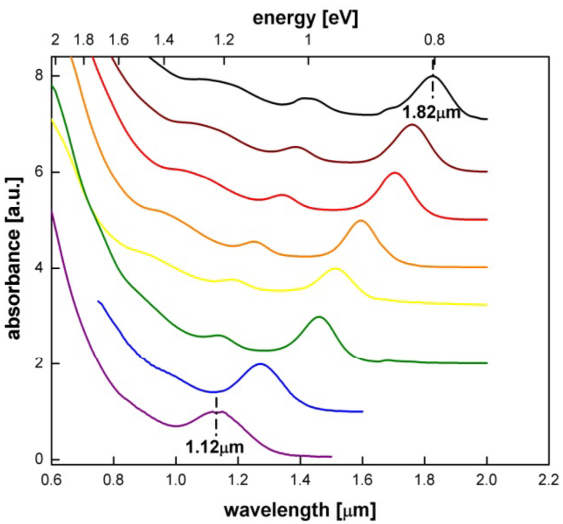
QD-Carbon Nanotube / PVK Polymeric Nanocomposite

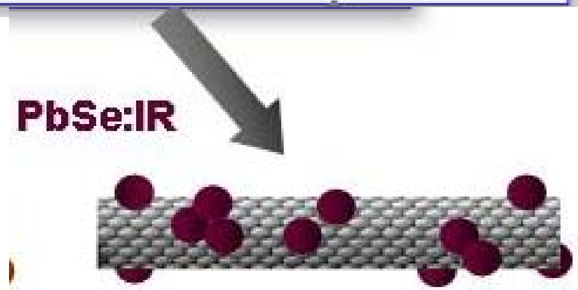




Carbon Nanotubes Coupled with Quantum Dots

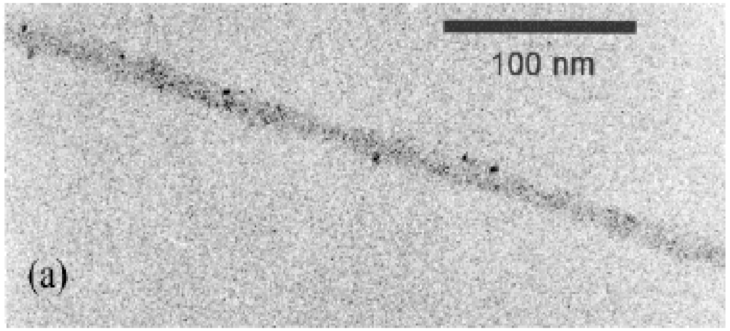






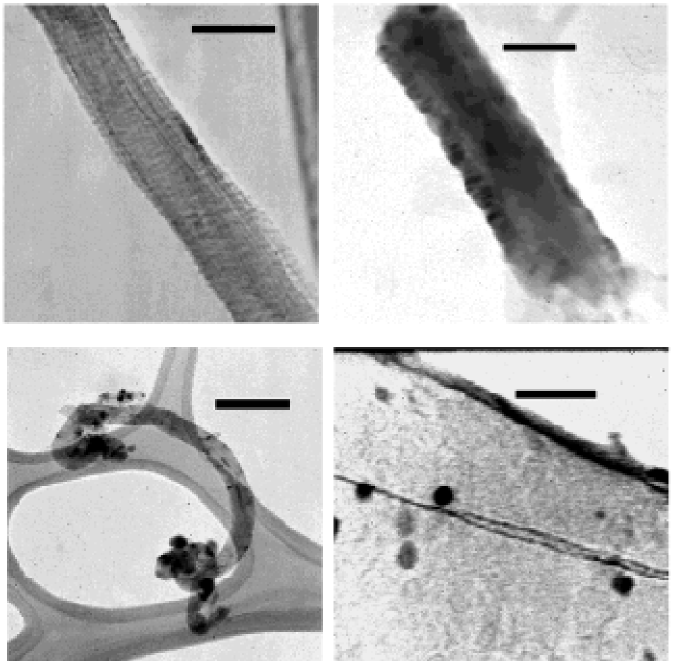
SWCNT-PbSe QDs

SWCNT-CdSe



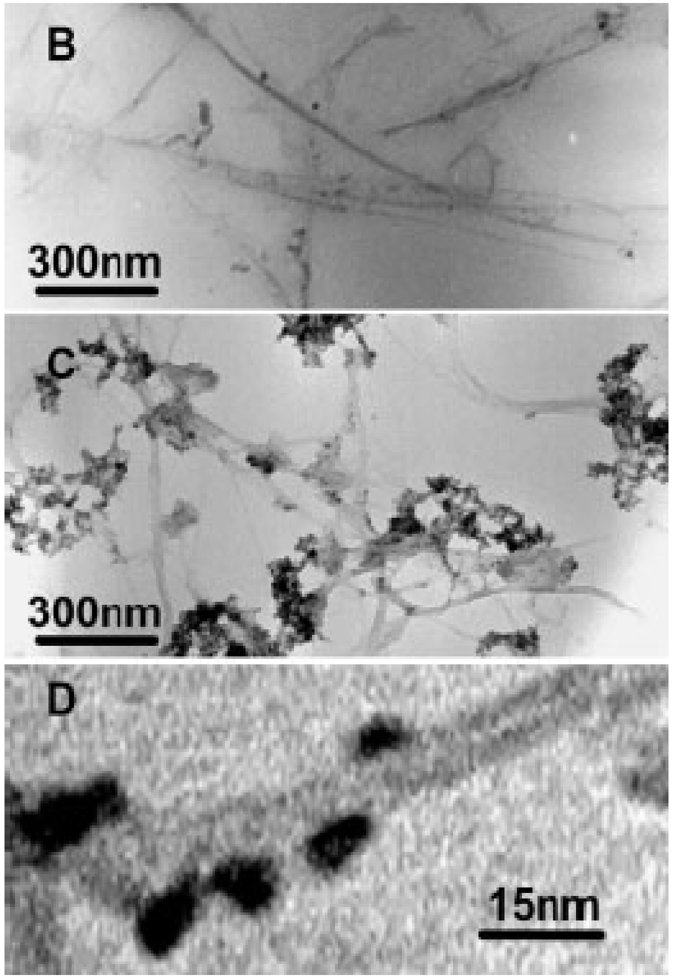
J. M. Haremza et al, Nano Lett. 2, 1253 (2002)

SWCNT-CdSe



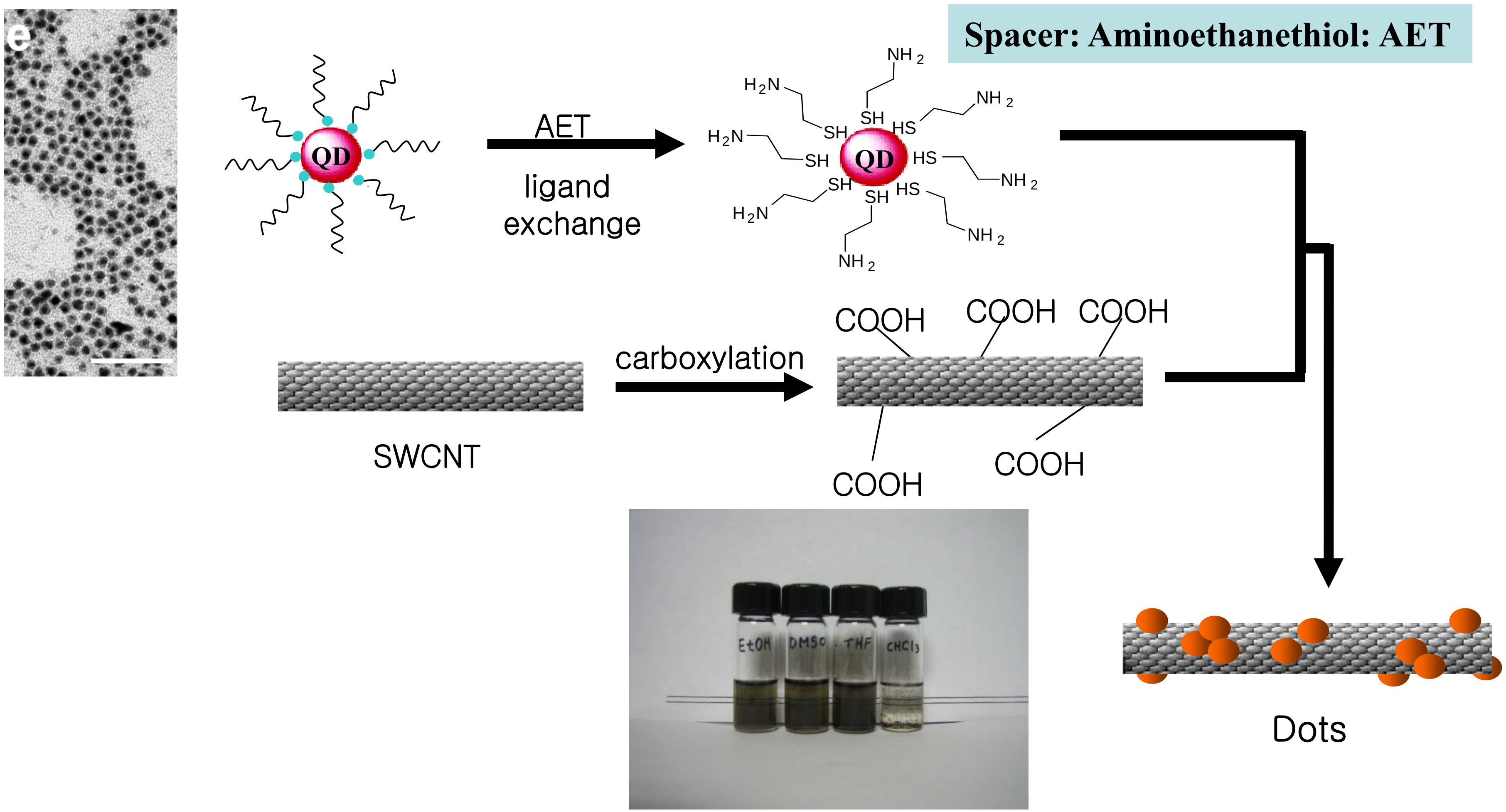
S. Banerjee et al, Nano Lett. 2, 195 (2002)

SWCNT-CdS

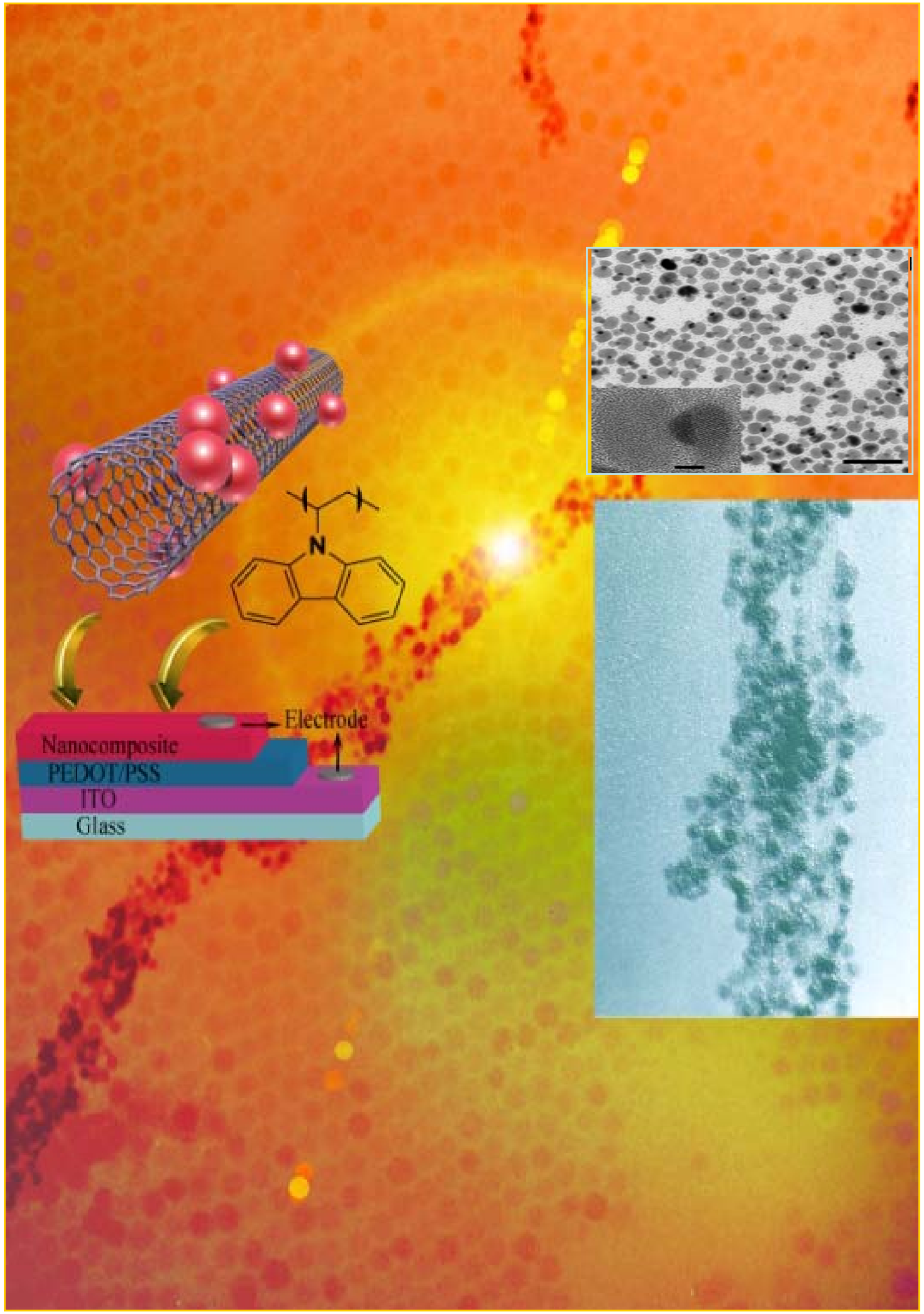


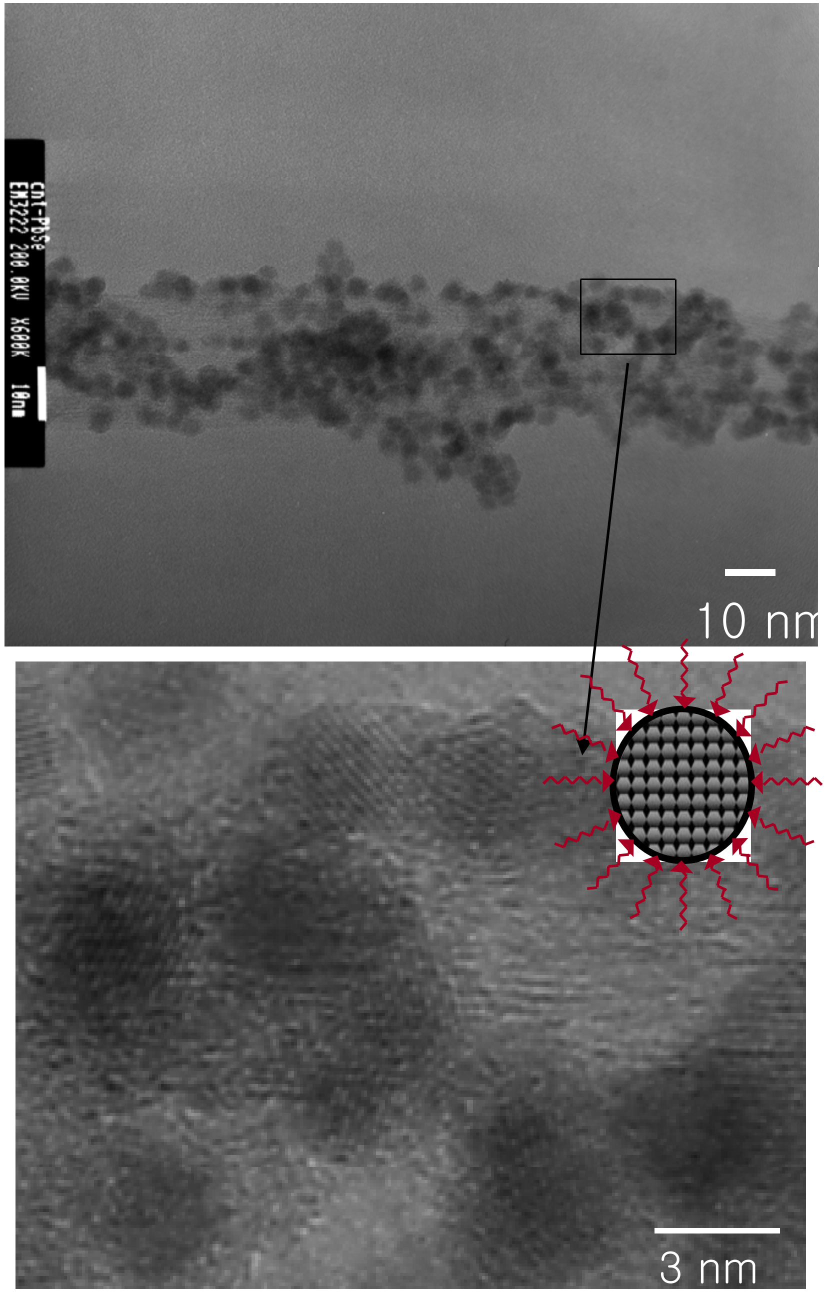
I. Robel et al,
Adv. Mater. 17, 2458 (2005)

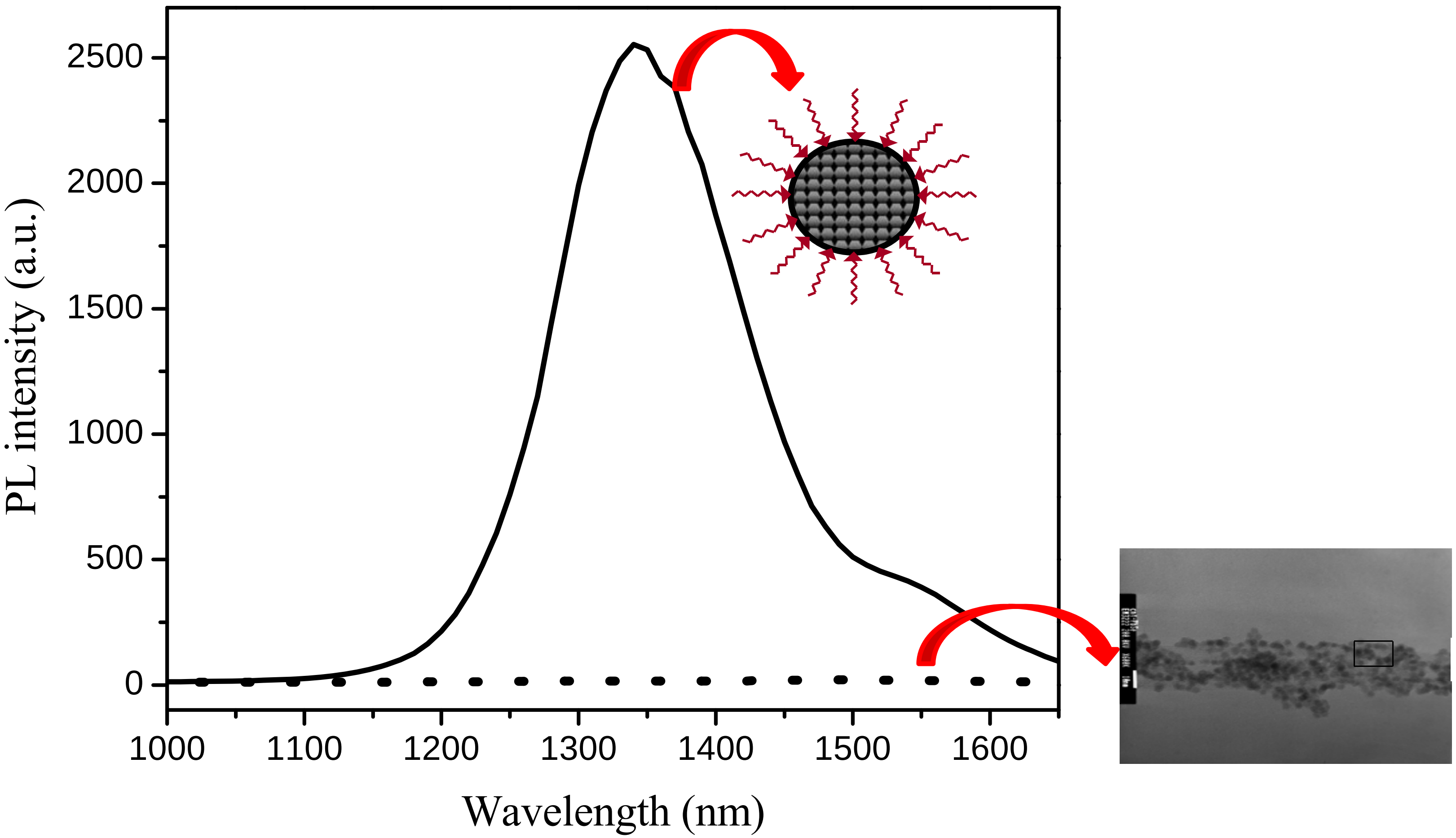
QD-SWCNT-Polymer Nanocomposites for Photovoltaics



A variety of QDs active from UV to IR enables us to access a wide part of the solar spectrum

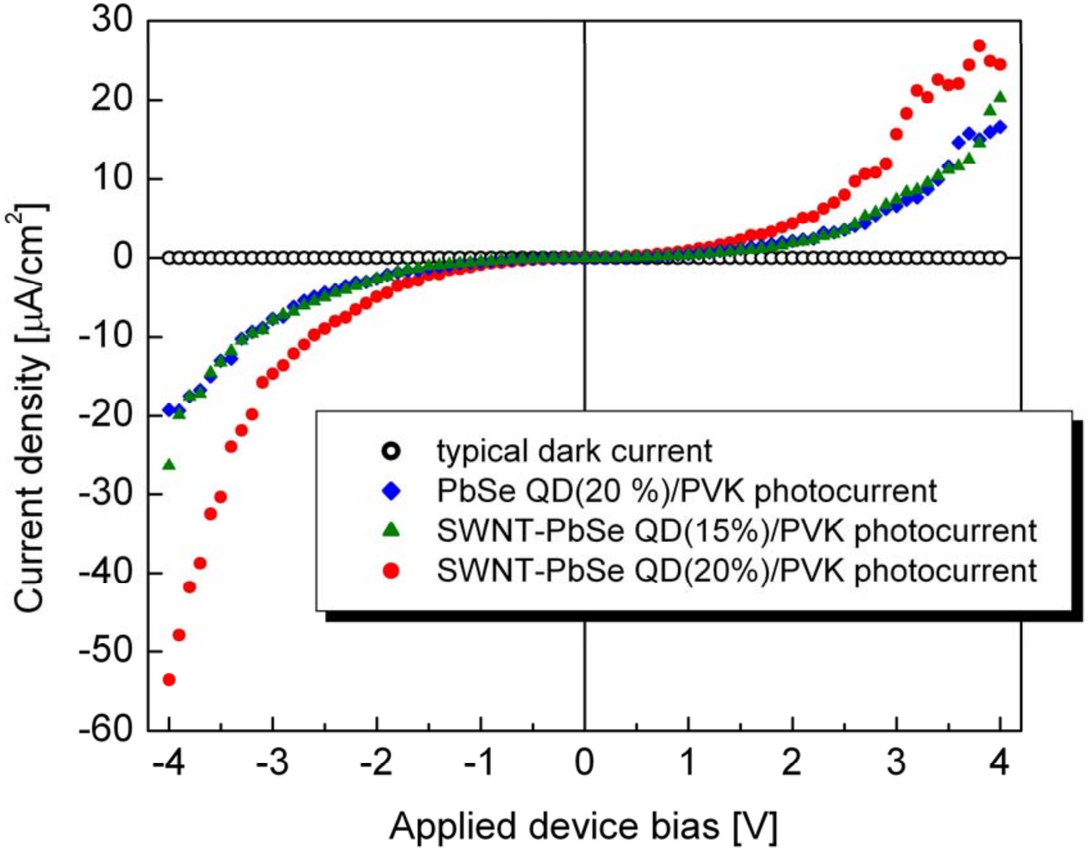

N
Electrode
Nanocomposite
PEDOT/PSS
ITO
Glass

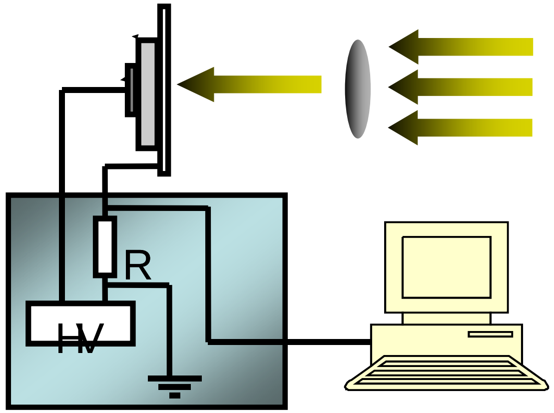

10 nm
3 nm



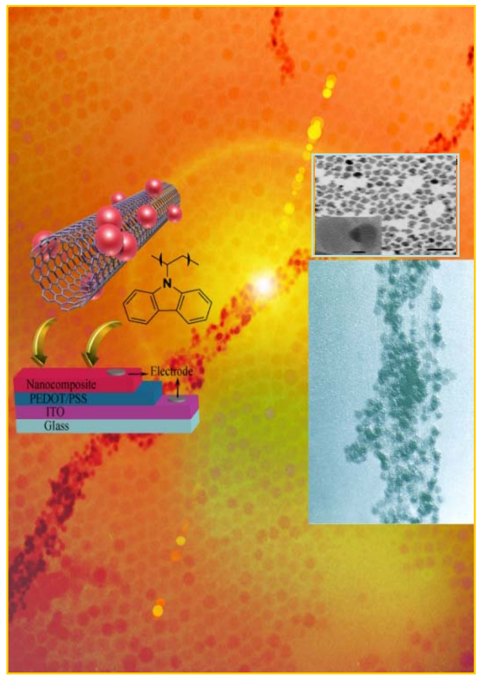
PL spectra of PbSe QDs (solid line) and SWNT-PbSe (dotted line) in tetracholoethylene colloidal suspensions. The concentration of PbSe QDs was the same in both cases.

I-V Characteristics of PbSe QD/PVK and SWNT-PbSe /PVK Device in Dark and under Illumination





Keithley source meter



***Adv. Mater.*, 19, 232-236 (2007) / US Patent 2010-0025662 A1, 2011**

ACS *"Heart Cut"* Research Highlight, 2007

Contents

- Introduction
- Quantum Dot-based Hybrids
  * Enhancing the Photocurrent Density
  * Photopatternable Quantum Dots
- Low Bandgap Polymers
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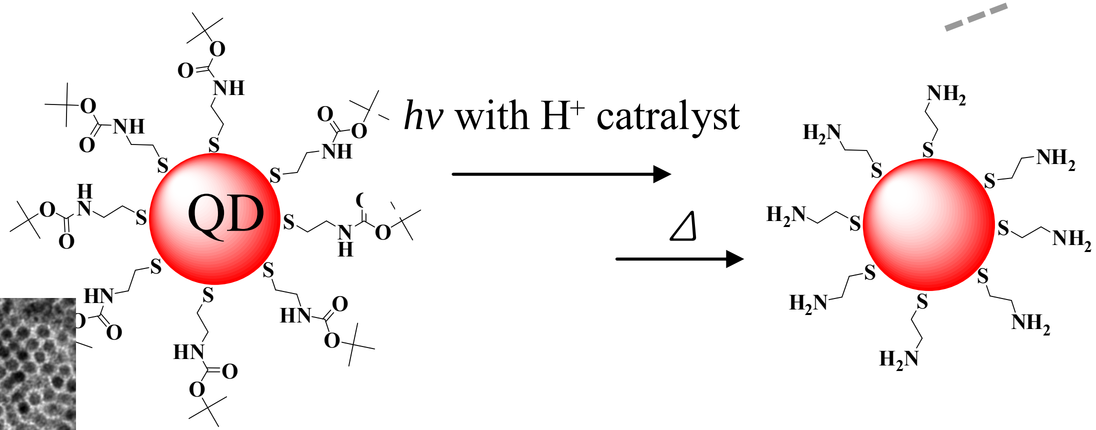
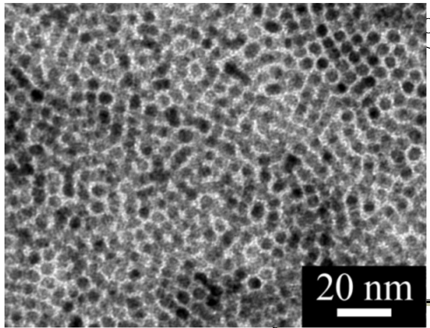
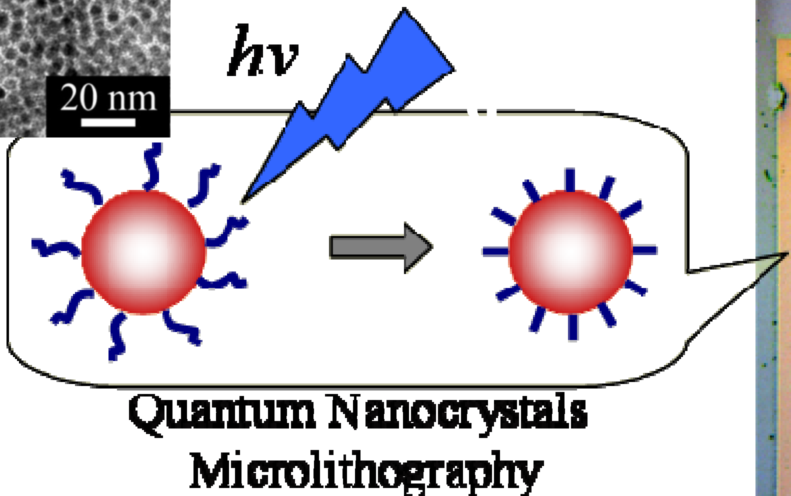
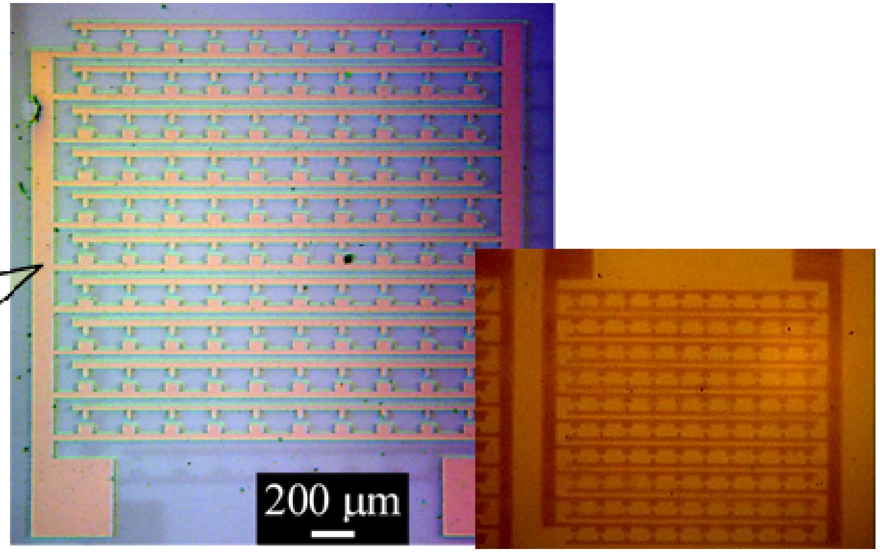
Surface Functionalization for Photo-Patternable QDs

Chemical Amplification Reaction



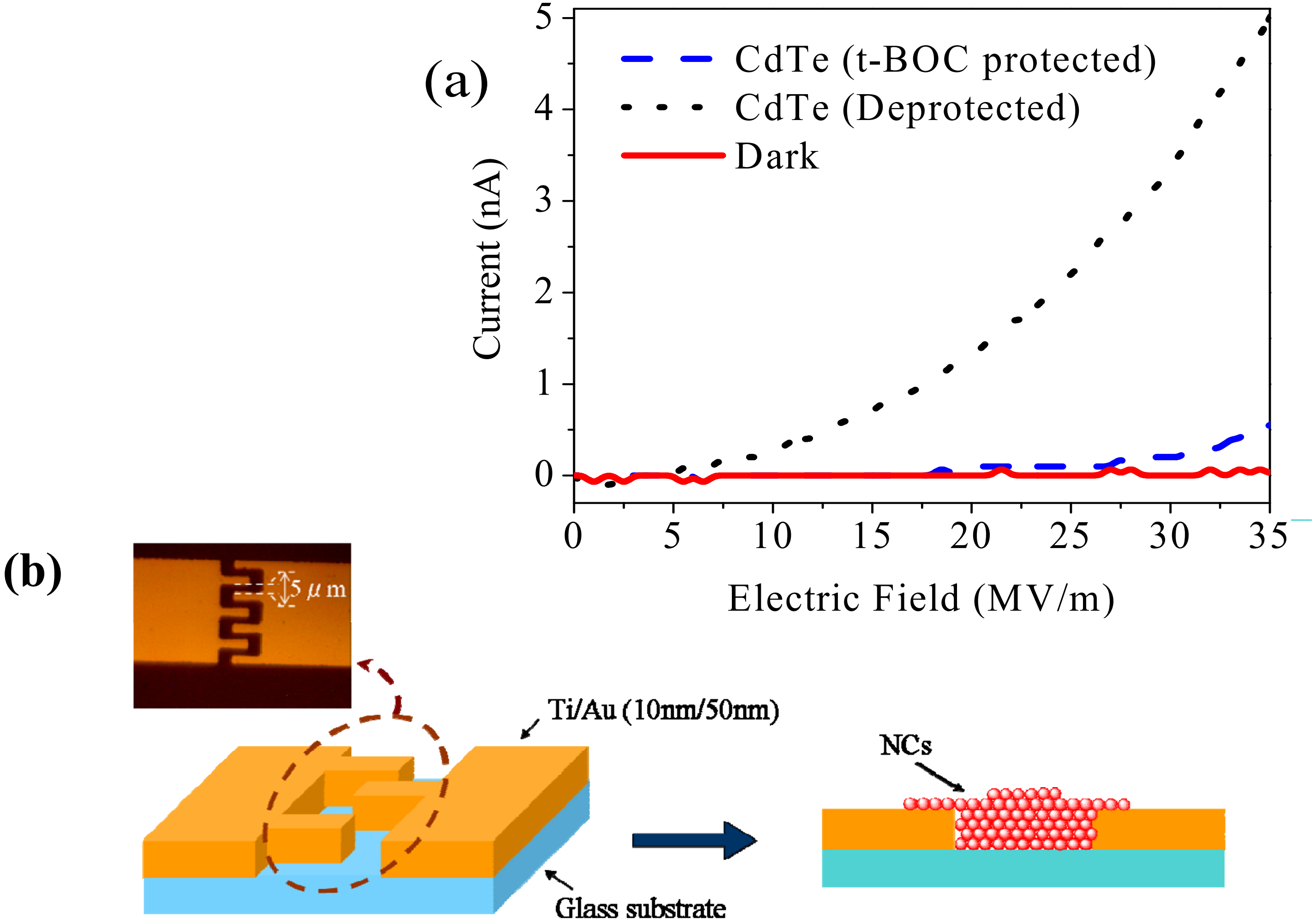






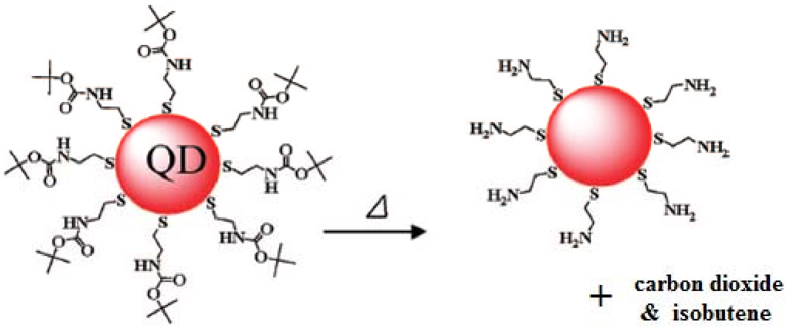
Nano Lett., 8, 3262(2008)

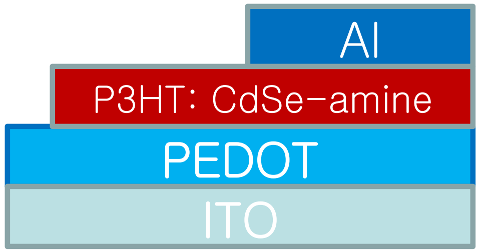
Photocurrent Measurements of Photopatternable QDs



Current-voltage curves (a) in the dark or with white light (100 mW/cm^2) illumination for a film of *t*-BOC protected and deprotected CdTe nanocrystals (measured at the voltage scan rate is 1 V/s). The channel length is 5 µm. MSM device structure (b) for photoconductivity measurement.

Polymer Nanocomposite Photovoltaics utilizing CdSe QDs Capped with a Thermally Cleavable Solubilizing Ligand





Solar Cell Device Structure

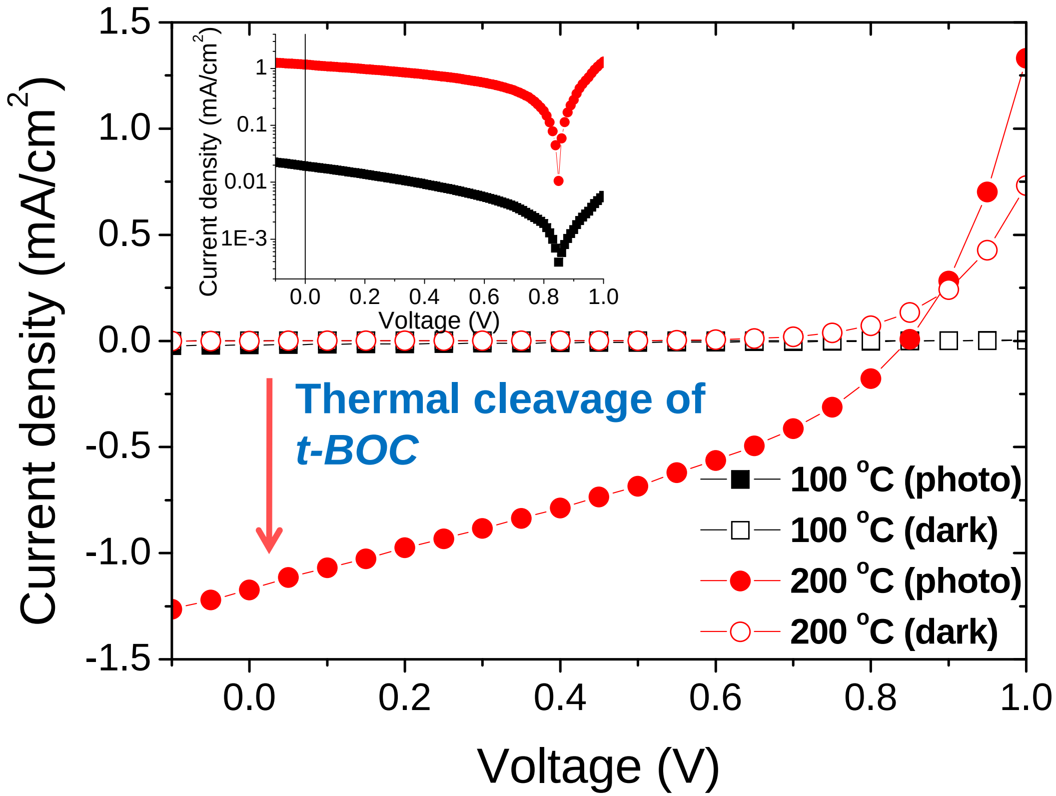
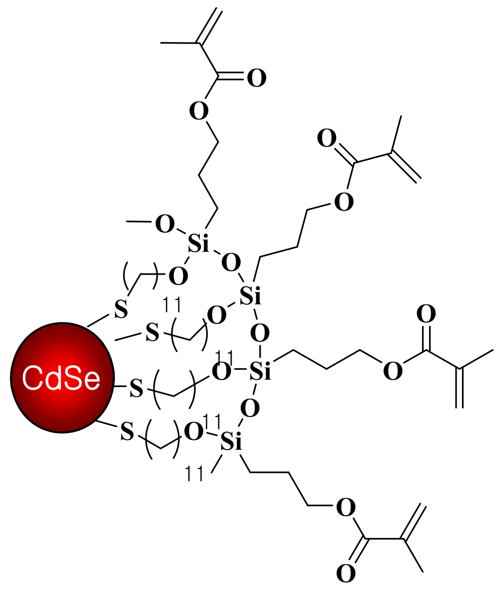


TABLE I. Summary of device performance in P3HT:CdSe-*t*Boc (10:90 wt %) blend film with different heating temperatures for *t*BOC deprotection

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

***Appl. Phys. Lett.*, 94, 133302 (2009)**



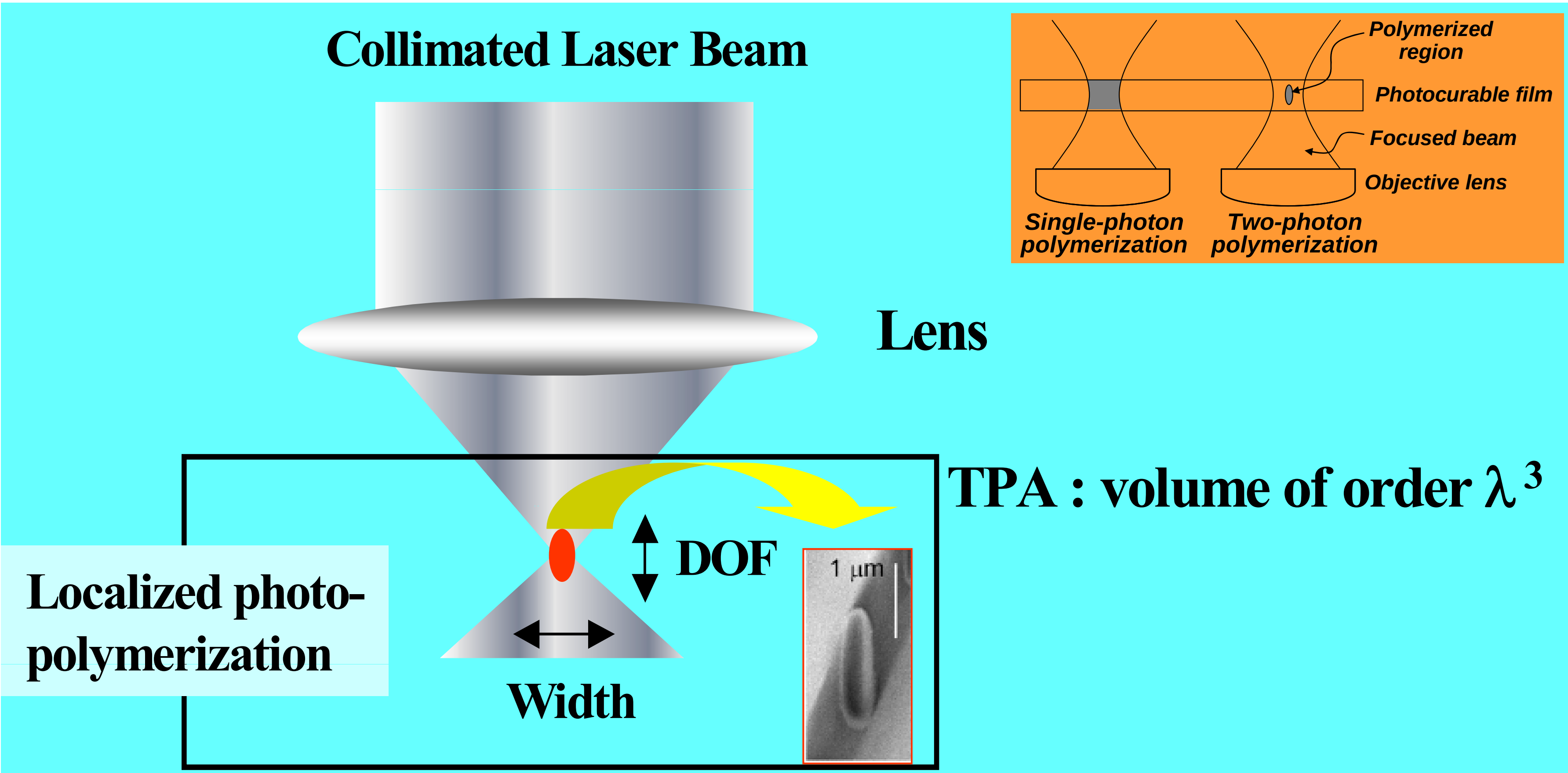
QD 1

UV: 552nm

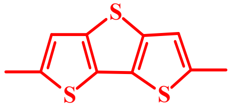
PL: 568nm

3-D Lithographic Microfabrication

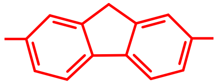
♦ Localized photochemistry by TPA process



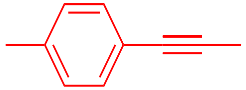
Use of longer radiation wavelengths in TPA process is possible to achieve the better penetration depth in the medium



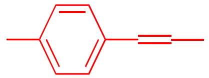
DTT



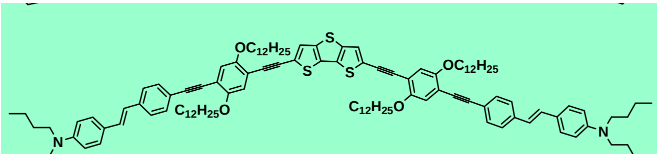
Flu



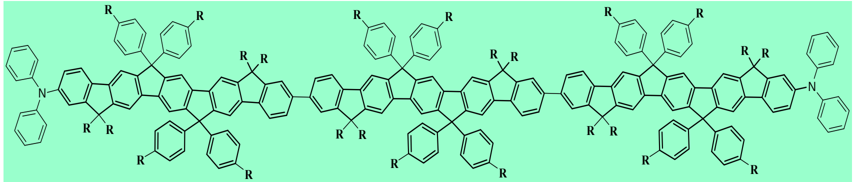
PE



PV

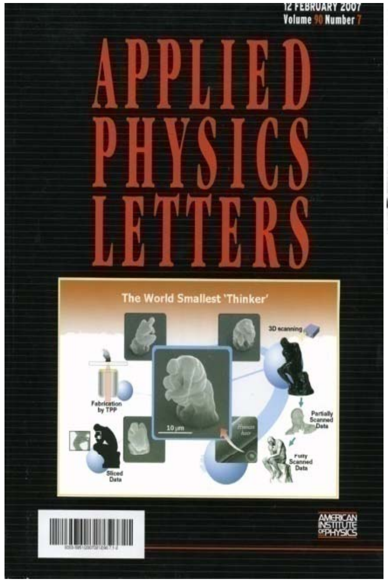


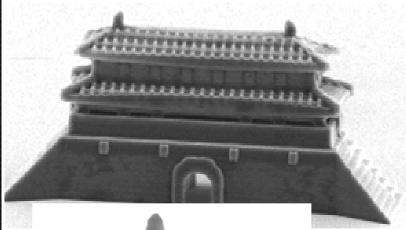
NBu2-DTTPE-NBu2

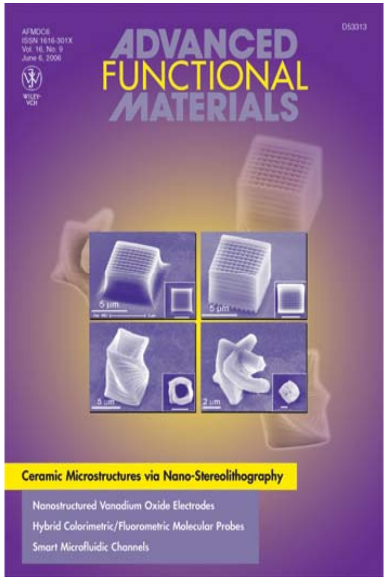


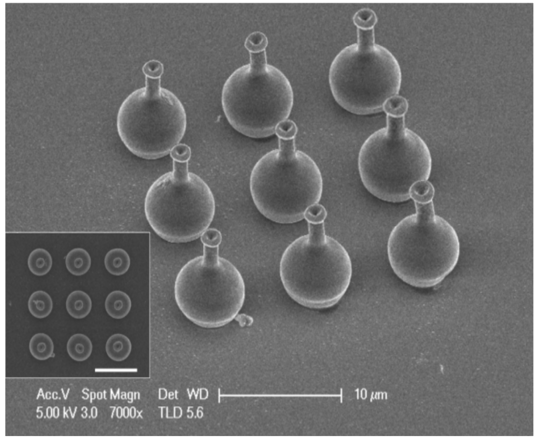
Polymers

Ceramics

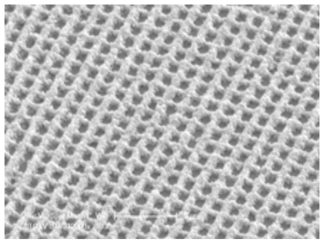


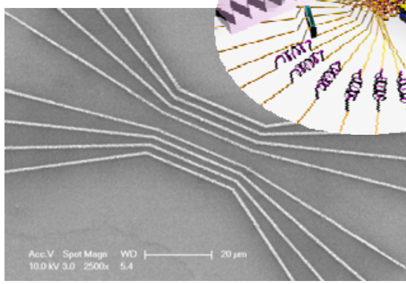


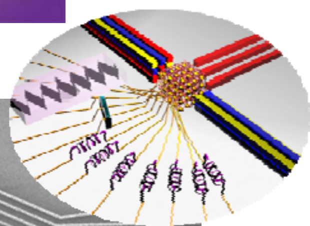




Metals







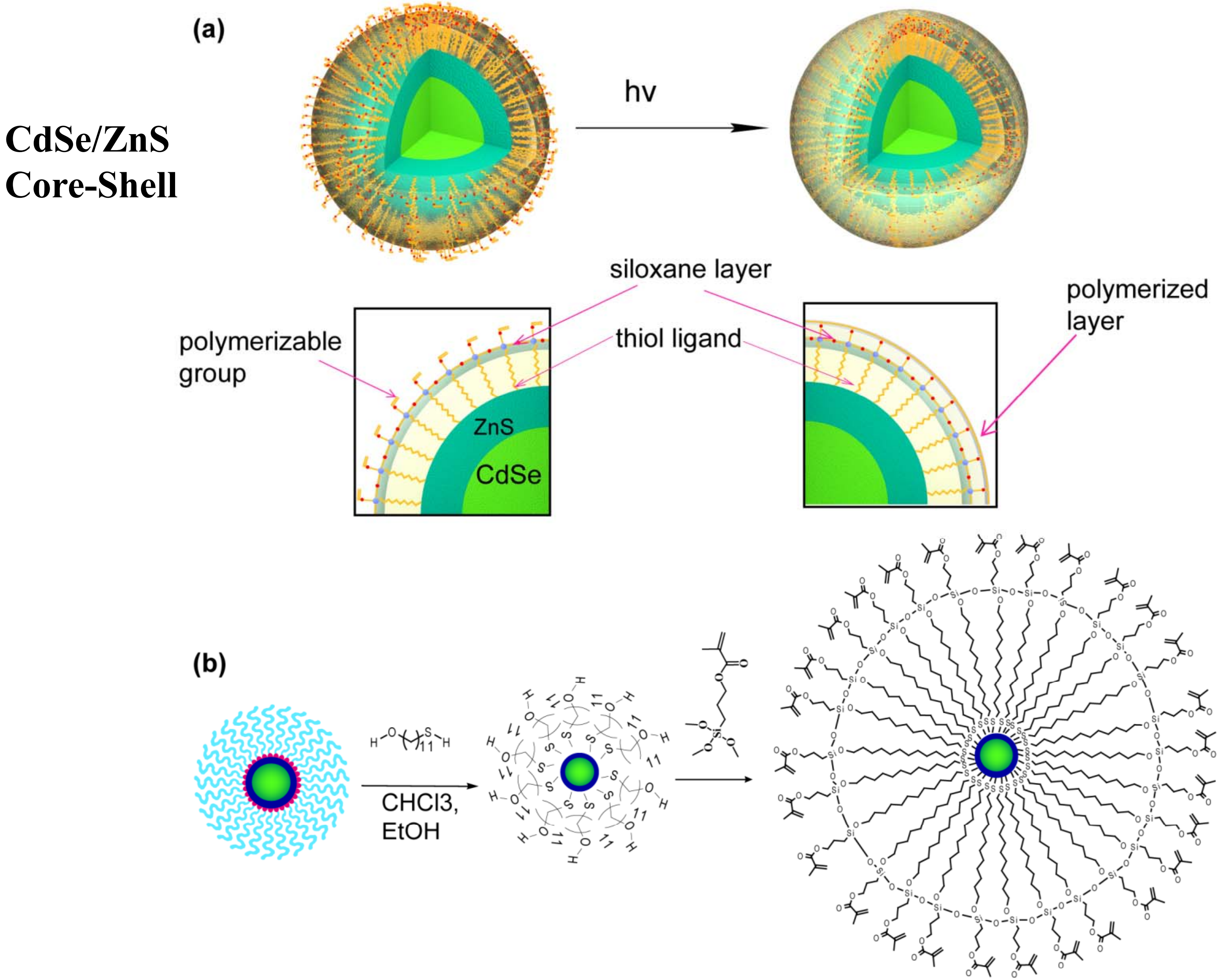
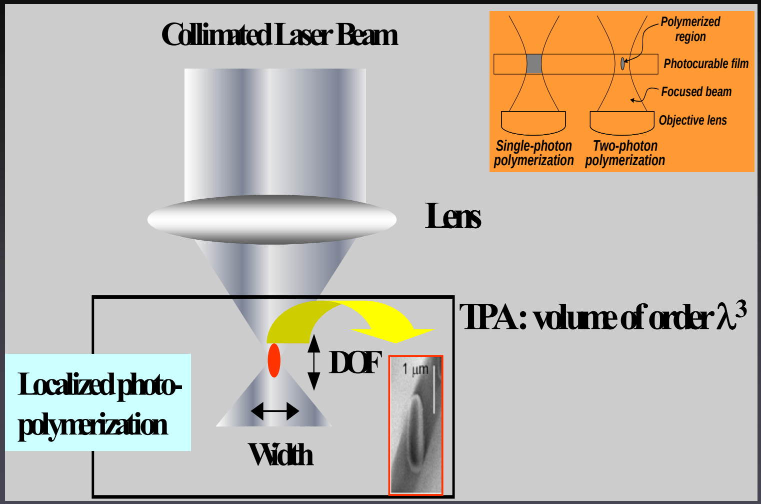
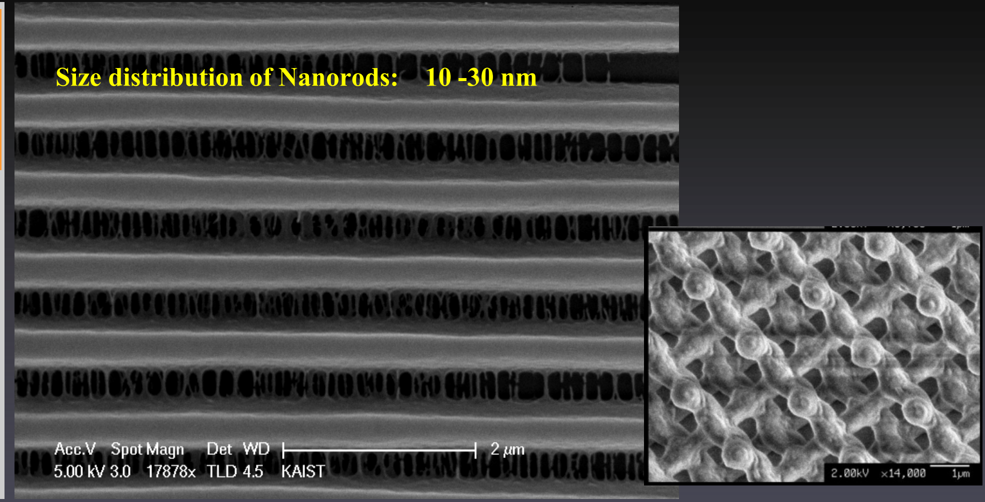
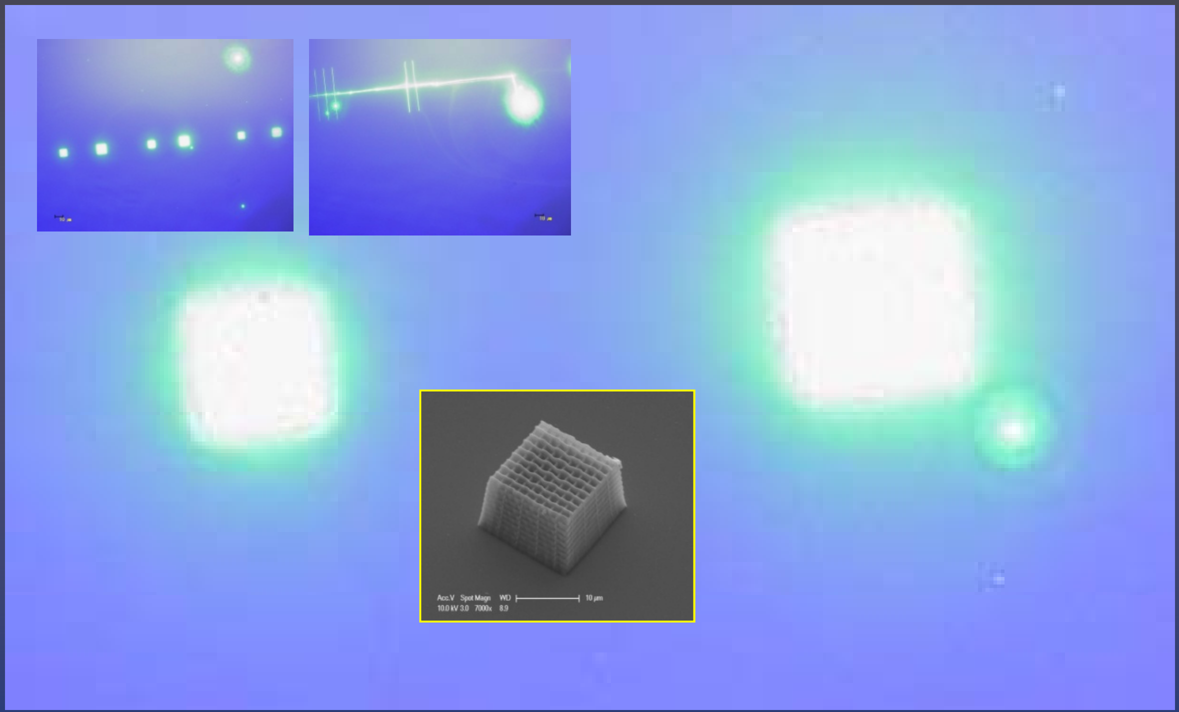


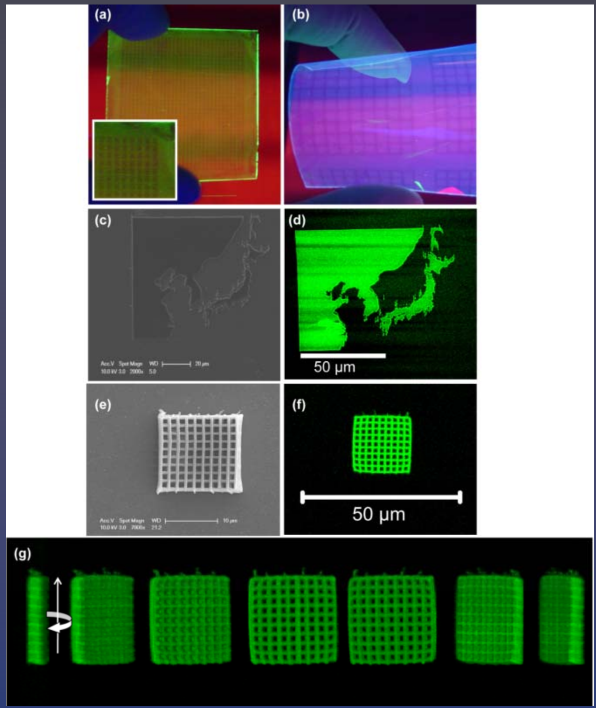
Figure (a) shows the photocuring of working acrylate functionalized quantum dots with its layer structure, (b) Shows the synthesis scheme for the acrylate functionalized photopatternable quantum dots.

Photopatterns by Using CdSe/ZnS Core-Shell QDs

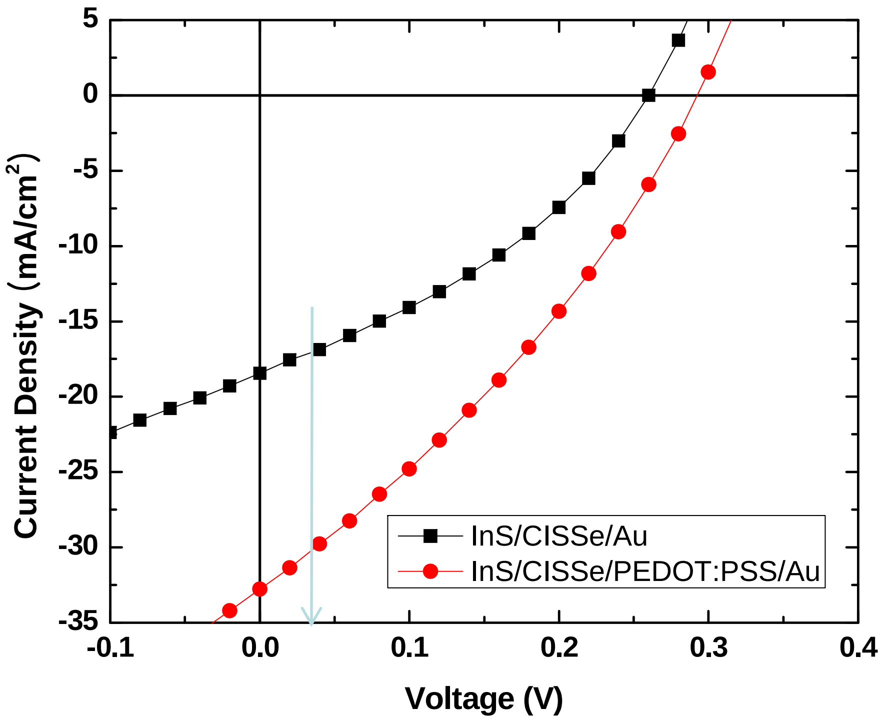




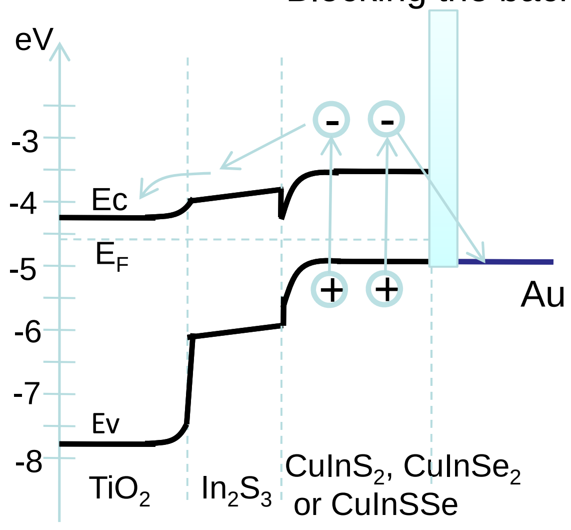




Polymer Blocking Layer Effect on In_2S_3/CuInSSe Solar Cell



PEDOT:PSS
Blocking the back recombination



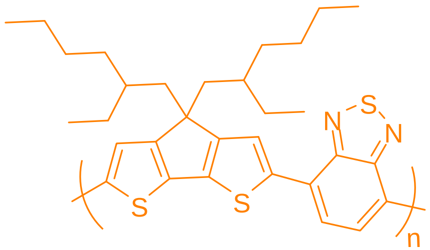
	Voc (V)	Jsc(mA/cm²)	FF(%)	PCE(%)
w/o PEDOT:PSS	~0.26	18.4	35.3	1.69
with PEDOT:PSS	~0.29	33.5	31.9	3.16

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

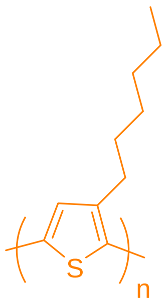
➔PEDOT:PSS effectively blocks electrons & transports holes

Prasad et.al, 2009

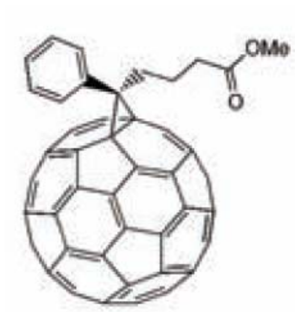
Low-Bandgap Conjugated Polymers



PCPDTBT



P3HT



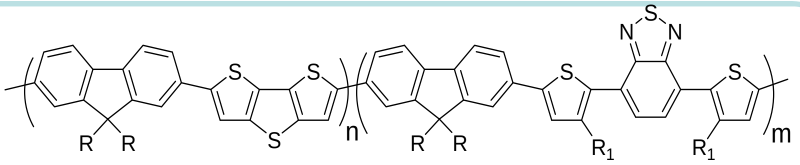
PCBM

$PC_{70}BM$

	PCPDTBT	P3HT
	D-A concept	Rigiospecific Structure
Optical Bandgap:	1.52 eV	1.90 eV

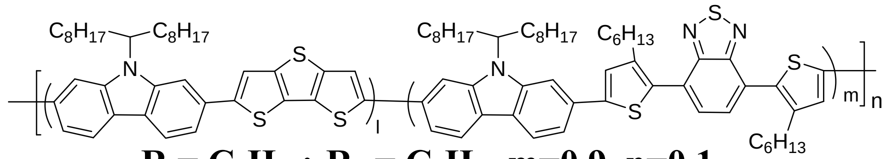
Low Bandgap Conjugated Copolymers: PFTB & PCTB

PFTB



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

PCTB

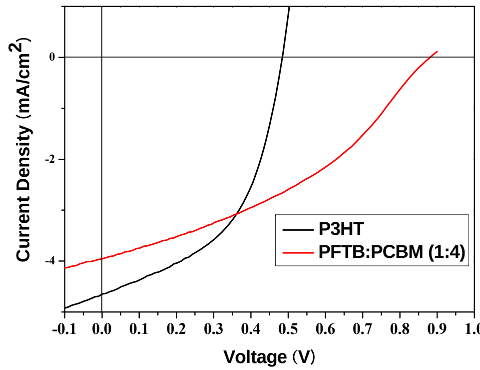


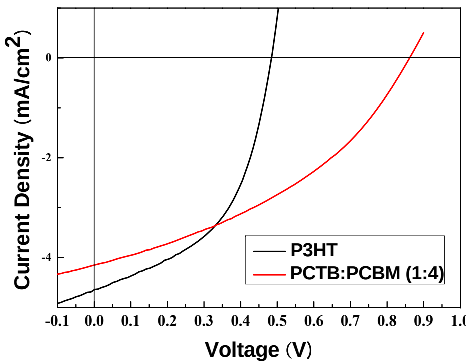
R = C_8H_{17}: R_1 = C_6H_{13} m=0.9, n=0.1

PFTB Abs: λ_{max}	PFTB PL : λ_{max}	PCTB Abs: λ_{max}	PCTB PL : λ_{max}
521 nm	642 nm	521 nm	642 nm
519 nm (with PCBM 1:4)	642 nm (with PCBM 1:4)	519 nm (with PCBM 1:4)	643 nm (with PCBM 1:4)

I-V Characteristics and Solar Cell Efficiency

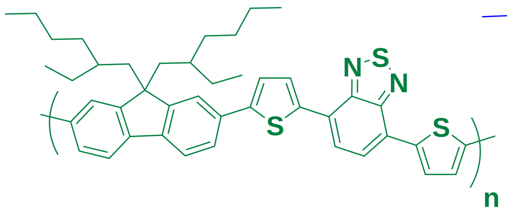
Device	*Jsc* *(mA/cm^2)*	*Voc* *(V)*	*FF* *(%)*	Solar Efficiency (%)
P3HT/PCBM (1:0.8)	4.234	0.485	49.68	1.02
PFTB/PCBM (1:4)	3.596	0.881	37.64	**1.19**
PCTB/PCBM (1:4)	**3.782**	**0.862**	**38.74**	**1.26**



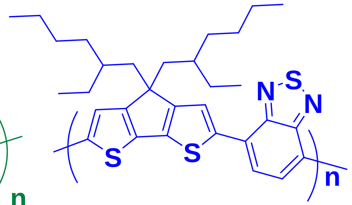


Development of Efficient NIR Polymers;

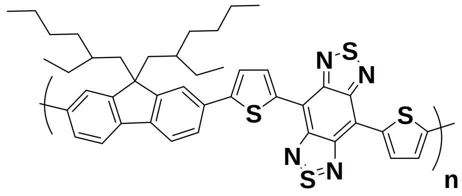
Synthesis of the Low bandgap Polymers



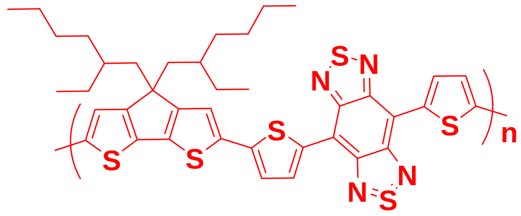
PFTTBT



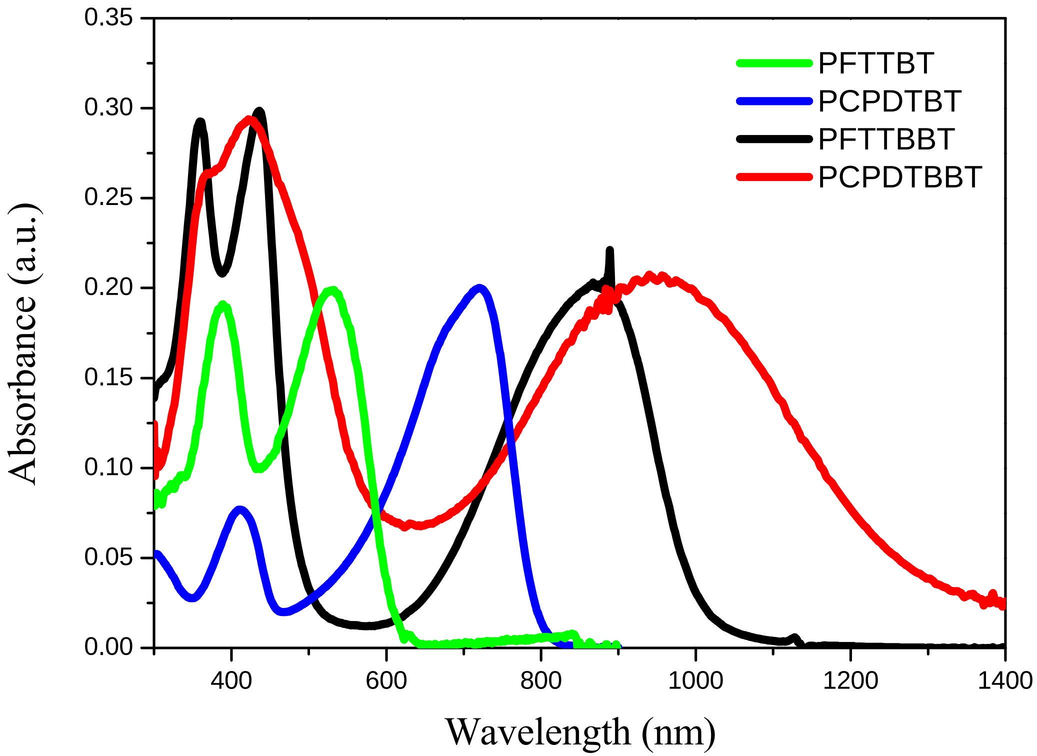
PCPDTBT



PFTTBBT



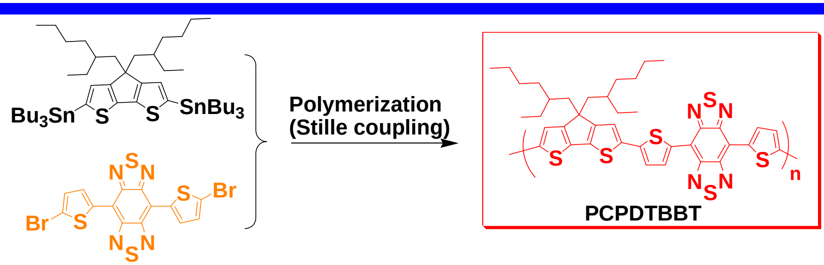
PCPDTBBT

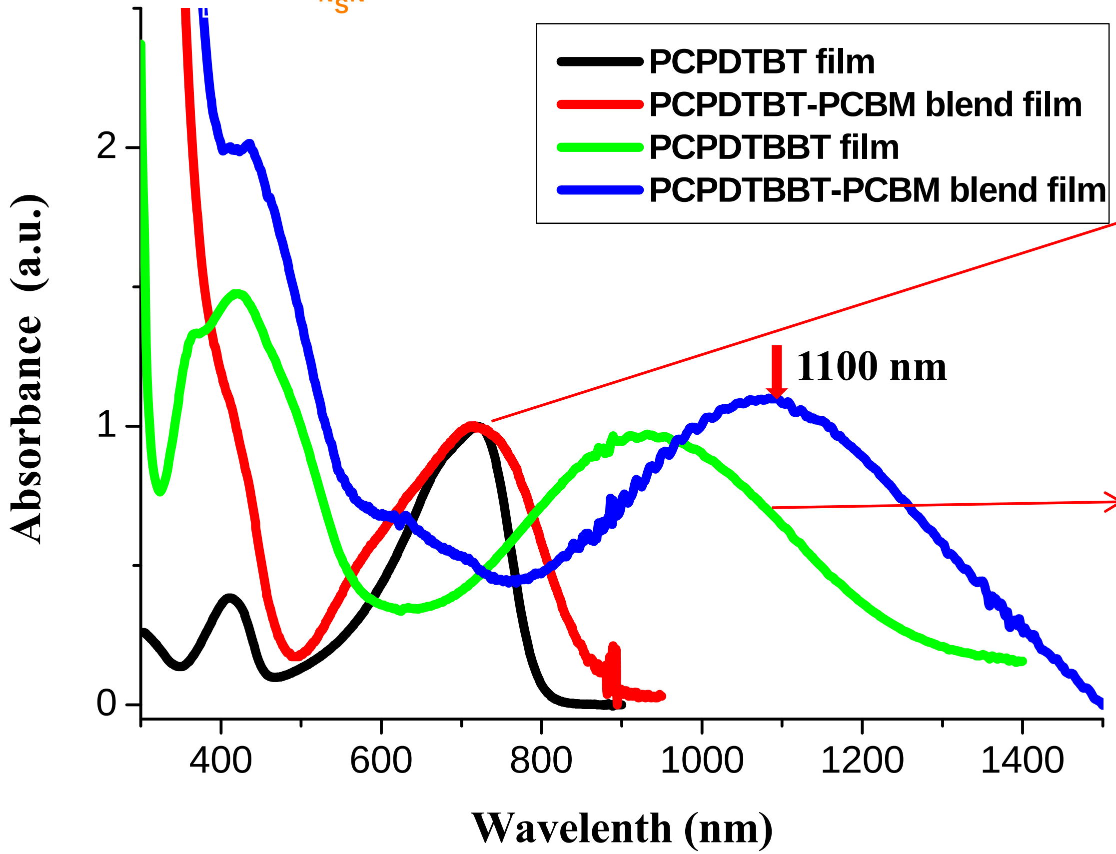


Optical properties of various polymers

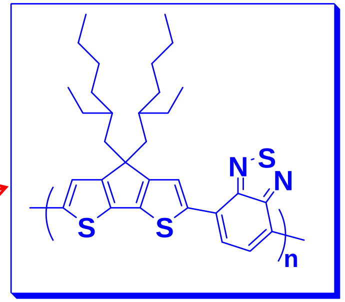
Polymer	Abs. λmax.	Opt. band gap
PFTTBT	530 nm	1.98 eV
PCPDTBT	718 nm	1.52 eV
PFTTBBT	868 nm	1.19 eV
PCPDTBBT	950 nm	0.92 eV

Comparison of UV-vis Absorption of Low Bandgap Polymers

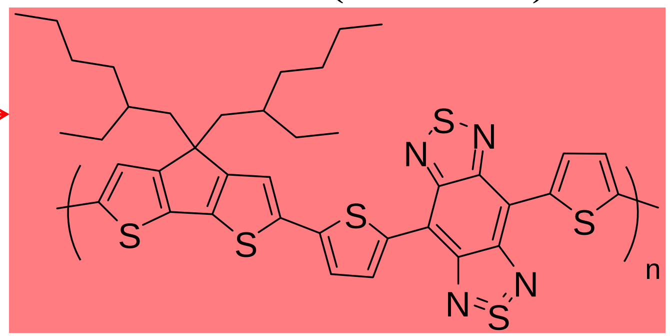




PCPDTBT (by Heeger's group)



PCPDTBBT (Our Work)



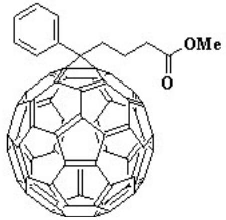
UV-vis absorption spectra of the PCPDTBT and PCPDTBBT Polymer films and the polymer-PCBM blend films

Contents

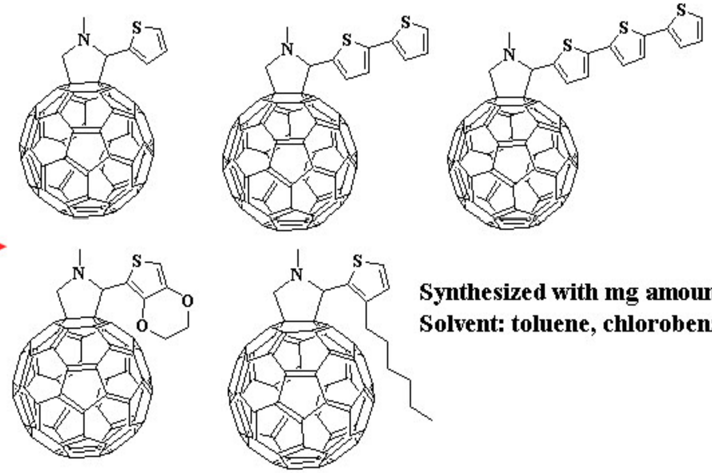
- Introduction
- Quantum Dot-based Hybrids
  * Enhancing the Photocurrent Density
  * Photopatternable Quantum Dots
- Low Bandgap Polymers
- **C60 Derivatives**
- Summary

C60 Derivatives as Acceptors in Hybrid Bulk Heterojunction Solar Cells

Acceptors
(C_{60} Derivatives)

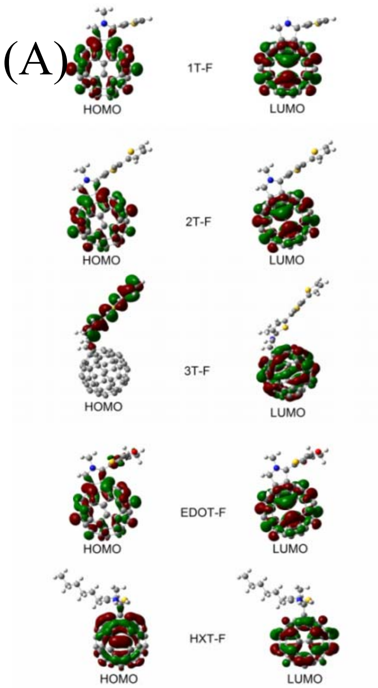


PCBM



Synthesized with mg amount
Solvent: toluene, chlorobenzene

(A)



(B)

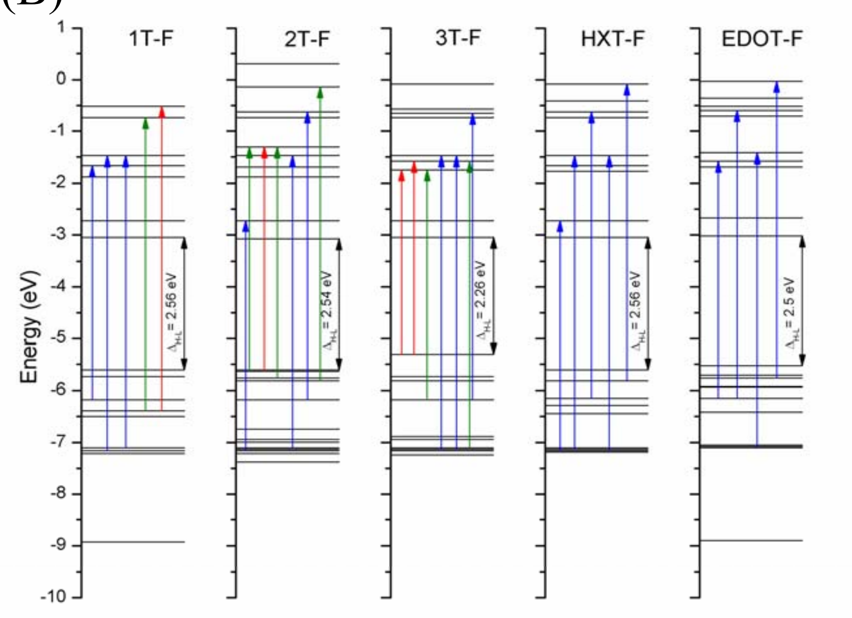
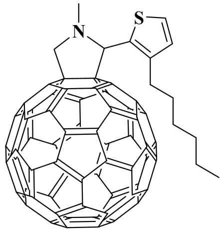


Fig. (A) The contour plots of the HOMOs (left side) and the LUMOs, right side) of all investigated dyads.
(B) Electronic energy levels of an isolated dyads. Vertical arrows represent the most probable transitions (with oscillator strength higher than 0.1. Blue, red, and green arrows corresponds to the LE(F), LE(T), and ICT transitions, respectively.

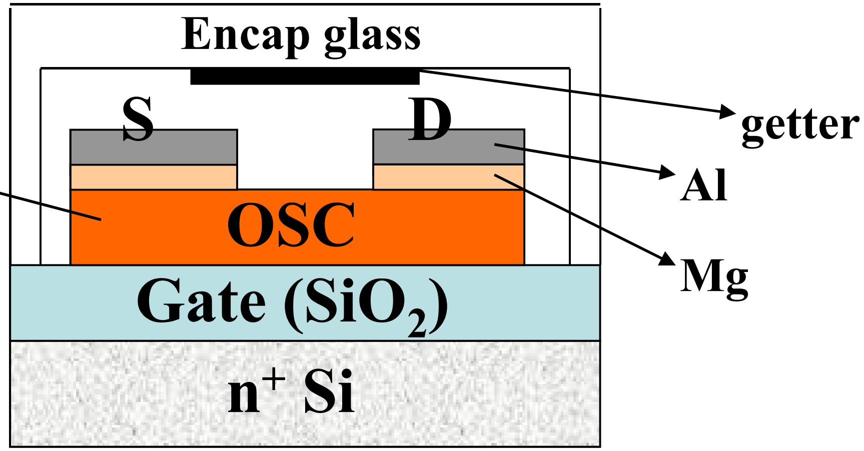
***Chem. Phys. Lett.* 479 , 224 (2009) / *Synth. Met.* 159, 2539 (2009)**

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



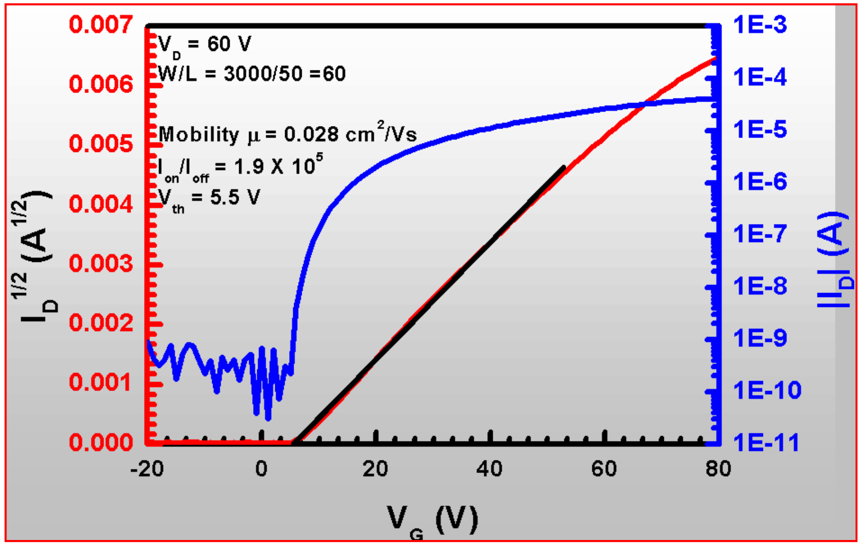
Fu-Hexyl

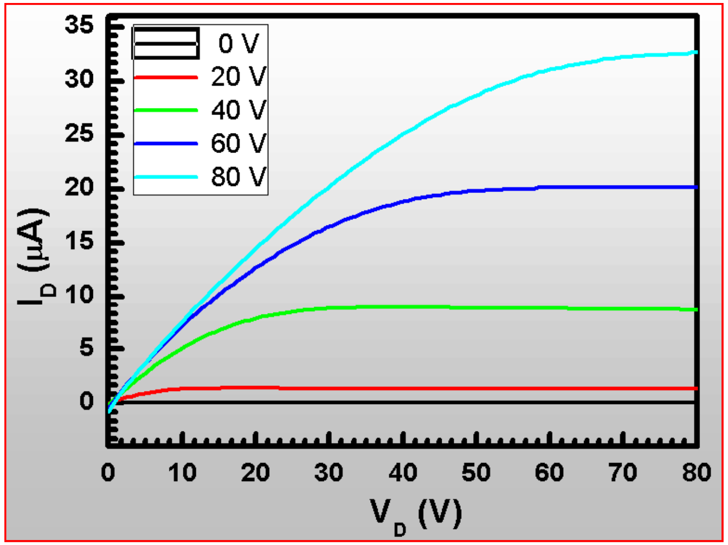
Inkjet printing (0.5wt% Fu-Hexyl in chlorobenzene)



μ=0.028 $cm^2/V\cdot s$ (0.0058 $cm^2/V\cdot s$ for PCBM)

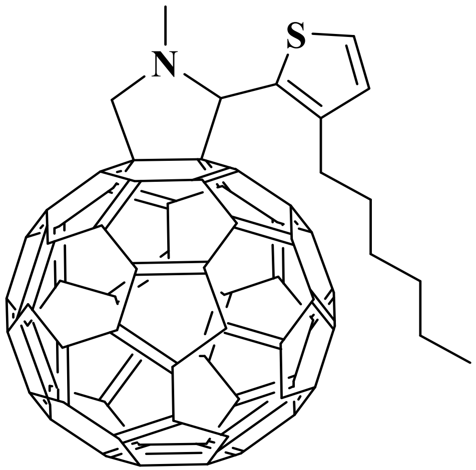
On-off ratio = 1.9 × 10^5



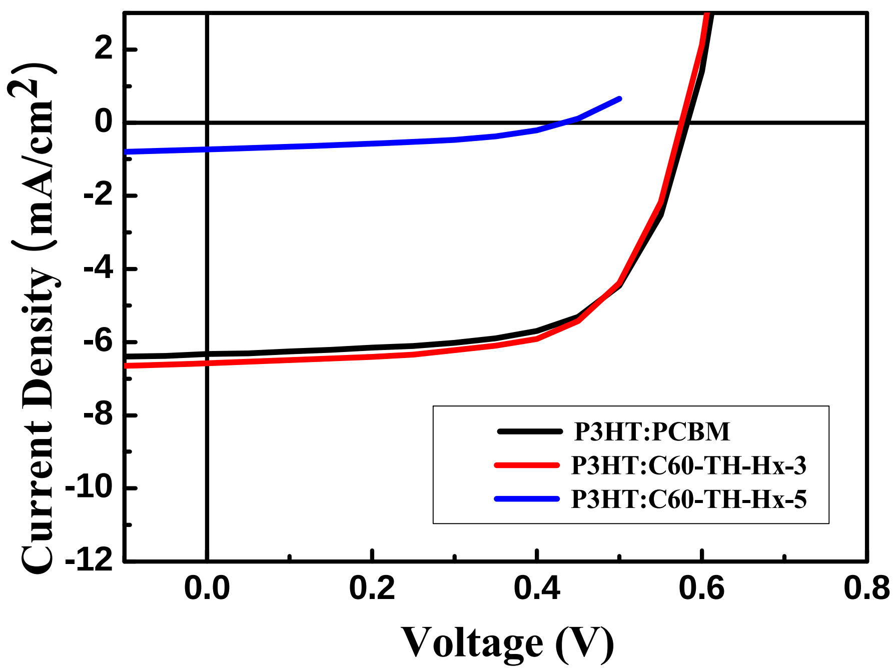


Org. Electron, 10, 1028 (2009)

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

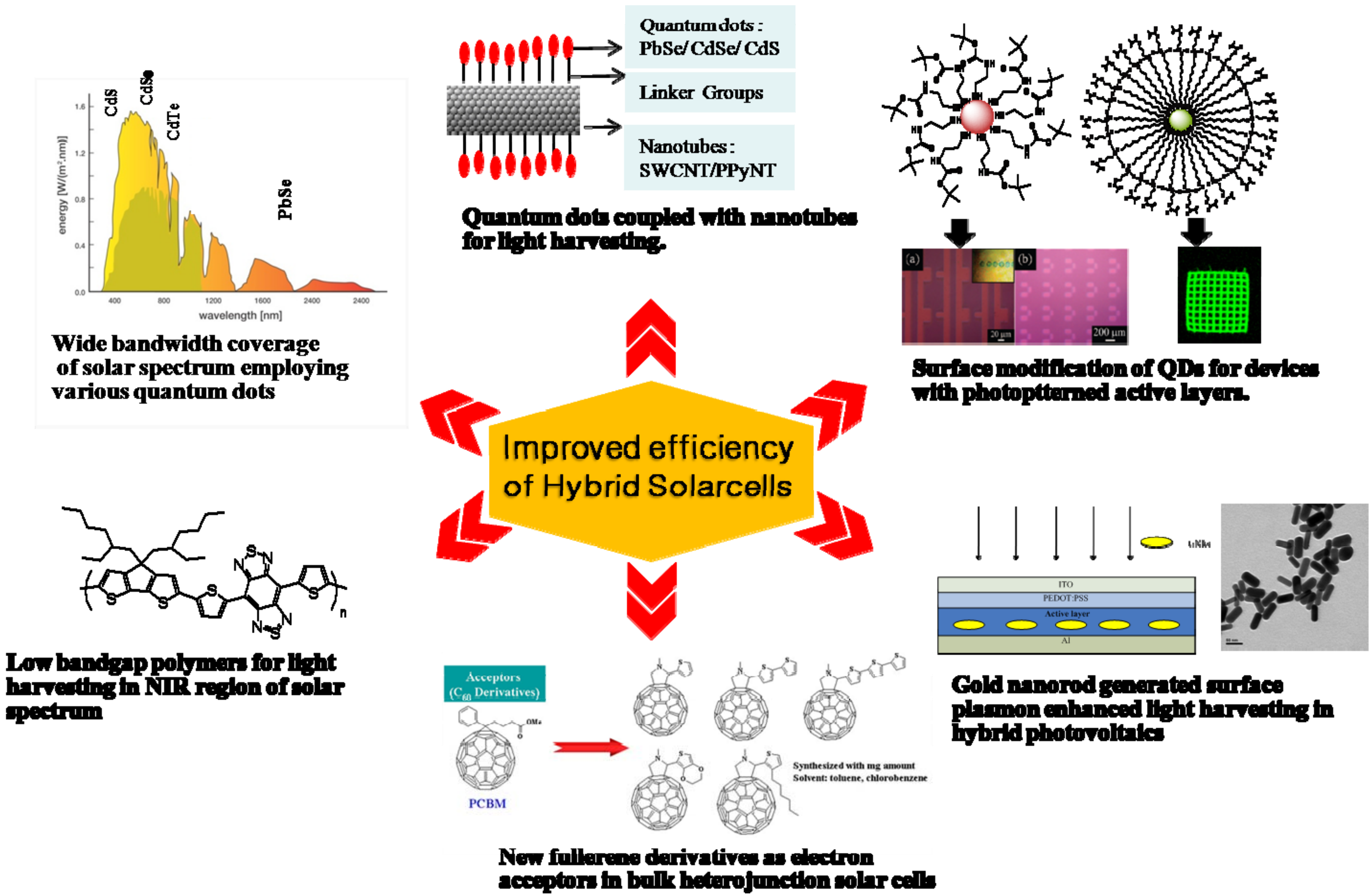


Fu-Hexyl



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

Graphic Summary



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