ORGANIC/INORGANIC INTERFACES IN PHOTOVOLTAICS

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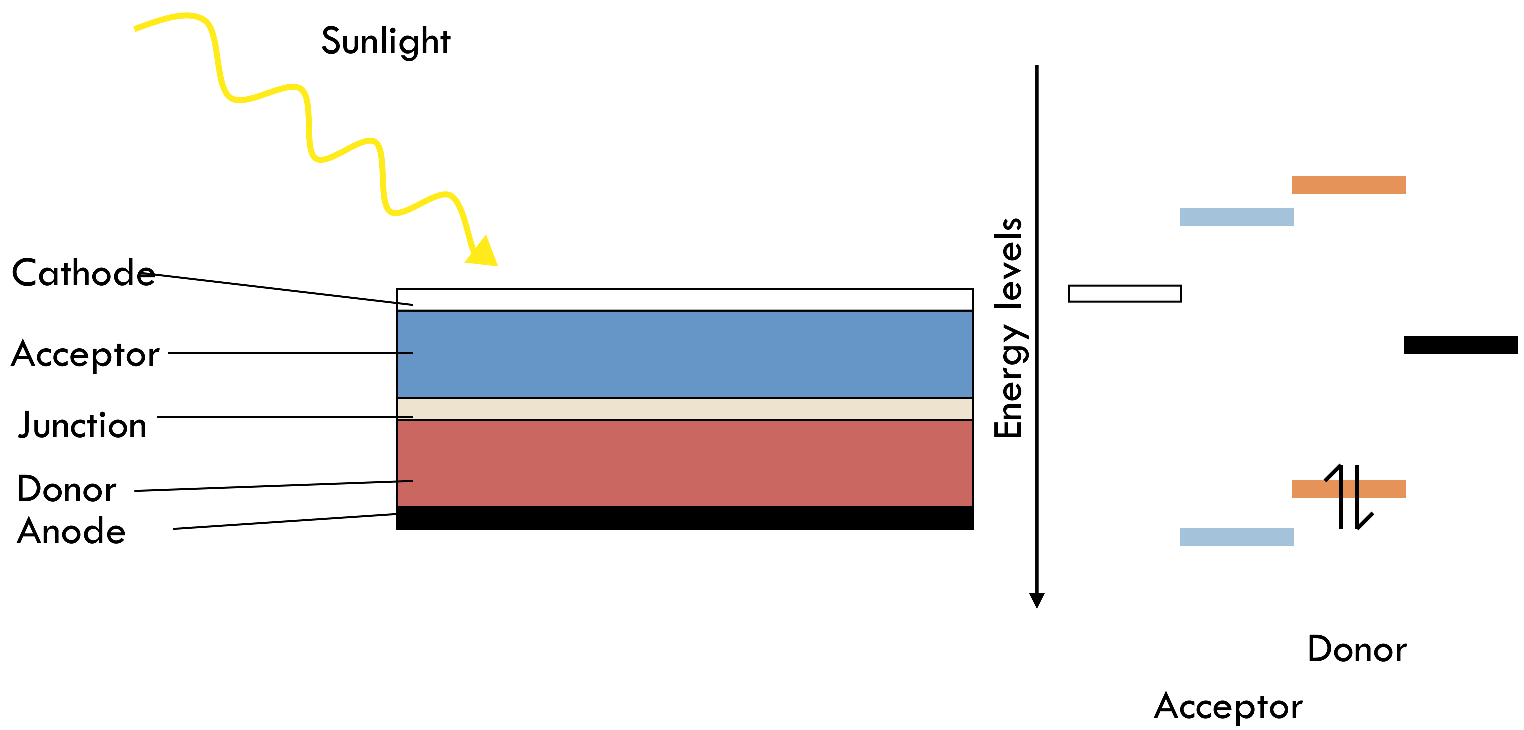
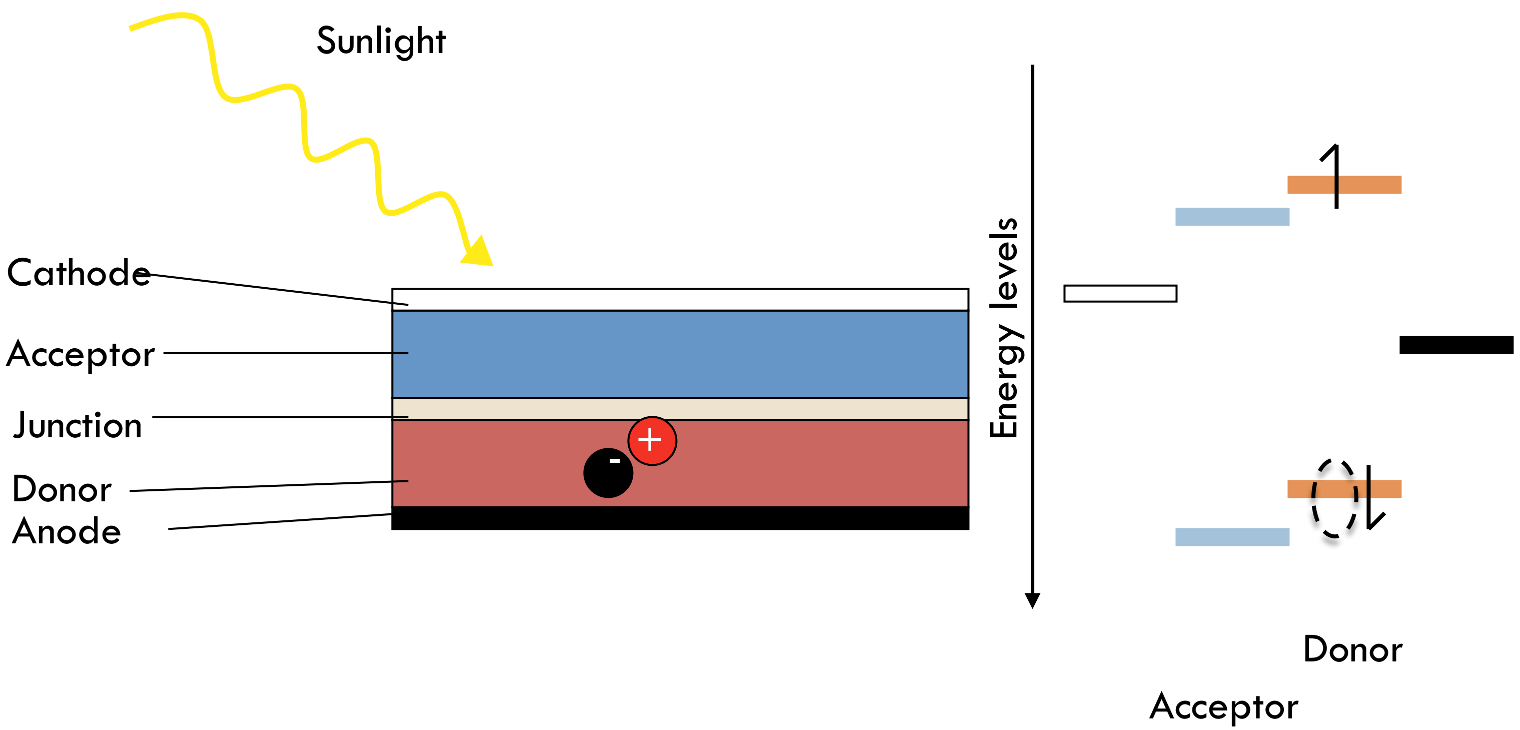
Outline

- Introduction to organic photovoltaic devices
- Examination of different interfaces
- Electrode/polymer interfaces
- Interfaces within the active layer

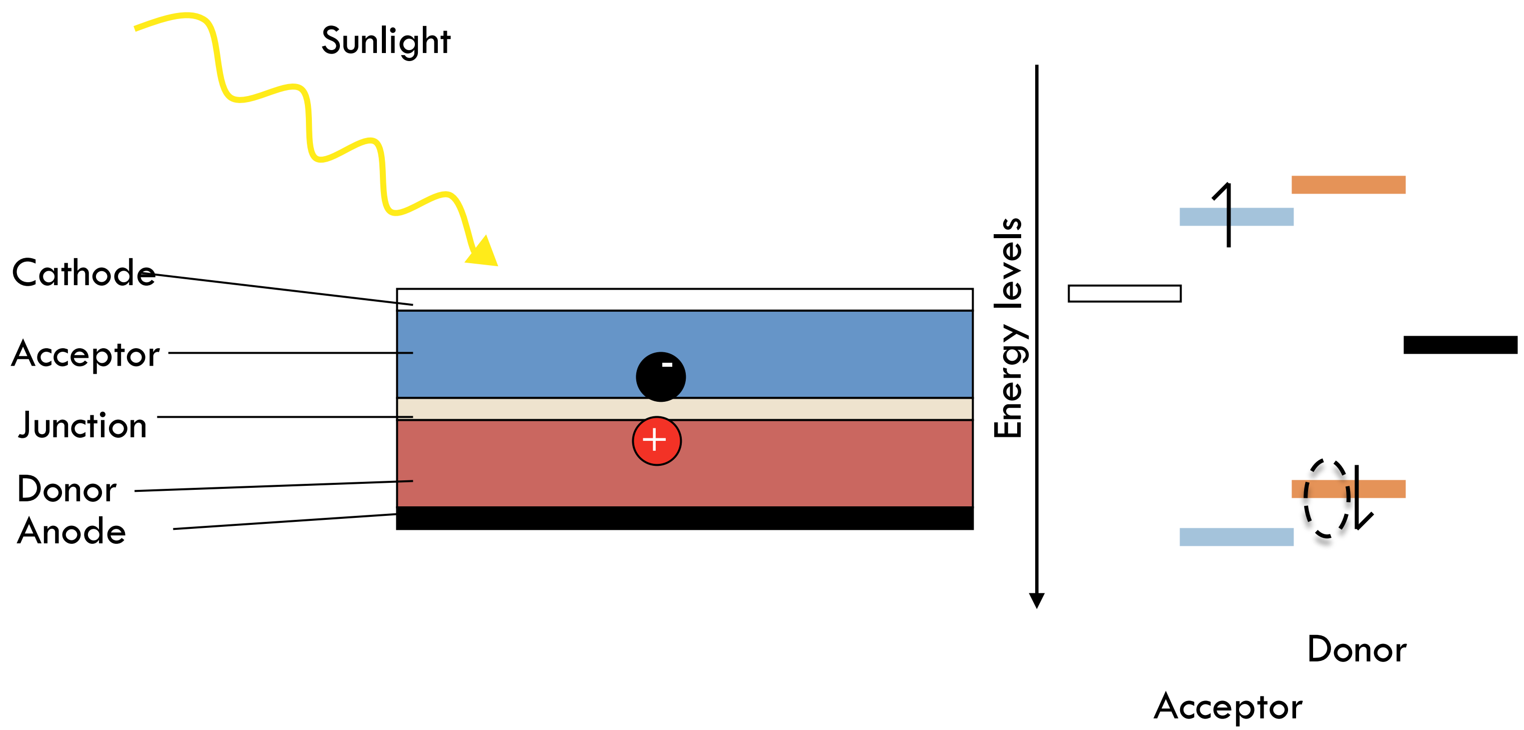
The photovoltaic effect



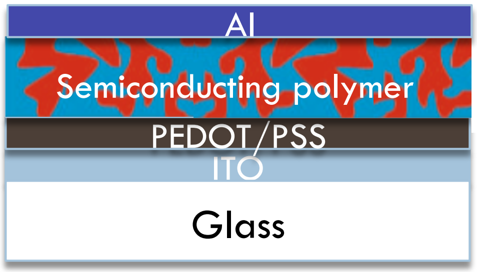
The photovoltaic effect



The photovoltaic effect



Bulk heterojunction devices



Chemical and physical treatments of ITO

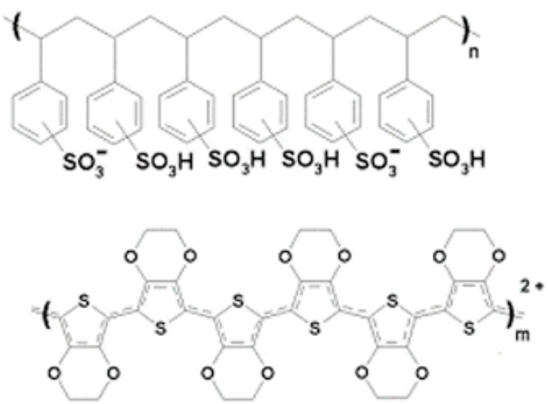
- Ultrasonic cleaning in organic solvents: This leads to some carbon contamination and keeps the work function of ITO at 4.5 eV.

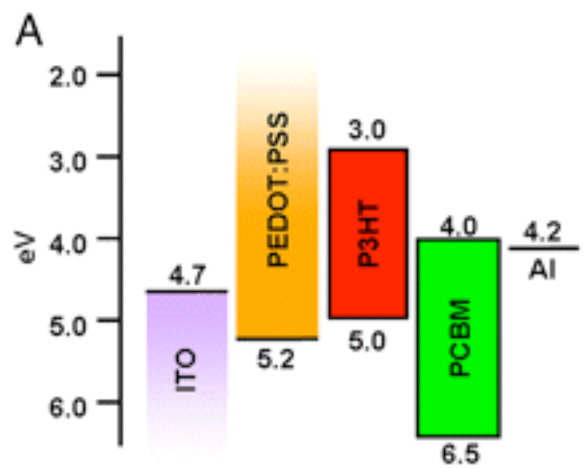
- UV ozone treatment: Increases the workfunction to 4.8 eV.

- Wet cleaning (aquaregia (HNO_3, HCl, H_2O)), dry-celaning; oxygen or argon plasma were found to increase the work function.

K. Sugiyama et al. J. Appl. Phys. **87**, 295, 2000.
J. S. Kim et al. J. Appl. Phys. **84**, 6859, 1998.

PEDOT/PSS





- Smoothens the ITO surface
- Prevents short-circuiting
- Water soluble polymer allowing for fabrication layered device

PEDOT/PSS

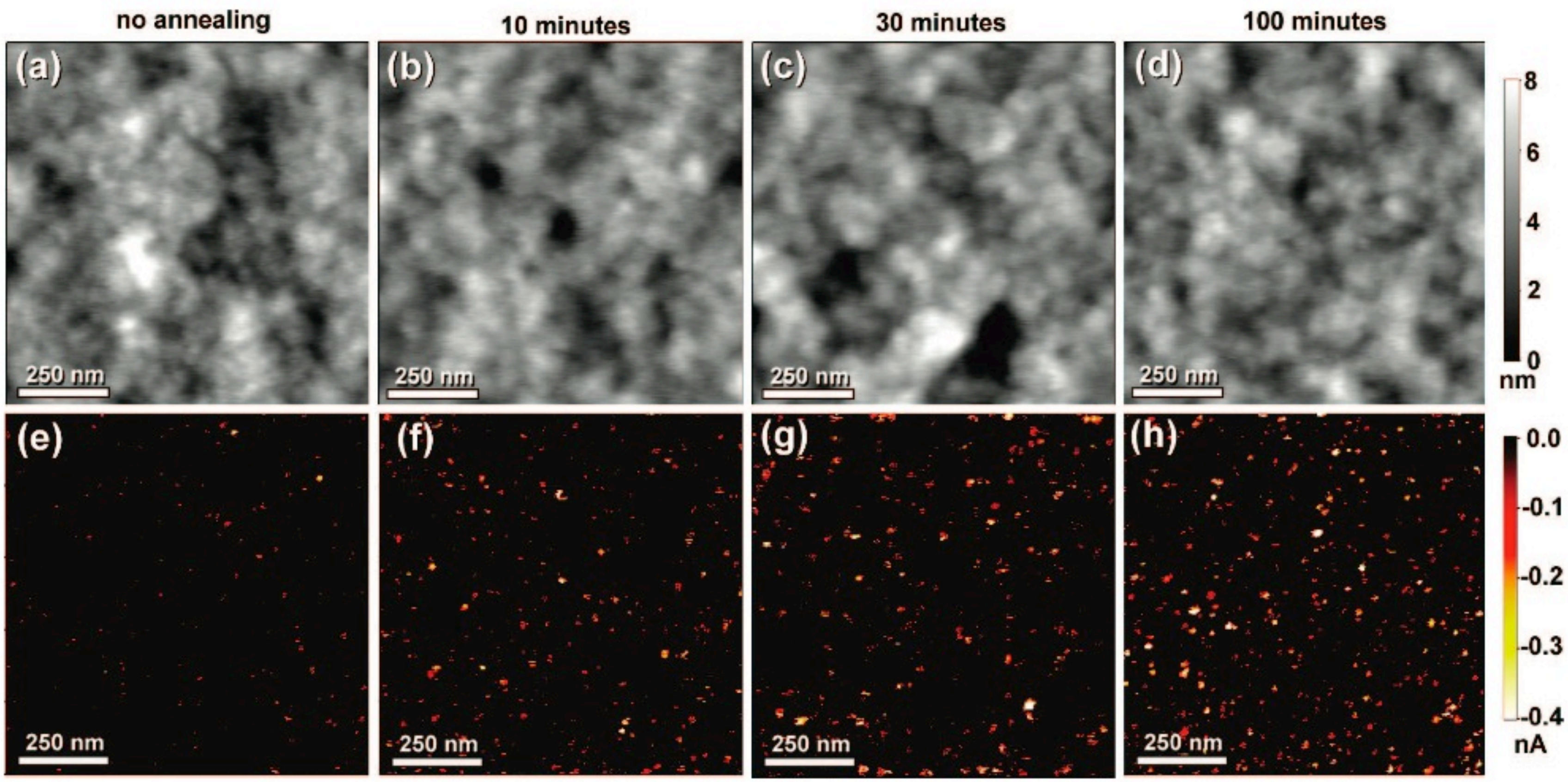


Figure 4. 1 μm^2 area c-AFM study of the effects of annealing on the PEDOT:PSS films. The topography (a–d) appears to change very little through the course of annealing. In the c-AFM images (e–h), gathered at –500 mV, the number of conductive pathways increase as function of the annealing time. Reported time at 140 °C: (a and e) 0 min, (b and f) 10 min, (c and g) 30 min, (d and h) 100 min.

J. Phys. Chem. C, 2008, **112**, 7922.

PEDOT/PSS

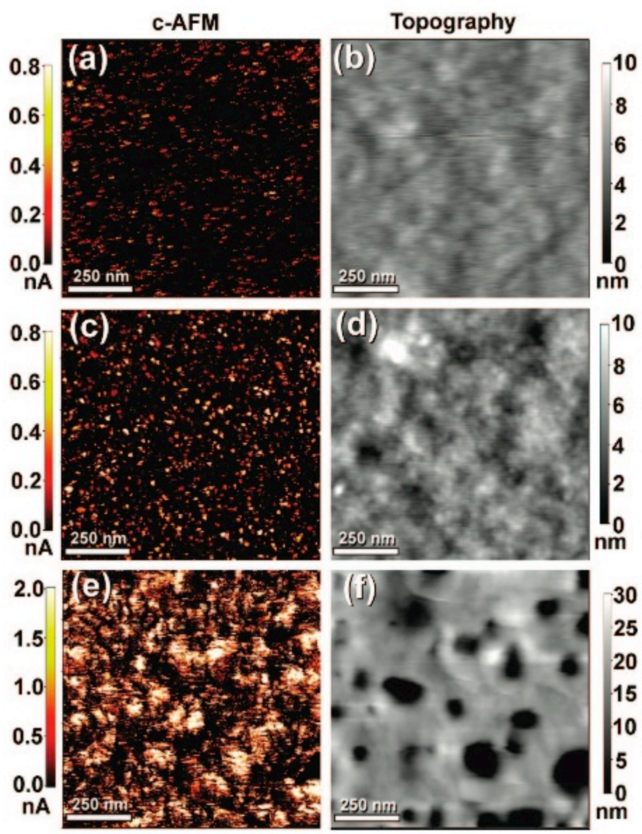


Figure 5. Examination of three different PEDOT grades on ITO surfaces: c-AFM images (a, c, and e) and corresponding topography images (b, d, and f) of Bayton 4083 (a and b) gathered at +500 mV, a higher-conductivity formulation called 4071, or "P", (c and d) gathered at +10 mV, and a ultrahigh conductivity grade "F-HC", (e and f) gathered at +3.5 mV.

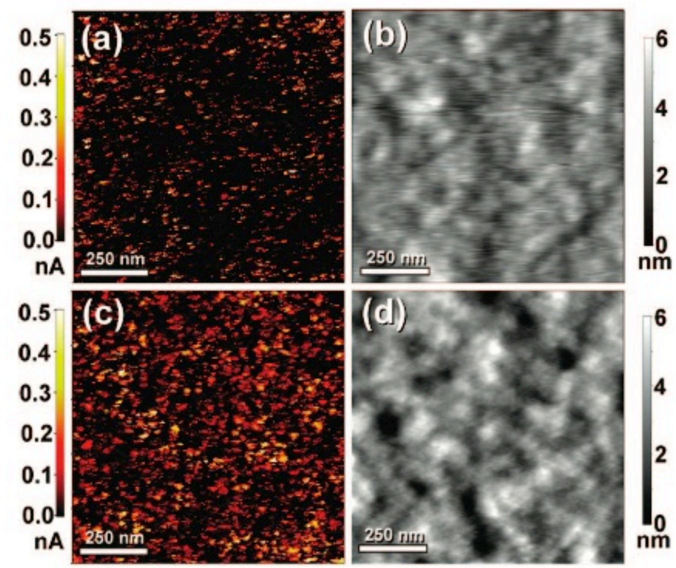
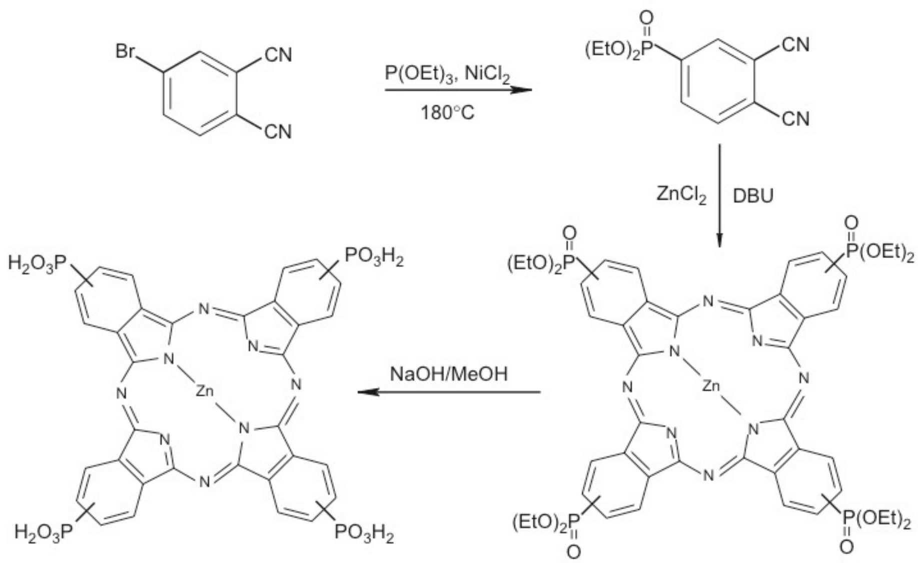


Figure 6. c-AFM (+500 mV, a and c) images of a PEDOT surface on ITO, annealed for 30 min at 140 °C before (a and b) and after (c and d) spin coating a neat chlorobenzene solution on top.

J. Phys. Chem. C, 2008, **112**, 7922.

Monolayers on ITO



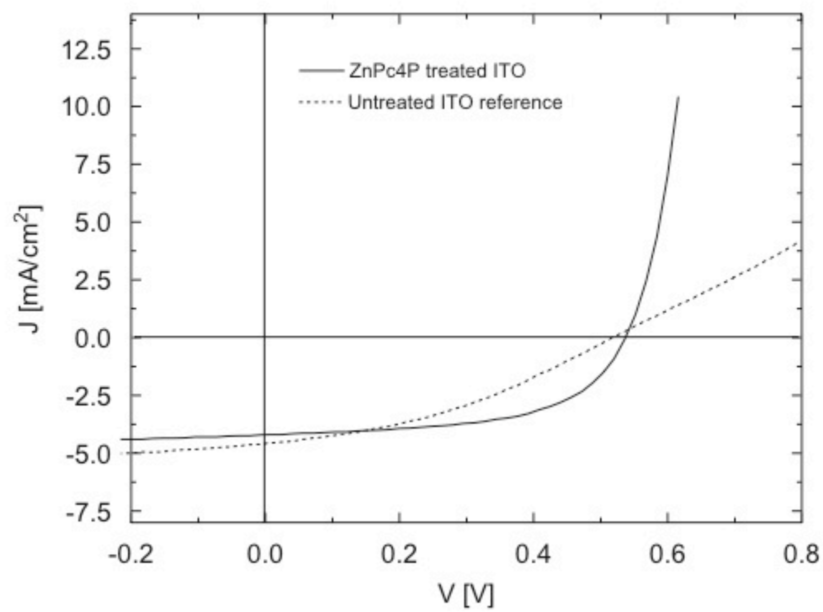
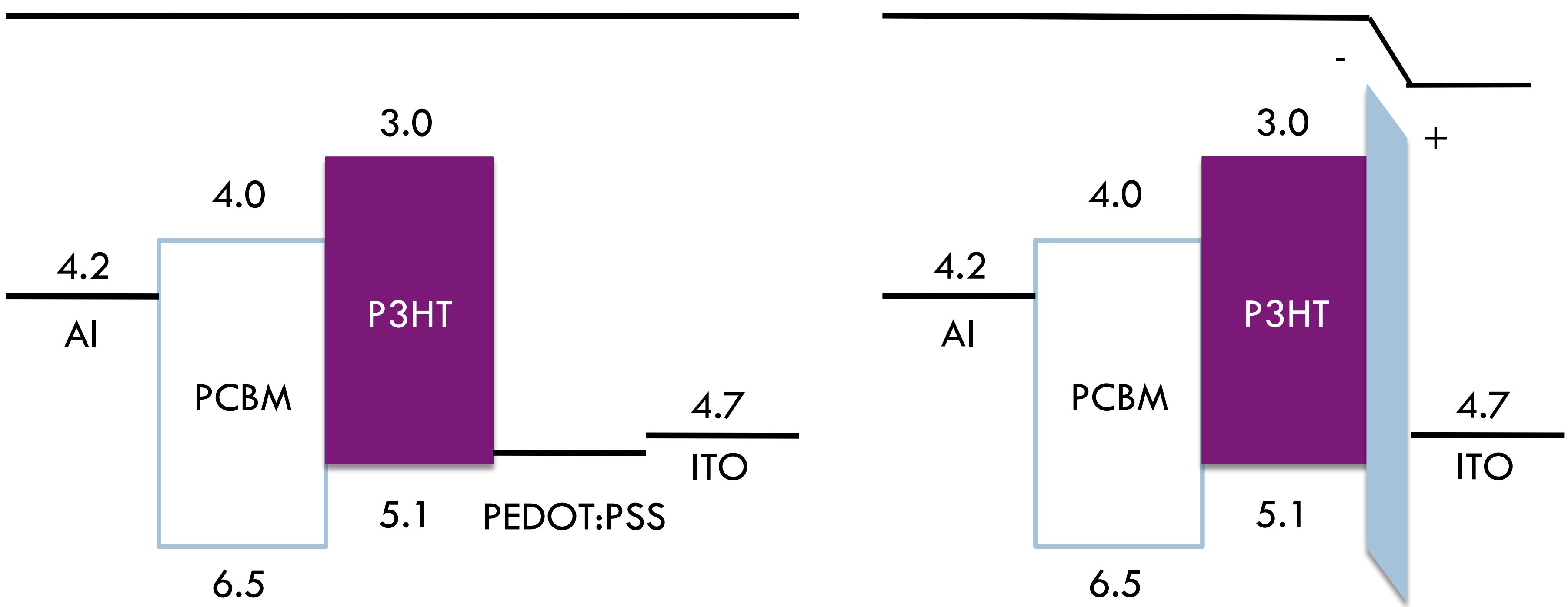


Fig. 2. *J–V* characteristics of ITO/ZnPc/C_{60}/Al solar cells under one sun AM1.5 illumination produced on untreated ITO (dashed line) and ZnPc4P treated ITO (solid line).

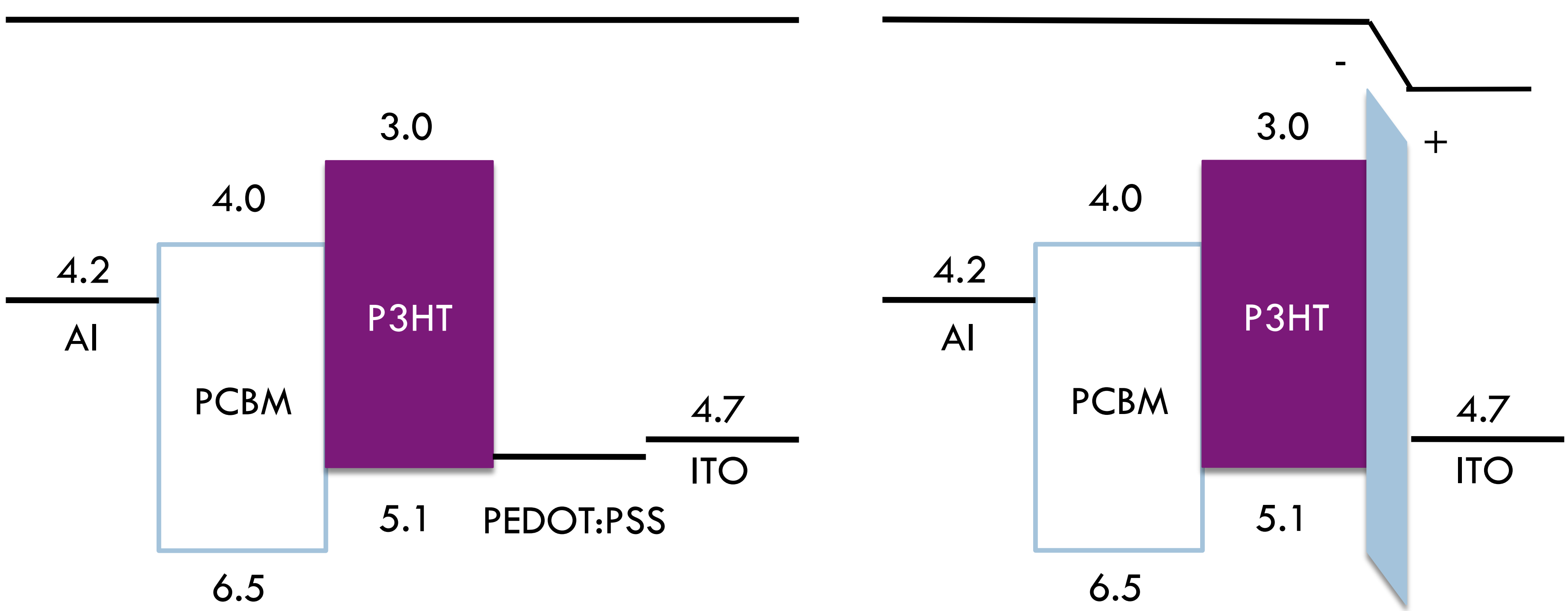
Sol. Energy Mater. Sol. Cells, 2008, **92**, 393.

Affecting the electrode work function



- The dipole induces a step in the local vacuum level due to electric field in the area
- Dipole pointing towards the surface effectively reduces the work function
- Dipole pointing away the surface effectively increases the work function

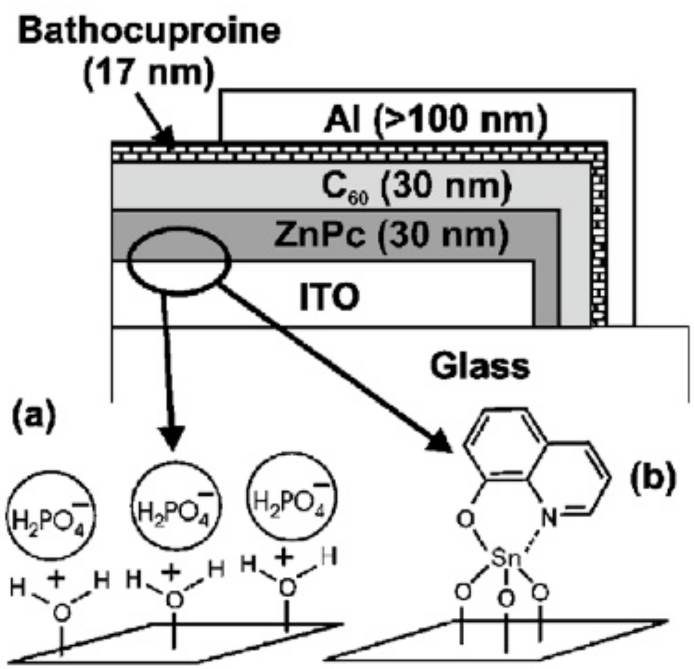
Affecting the electrode work function



$$\Delta V = \frac{N_{sl}\mu\cos\theta}{\varepsilon_r\varepsilon_0}$$

Monolayers on ITO

- Adjust the work function of the metal using dipolar molecules
- Reduce interface defects
- Use small molecules to prevent introducing insulating layer



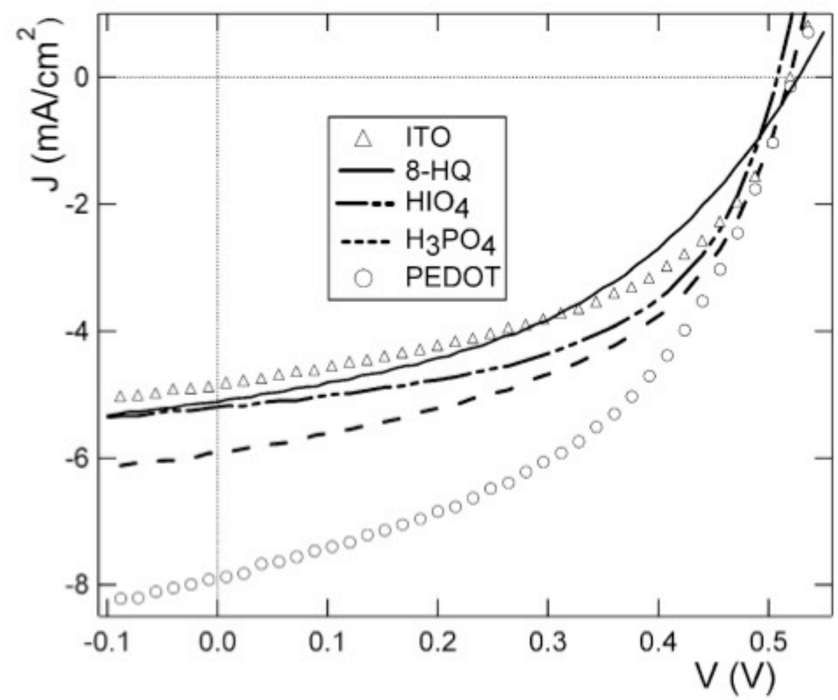


Fig. 2. $J-V$ characteristics of solar cells under one sun AM1.5 illumination with different ITO treatments compared to untreated ITO.

Thin solid films, 2005, **488**, 270.

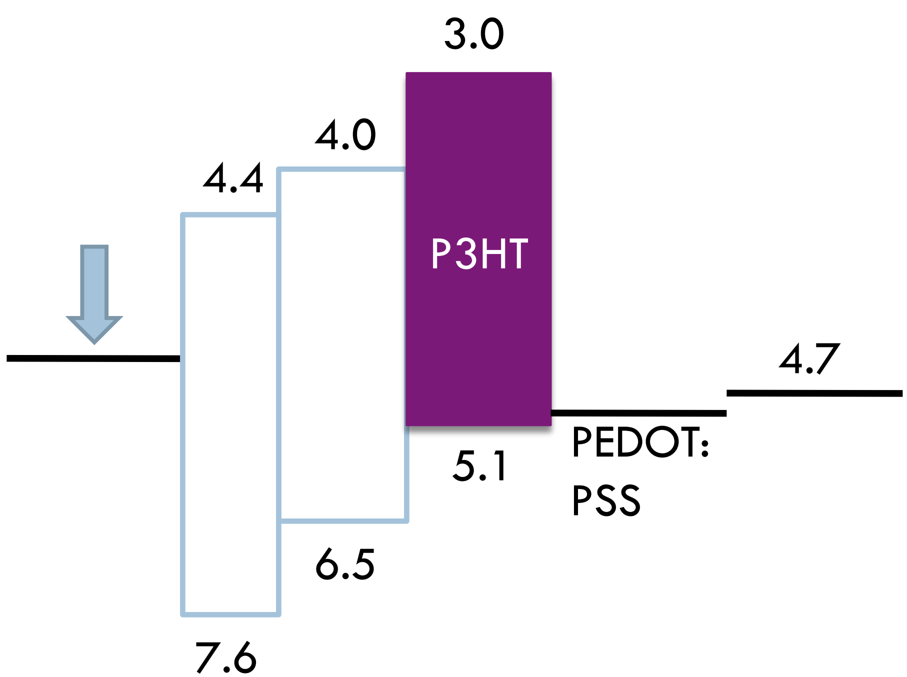
Monolayers on ITO

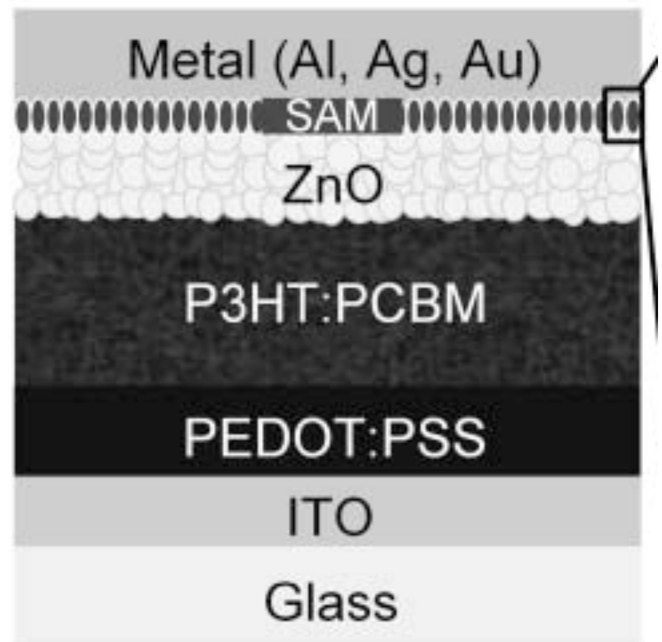
	J_{sc} (mA/cm^2)	V_{oc} (V)	FF (%)	R_s (Vcm^2)	Φ (eV)[3]		η (%)
					Published data	KPFM	
ITO	4.8	0.52	49	1.6	3.9–4.5 [11,18,19]	4.30±0.01	1.2
8-HQ	5.1	0.53	43	14.8	DΦ=+0.47 [14]	4.140±0.006	1.2
HIO_4	5.2	0.54	51	1.2	–	4.991±0.007	1.4
H_3PO_4	5.9	0.52	50	1.0	5.1 [11]	5.030±0.017	1.5
PEDOT	7.9	0.52	46	4.6	5.2–5.3 [9]	–	1.8

- 8-HQ shows little difference in device performance
- Acidic moieties increase the work function of ITO

Thin solid films, 2005, **488**, 270.

Affecting the electrode work function

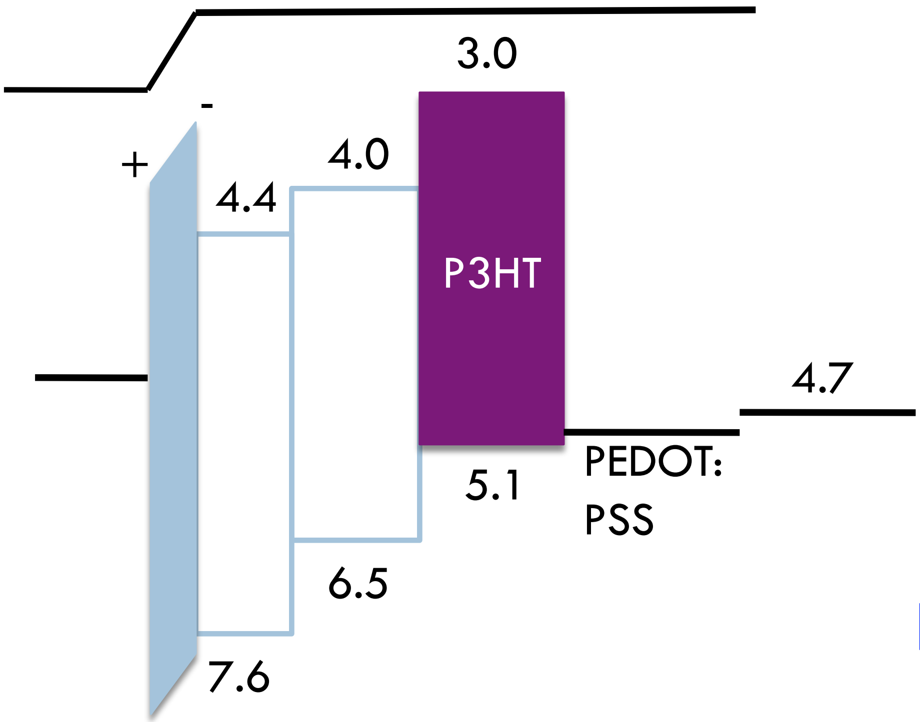


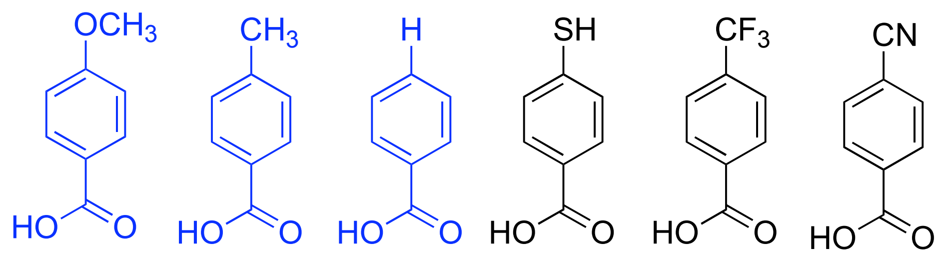


- ZnO acts as hole blocking layer, optical spacer, and acts as a barrier against water/oxygen.
- Wanted to use a higher work function metal to improve stability of top electrode.
- Also, introduces the possibility of an all solution-processed device.

Adv. Mater., 2008, **20**, 2376.

Affecting the electrode work function





-3.9D -2.9D -2.0D 1.5D 2.1D 3.7D

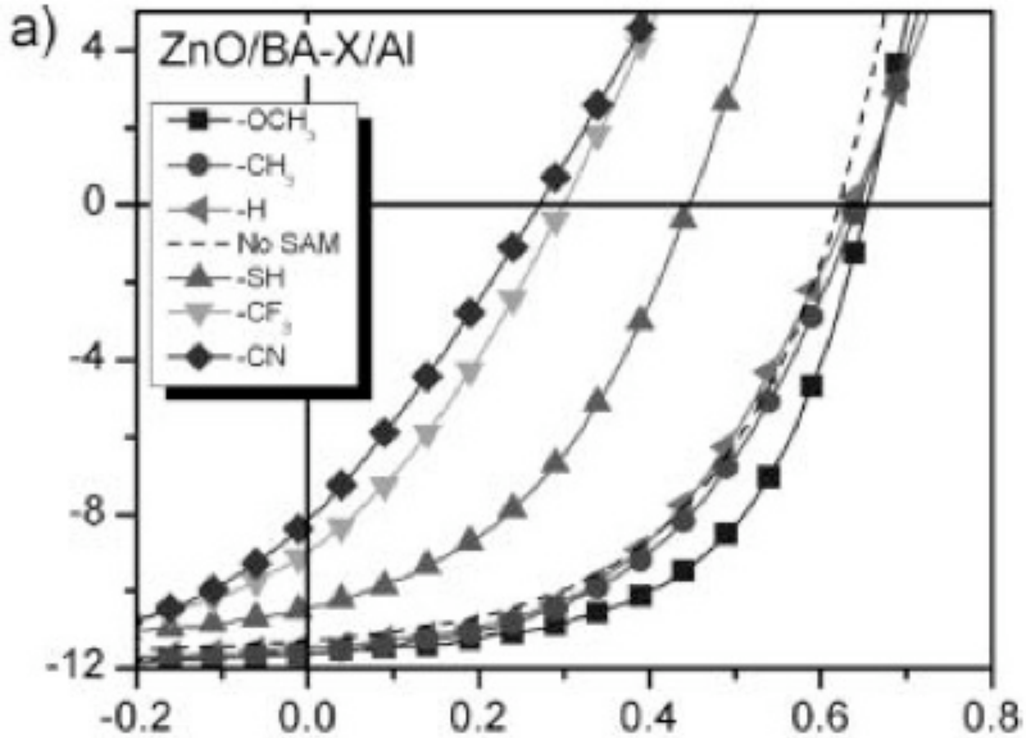
Dipole pointing away from ZnO

Expect top electrode work function to decrease

Expect device performance to improve

Adv. Mater., 2008, **20**, 2376.

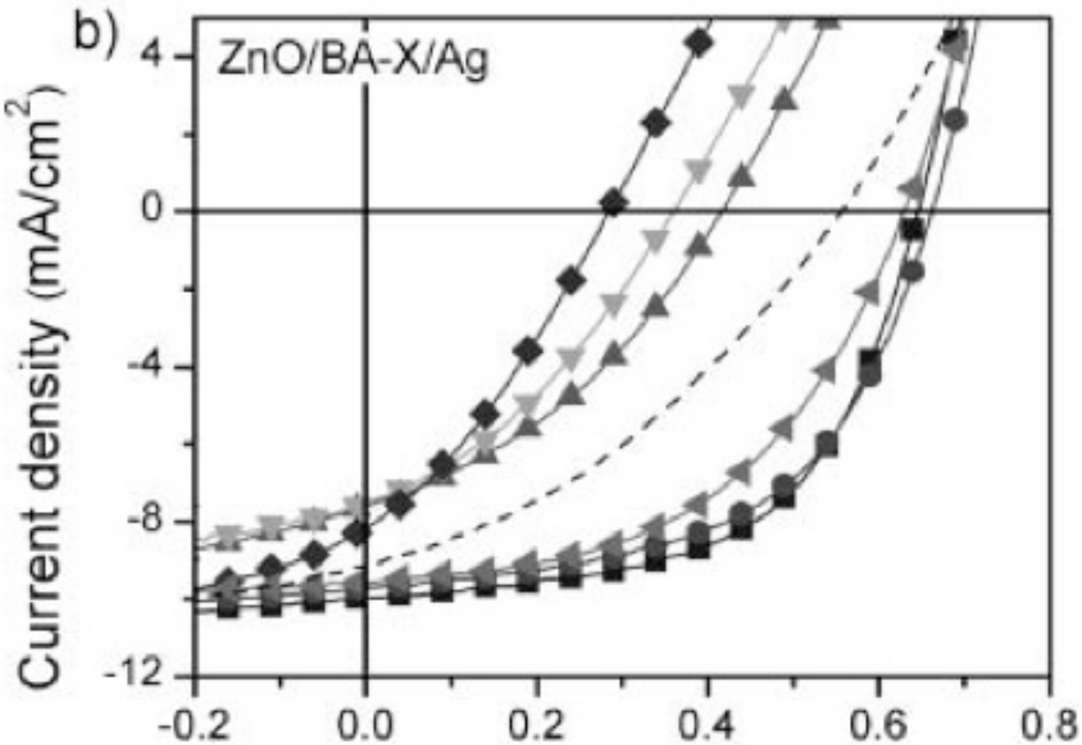
Affecting the electrode work function



4.2%

Adv. Mater., 2008, **20**, 2376.

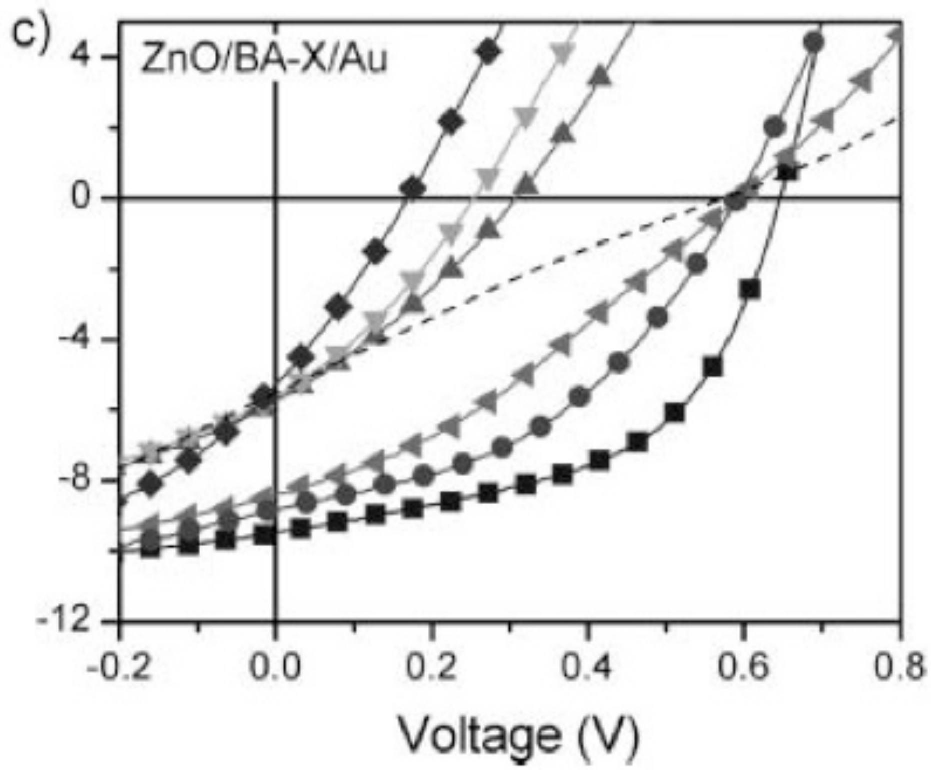
Affecting the electrode work function



3.65%

Adv. Mater., 2008, **20**, 2376.

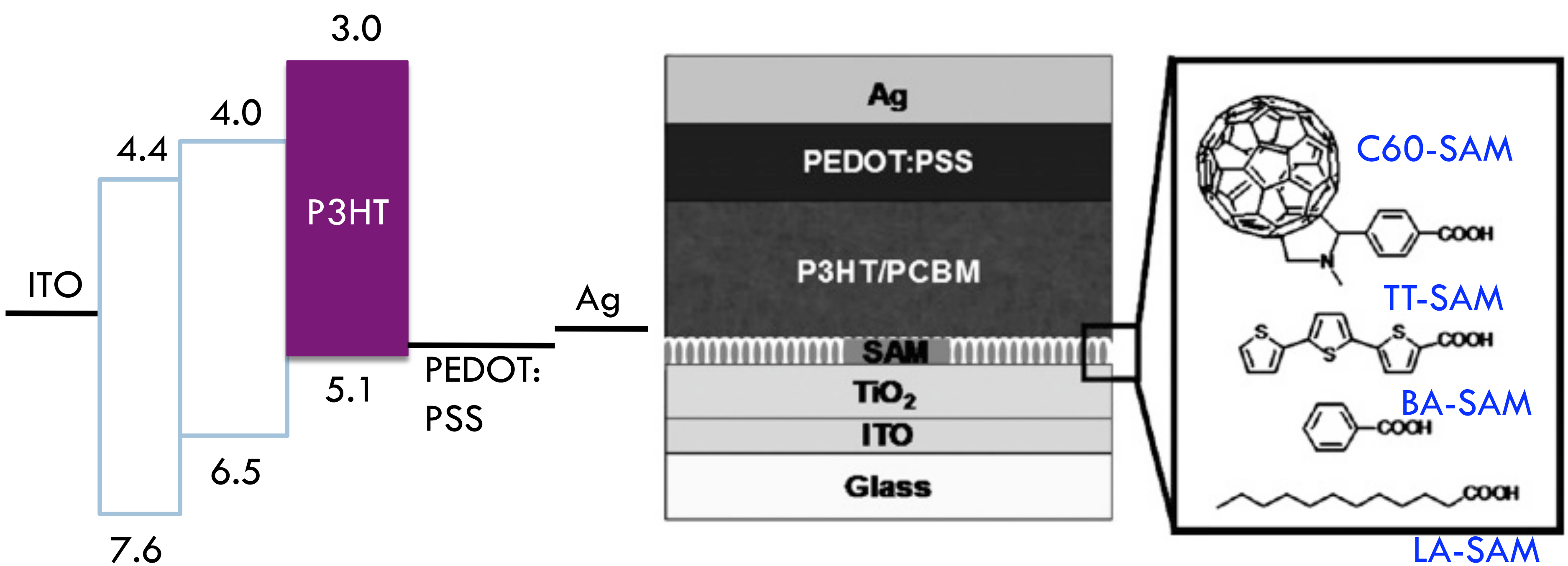
Affecting the electrode work function



3.22%

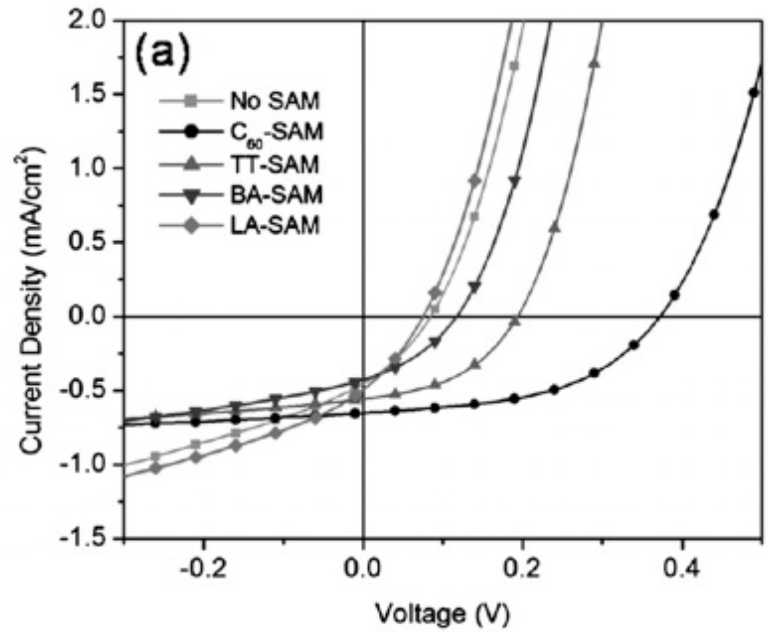
Adv. Mater., 2008, **20**, 2376.

Inverted solar cell structure



J. Mater. Chem., 2008, **18**, 5113.

Inverted solar cell structure



C60>TT>BA>LA>None

SAM	V_{oc}/V	J_{sc}/mA cm ^{2}	FF (%)	η (%)	Rectification ratio
None	0.08	0.45	31.5	0.01	4 10^{2}
C_{60}	0.37	0.65	49.1	0.12	3 10^{4}
Terthiophene (TT)	0.19	0.56	44.1	0.05	2 10^{3}
Benzoic acid (BA)	0.12	0.43	35.7	0.02	2 10^{2}
Lauric acid (LA)	0.07	0.49	30.6	0.01	4 10^{2}

J. Mater. Chem., 2008, **18**, 5113.

Inverted solar cell structure

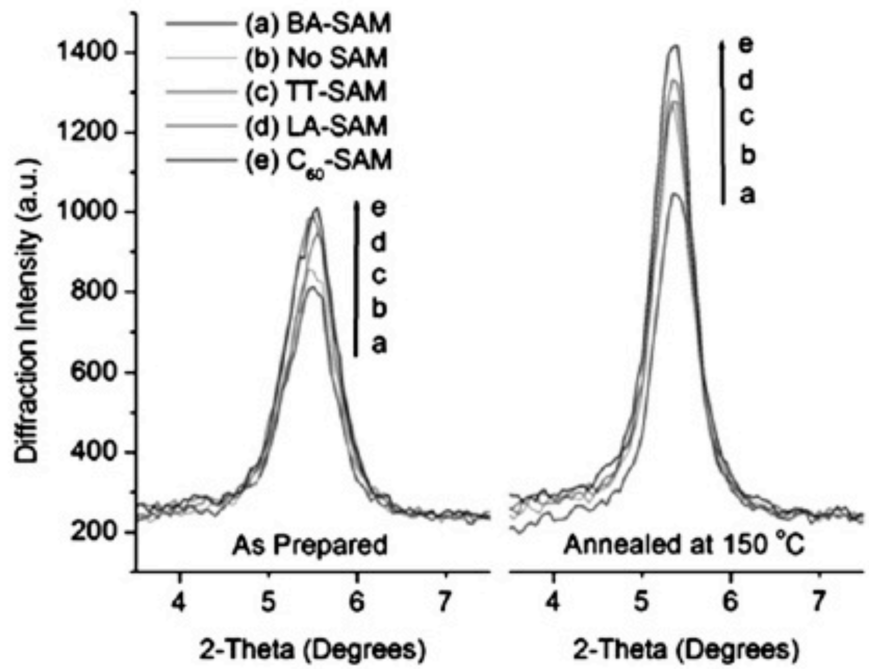
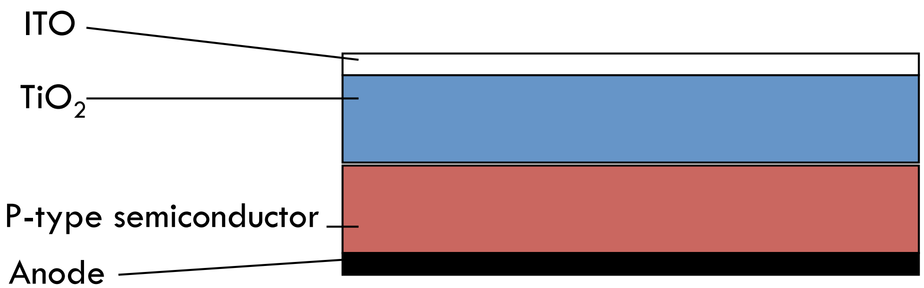


Fig. 6 X-Ray diffraction spectra of the P3HT (100) peaks before and after thermal annealing at 150 °C on bulk heterojunction devices modified with and without SAMs.

- SAMs can affect work function of the metal/metal oxide
- Allow for vertical segregation
- Alter the crystallinity in your thin film structure

J. Mater. Chem., 2008, **18**, 5113.

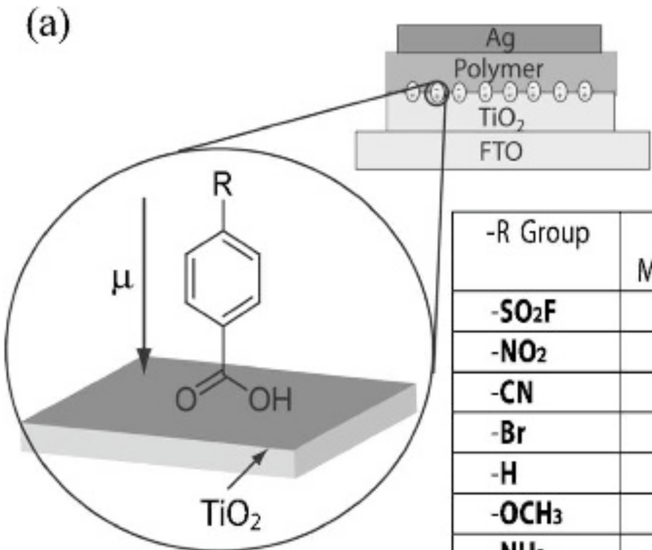
Organic-inorganic hybrid device



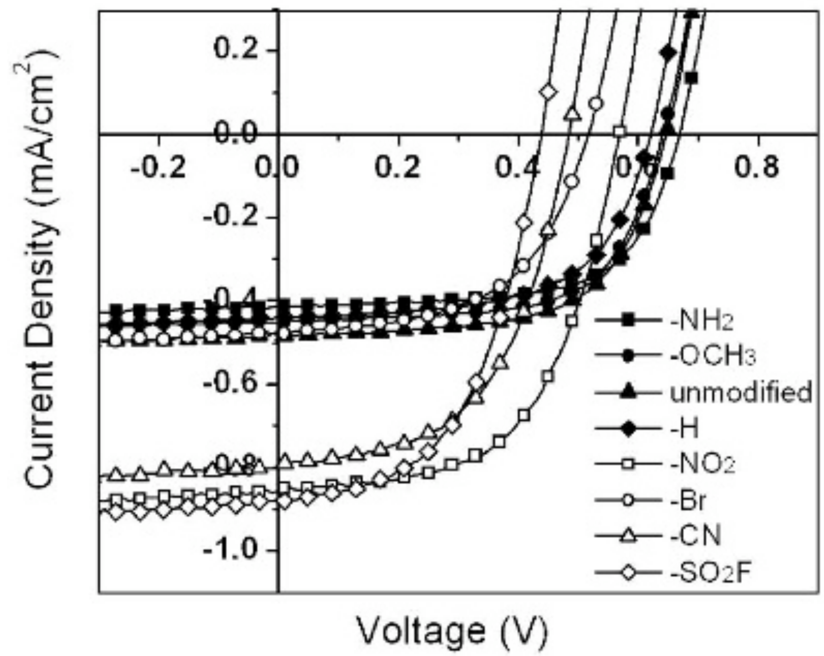
- Offer the best of both worlds
  - -Stability and improved efficiency from the inorganic
  - -Cheapness from the organic

- In reality, efficiencies are extremely low – P3HT/TiO_2 devices have a PCE of approx. 0.1-0.2%

Organic-inorganic hybrid device



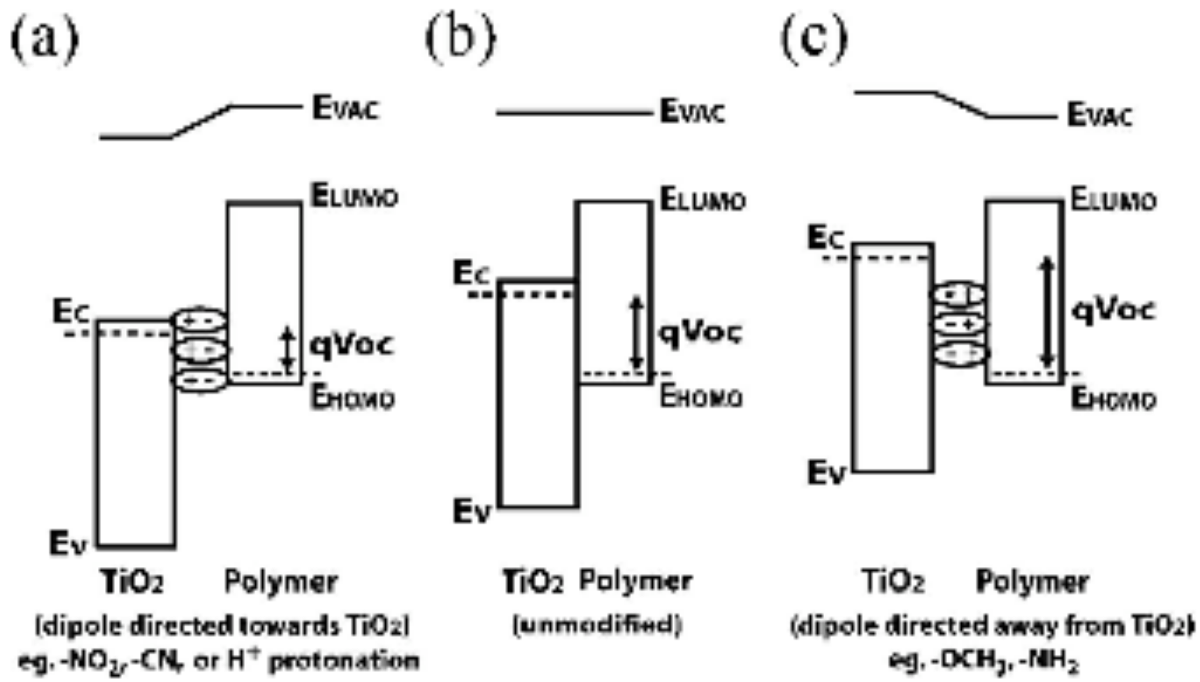
-R Group	Dipole Moment (D)
-SO2F	4.5
-NO2	3.8
-CN	3.4
-Br	1.4
-H	-2.1
-OCH3	-3.9
-NH2	-4.5



- When dipole is pointing towards the surface, J_{SC} increases and V_{OC} decreases. Overall PCE is improved.

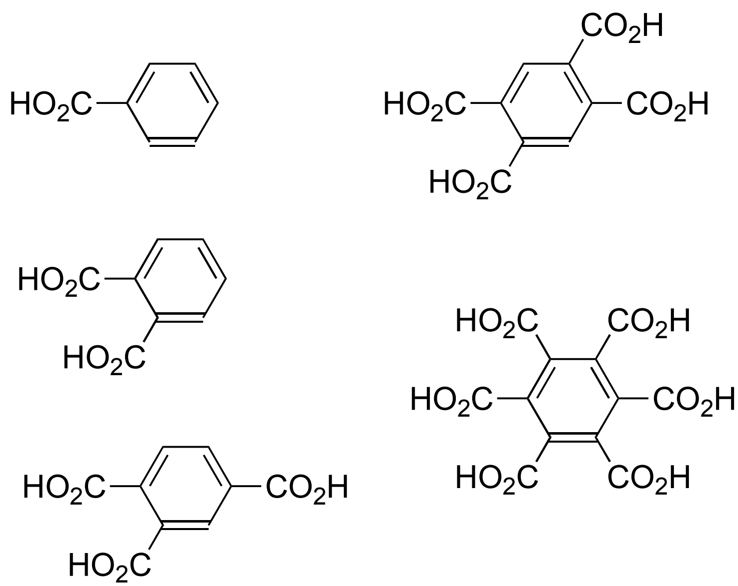
J. Appl. Phys., 2007, **101**, 114503.

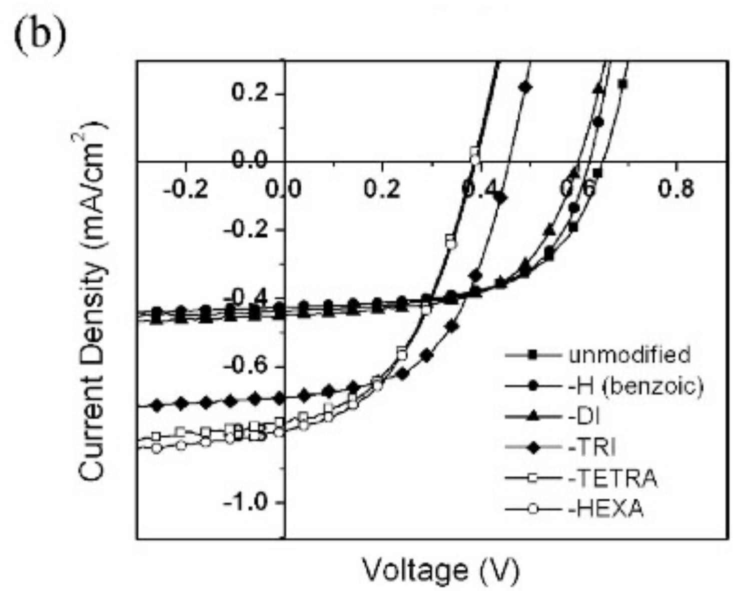
Organic-inorganic hybrid device



J. Appl. Phys., 2007, **101**, 114503.

Organic-inorganic hybrid device

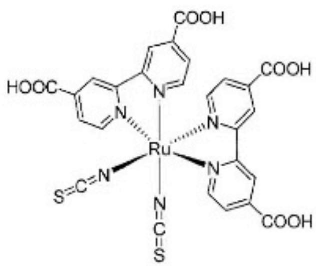




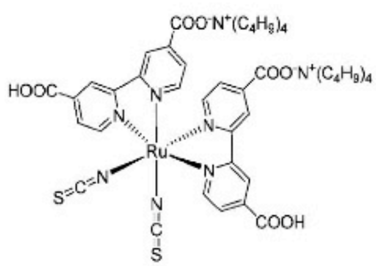
- H^+ ions accumulate on the surface, effectively creating a surface where the dipole is pointing towards TiO_2.

J. Appl. Phys., 2007, **101**, 114503.

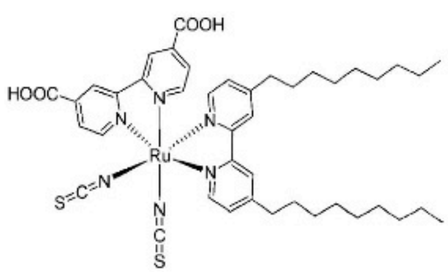
Organic-inorganic hybrid device



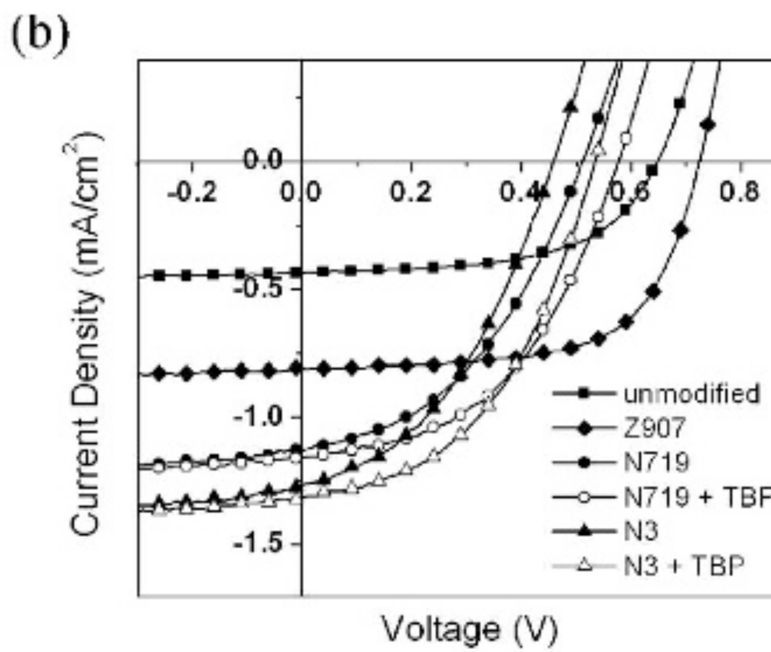
N3



N719

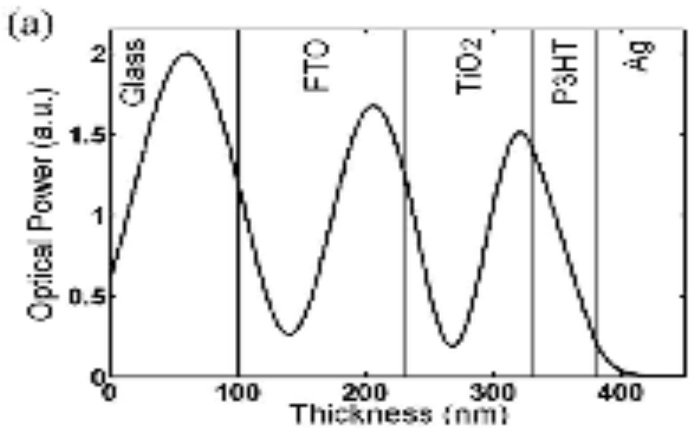


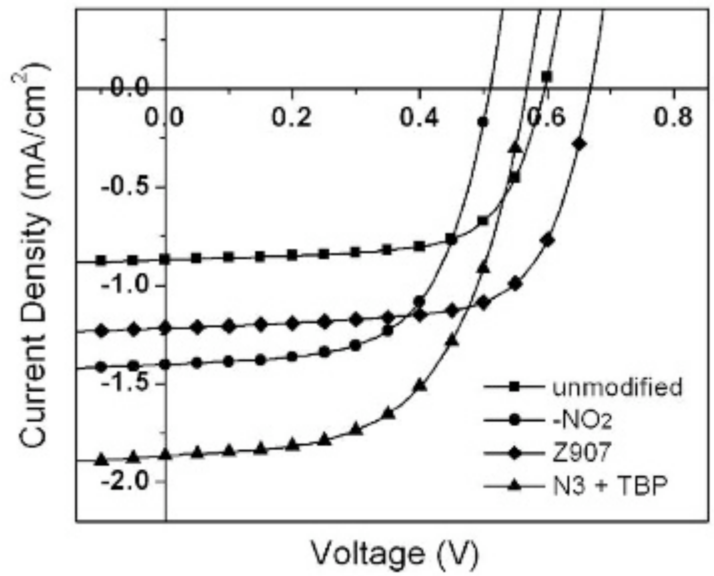
Z907



J. Appl. Phys., 2007, **101**, 114503.

Organic-inorganic hybrid device

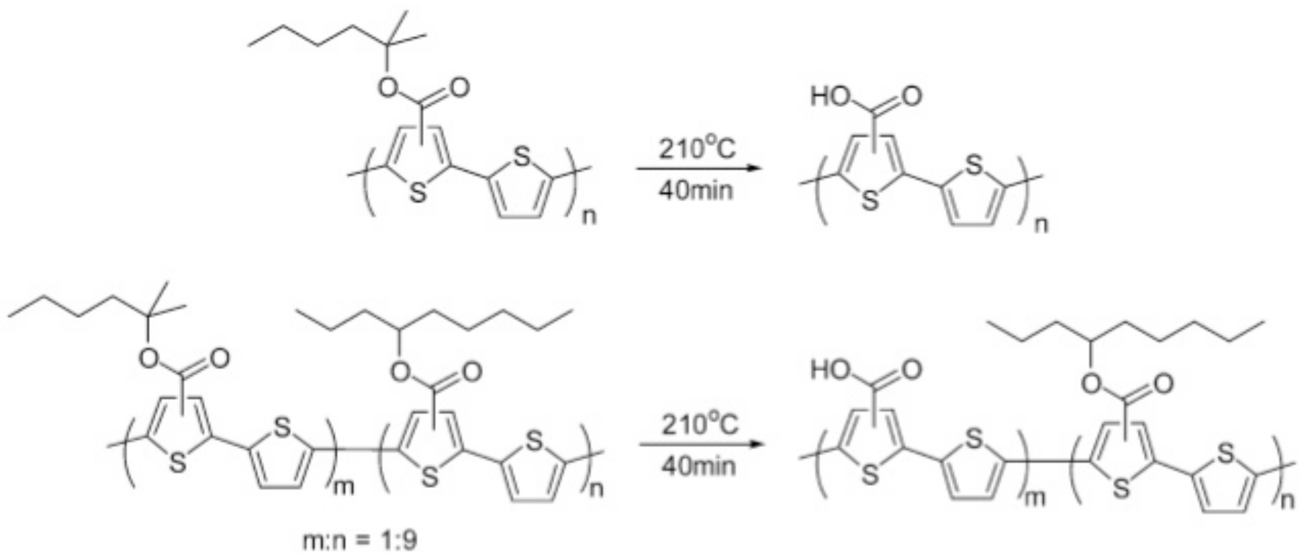




Devices	J_{sc} (mA/cm^2)	V_{oc} (V)	FF	η (%)	Estimated J_{sc} (mA/cm^2)
Unmodified	0.85	0.60	0.67	0.34	0.80
$-NO_2$	1.40	0.51	0.62	0.44	1.56
Z907	1.21	0.67	0.69	0.56	···
N3+TBP	1.86	0.57	0.57	0.60	1.92

J. Appl. Phys., 2007, **101**, 114503.

Organic-inorganic hybrid device

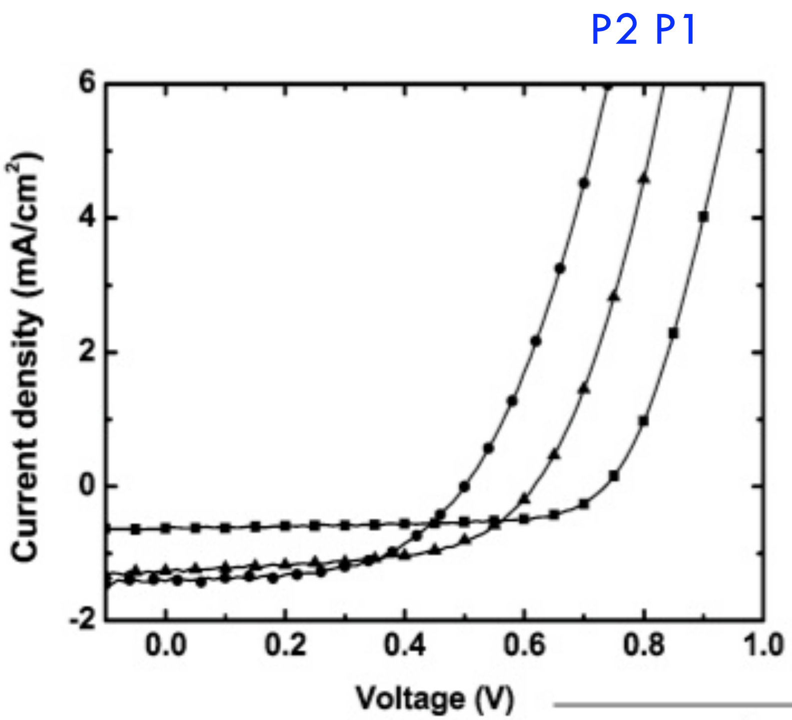


P1

P2

J. Appl. Phys., 2007, **101**, 114503.

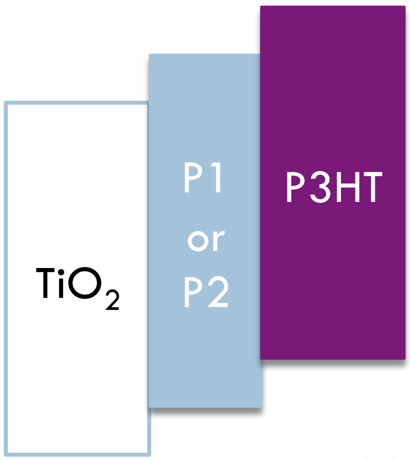
Organic-inorganic hybrid device



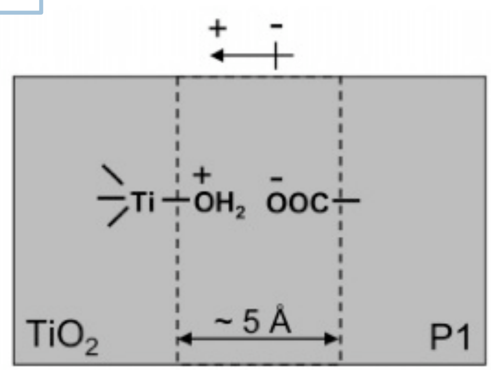
device	J_{sc} (mA/cm^2)	V_{oc} (V)	FF^b
FTO/TiO_2/P3HT/Ag	0.63	0.73	0.64
FTO/TiO_2/P2/P3HT/Ag	1.26	0.62	0.56
FTO/TiO_2/P1/P3HT/Ag	1.41	0.50	0.54

J. Appl. Phys., 2007, **101**, 114503.

Affecting the V_{OC}



- !V_{OC} is related to the difference between HOMO of donor and LUMO of acceptor.



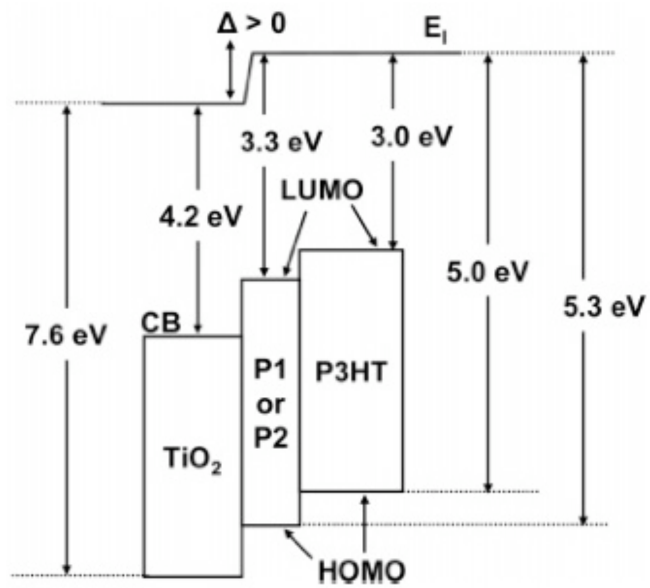


TABLE 1: Kelvin Probe Measurements of the Work Function of Several Films[a]

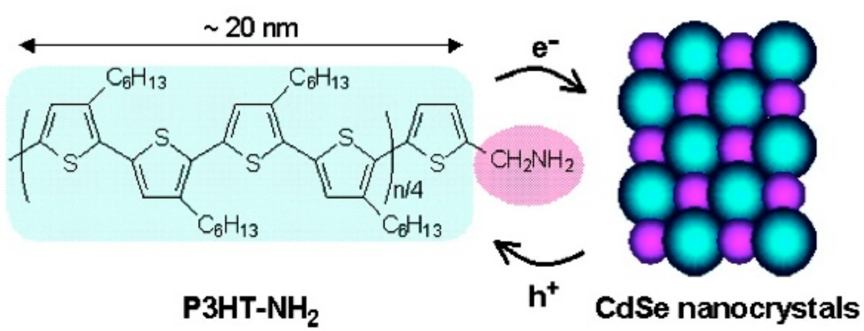
sample	FTO	FTO/TiO_2	FTO/TiO_2/P3HT	FTO/TiO_2/P1	FTO/TiO_2/P2
work function (eV)	4.91 ± 0.01	4.51 ± 0.02	4.45 ± 0.01	4.73 ± 0.01	4.57 ± 0.01

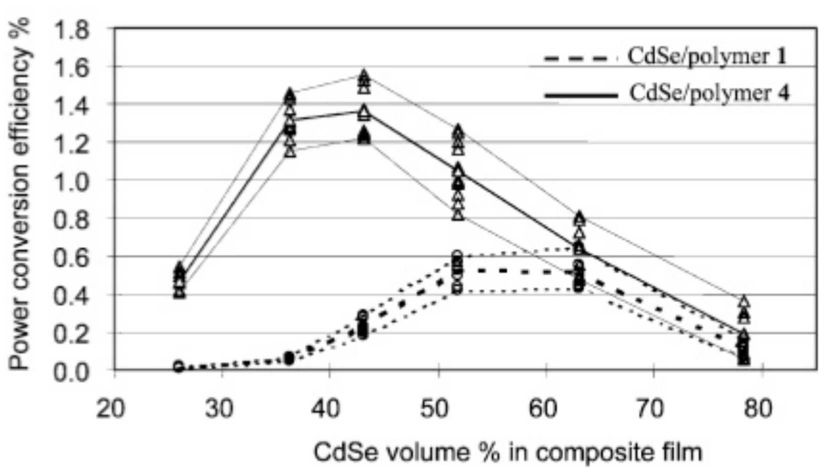
[a] The thicknesses of the TiO_2, P3HT, P1, and P2 are 50, 5, 5, and 5 nm, respectively.

J. Appl. Phys., 2007, **101**, 114503.

P3HT/III-V nanoparticle OPVs

- Potentially solves exciton diffusion problem
- Nanoparticle absorbs light as well
- Possibility of multi-exciton formation





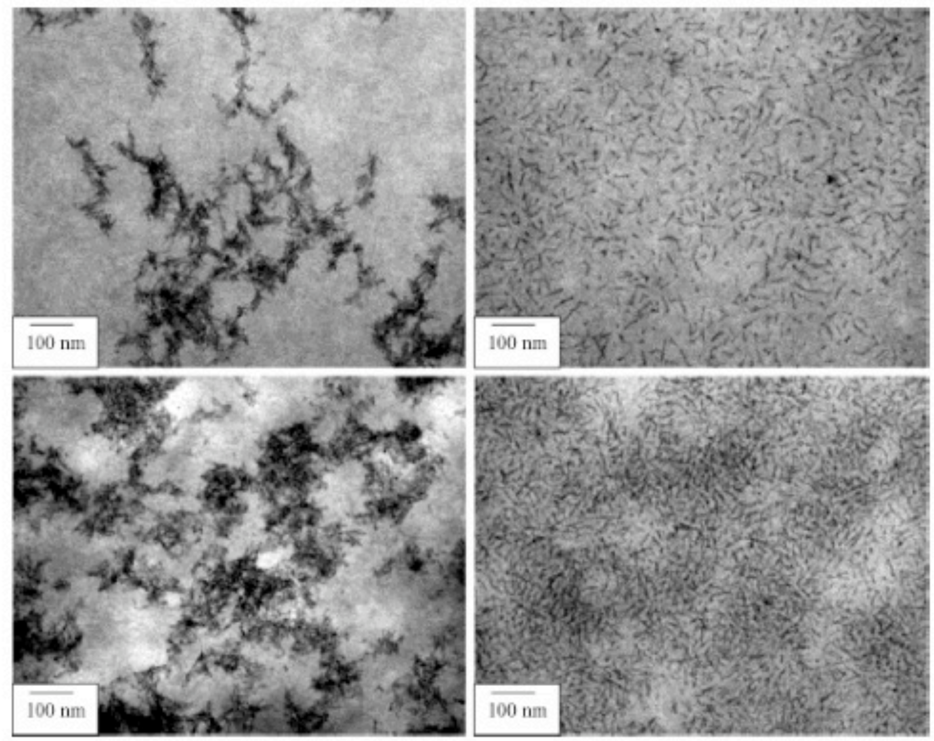


Figure 1. TEM images of four films consisting of CdSe (20 wt %)/polymer **1** (top left), CdSe (20 wt %)/polymer **4** (top right), CdSe (40 wt %)/polymer **1** (bottom left), and CdSe (40 wt %)/polymer **4** (bottom right), respectively.

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