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# Characterization of N, N'-bis-2-(1-hydroxy-4-methylpentyl)-3, 4, 9, 10-perylene bis (dicarboximide) sensitized nanocrystalline TiO<sub>2</sub> solar cells with polythiophene hole conductors

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## Abstract

We have fabricated solid-state, dye-sensitized nanocrystalline TiO<sub>2</sub> solar cells (DSSC) based on perylene derivative dye, N,N'-bis-2-(1-hydroxy-4-methylpentyl)-3,4,9,10-perylene bis (dicarboximide) (HMPER) with two different polythiophenes as hole conductors; i.e. poly (3-octyl thiophene) (P3OT) and poly (3-hexyl thiophene) (P3HT), respectively. HMPER adsorbs strongly to the surface of nanocrystalline TiO<sub>2</sub> and inject electrons into TiO<sub>2</sub> conduction band upon absorption of light. Polythiophene derivatives are well-known materials as hole conductors in solid-state dye-sensitized solar cells. We obtained quite similar results with P3OT and P3HT yielding a short-circuit current density of around 80 μA/cm<sup>2</sup> and open-circuit voltage of around 0.7 V at 80 mW/cm<sup>2</sup> AM 1.5 light intensity. The results are compared with Ru-535 TBA-sensitized nc-TiO<sub>2</sub> cells prepared by using the same polythiophene derivatives.

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**Keywords:** Dye-sensitized solar cell; Perylenediimide; Nanocrystalline TiO<sub>2</sub>; Polythiophene

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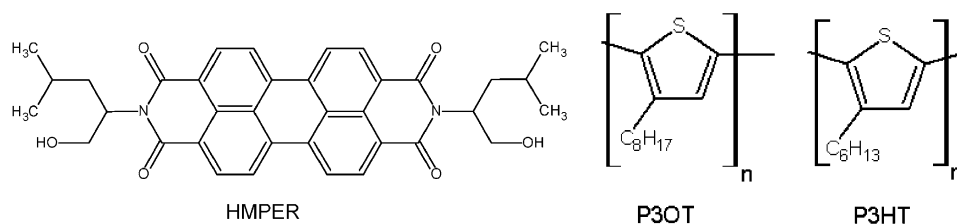
E-mail address: [icli@mail.ege.edu.tr](mailto:icli@mail.ege.edu.tr) (S. Icli).

## 1. Introduction

Since the report on high power conversion efficiency [1] dye-sensitized nanocrystalline TiO<sub>2</sub> solar cells (nc DSSCs), based on photosensitization of nanocrystalline TiO<sub>2</sub>, are regarded as a potentially low-cost alternative to conventional solid state devices. DSSCs with I<sup>-</sup>/I<sub>3</sub><sup>-</sup> electrolyte show power conversion efficiencies of >10% [2]. Their commercialization is still hindered due to stability problems like evaporation of the electrolyte, degradation of the dye as well as by technological problems of the large area module production in presence of liquid electrolyte. In order to overcome these problems, efforts are on-going to replace the liquid electrolyte with a solid analog (i.e. polymer electrolyte or hole conductor). These approaches aims to replace the liquid electrolyte with, (i) a polymer gel electrolyte that conduct ions [3], (ii) p-type inorganic materials such as CuI, CuSCN, and (iii) organic hole conductors such as triphenyldiamine (TPD) [4–7]. Bach et al. used an amorphous, organic hole transport material (HTM) to replace the electrolyte, in which positive charges are transported by hopping processes [8]. Furthermore, Gebeyehu et al. and Smestad et al. have used p-type semiconducting polymers that accept holes from the dye cation to replace liquid electrolyte [9–11]. A prospective hole conductor must have low optical absorption in the visible region of solar spectrum, reasonable hole conductivity, photochemical and physical stability and appropriate HOMO and LUMO energy levels for efficient charge transport in order to use for solid- state DSSCs. In most of previous studies on dye sensitization of nc-TiO<sub>2</sub> for solar cells Ru-complexes were used. Grätzel and co-workers reported the highest solar energy to electricity conversion efficiency with DSSCs, based on Ru-complexes and liquid I<sup>-</sup>/I<sub>3</sub><sup>-</sup> electrolyte [2]. The same group reported high photon to electron conversion efficiency (IPCE) (up to 33%) with solid-state DSSCs based on Ru-complex and p-type amorphous hole conductor (spiro-OMeTAD) [8].

In this work, the well-known polythiophene derivatives of poly (3-hexyl thiophene), P3HT, and poly (3-octyl thiophene), P3OT, are used to replace the liquid electrolyte. The charge injection dye is a perylenediimide (PDI) derivative, N, N'-bis-2-(1-hydroxy-4-methylpentyl)-3,4,9,10-perylene bis (dicarboximide), HMPER, as the photo-sensitizer on nc-TiO<sub>2</sub> (Scheme 1). PDIs absorb in the visible ( $\epsilon \approx 10^5 \text{ M}^{-1} \text{ cm}^{-1}$ ) and emit from the singlet state with a fluorescence quantum yield ( $\phi_f$ ) of unity [12,13]. Electron injection from the singlet excited state of the dye into the conduction band of the semiconductor is faster than from triplet states. PDIs have been used commercially as red pigments for half a century because of their chemical stability and light absorption [14]. The electron injection rate constants ( $k_{inj}$ ) of perylene dyes and Ru-complexes into the TiO<sub>2</sub> are relatively similar. Burfeindt et al [15] reported the  $k_{inj}$  value as  $5 \times 10^{13} \text{ s}^{-1}$  for perylene derivatives, whereas Kalyanasundaram and Grätzel et al gave this value as  $> 8 \times 10^{13} \text{ s}^{-1}$  for Ru-complexes [16]. The major advantage of PDI derivatives over Ru-complexes is that their synthetic pathway is easier and basic chemicals are at lower costs [14].

Solar cells fabricated using these materials clearly show a photovoltaic activity with similar efficiencies for both derivatives of polythiophenes through out both HMPER and Ru-535 TBA sensitization (Scheme 1).



Scheme 1.

## 2. Experimental section

### 2.1. Materials

Titanium isopropoxide (99%) was purchased from Acros. Titanium oxide nanocrystalline powder, P25, was obtained from Degussa. ITO-coated 1.1 mm glasses (sheet resistance  $13 \Omega/\square$ ) were purchased from Merck. Regioregular P3OT and P3HT were obtained from Aldrich and used as received. HMPER was synthesized and purified as described in Ref. [3]. Chlorobenzene purchased from Aldrich. Ruthenium 535 TBA obtained from Solaronix.

### 2.2. $TiO_2$ film preparation and dye sensitization

Two types of  $TiO_2$  layer were prepared, the first layer was a non-porous dense nanocrystalline  $TiO_2$  layer, to prevent short circuit in the solar cell [8], it was prepared by the sol–gel method. A titanium isopropoxide (99%) precursor was used to prepare a polymeric sol; 10.7 g of titanium isopropoxide were added to 44 g dry 2-propanol and stirred for 10 min on magnetic stirrer (Part A). In another beaker, 6.76 g water and 0.96 g  $HNO_3$  (65%) were added to 44 g dry 2-propanol for 10 min on magnetic stirrer (Part B). Part B was added droplet on Part A under vigorous stirring. After mixing the two parts the solution was remained under stirring for half an hour. At the end of this time the sol was ready to use.

This sol was coated on ITO electrodes by spin coating at 2000 rpm. The obtained film thickness was measured by Tencor Alpha Step 500 profilometer and observed around 100 nm.

The films were annealed at  $450^\circ C$  for 30 min to obtain anatase  $TiO_2$  films.

The second  $TiO_2$  layer is a thicker and mesoporous layer to adsorb the sensitizer dye on the surface. Commercially available nanocrystalline  $TiO_2$  powder P25 was used to prepare the coating paste. P25 is a product of Degussa AG, Germany; a mixture of 30% rutile and 70% anatase, BET surface area  $55 m^2$ . This is produced by flame hydrolysis of  $TiCl_4$ . The particle size of P25 is about 25 nm. The paste was prepared according to a procedure given by Nazeeruddin et al. [2]. The prepared  $TiO_2$  paste was coated onto conducting glass substrates by doctor blade technique. ITO-coated glasses were covered on two parallel edges with an adhesive tape (Scotch 3 M,  $\sim 40 \mu m$  thickness) to control the thickness. The paste applied was  $5\text{--}10 \mu l/cm^2$

by a glass rod. The coated substrates were dried at room temperature and annealed at 450 °C for 30 min with 10° C/min heating rate to obtain pure TiO<sub>2</sub> films. The obtained mesoporous TiO<sub>2</sub> film thicknesses were measured by Tencor Alpha Step 500 profilometer, being around 8 μm.

The prepared TiO<sub>2</sub> electrodes were dipped at least 3 h into a 5 × 10<sup>-4</sup> M HMPER solution in dry 2-propanol. At the end of this time the HMPER adsorbed TiO<sub>2</sub> substrates were washed with pure 2-propanol and dried under vacuum. For comparison, also TiO<sub>2</sub> electrodes sensitized by 0.3 mM Ru 535 TBA solution in dry ethanol were prepared. The sensitized electrodes were kept in vacuum to prevent adsorption of water on the TiO<sub>2</sub> surface.

The sensitized TiO<sub>2</sub> electrodes were coated with P3OT and P3HT by spin casting using 1% (w/w) solutions in dry chlorobenzene. The polythiophenes were coated at 1500 rpm and dried at 2000 rpm. After spin casting, the films dried completely in a high vacuum chamber for 30 min.

The cell preparation was completed by transferring the samples to a vacuum deposition chamber in an inert argon atmosphere glove box for evaporation of metal (Al, Ag, Au) back electrodes. Before the evaporation of metals, we evaporated a very thin layer (0.6 nm) of LiF to obtain good contact between polythiophene and metal [17]. The vacuum deposition process was controlled by a thickness monitor connected to a crystal oscillator. The evaporated metal thicknesses were 60 nm and evaporation rates were 0.1 nm s<sup>-1</sup>. The completed cell structure is given in Fig. 1. Ru-535 TBA sensitized nc-TiO<sub>2</sub> cell preparation was done throughout the same path by replacing HMPER with Ru-535 TBA.

### 2.3. Photovoltaic measurements of the solar cells

The photovoltaic performance of solid-state solar cells based on PDI sensitizers and polythiophene hole conductors was measured with a Keithley 2400 Source-Meter and data acquisition software. We employed an 80 mW/cm<sup>2</sup> AM 1.5 light

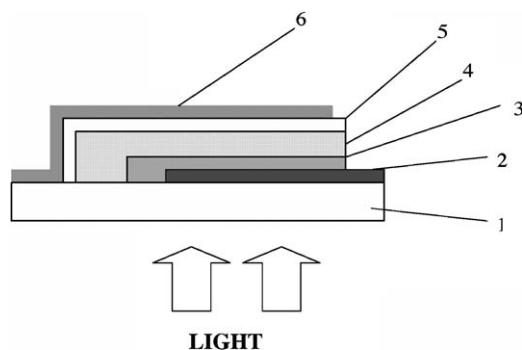


Fig. 1. Structure of photovoltaic devices; (1) glass substrate, (2) ITO layer, (3) compact TiO<sub>2</sub> layer, (4) conjugated polythiophene penetrated dye (Ru-535 TBA or HMPER) sensitized porous nc-TiO<sub>2</sub> layer, (5) LiF layer, (6) metal back electrode.

intensity by a solar simulator (KHS equipped with 750 W Xe lamp). The incident light intensity was calibrated with a reference solar cell produced by Fraunhofer ISE. All measurements of photovoltaic performances were proceeded in glove-box with inert Ar atmosphere. The measurements were made a day after the cell preparation and the average of three consecutive measurements were taken. No further long-term stability test was done.

### 3. Results and discussion

#### 3.1. Absorption, fluorescence and electrochemical properties:

Photophysical and electrochemical properties of HMPER are listed in Table 1. Fig. 2 shows the absorption and fluorescence spectra of HMPER in AcCN solution and adsorbed onto transparent TiO<sub>2</sub> film. The three absorption bands between 455 and 520 nm are typical for the lowest energy transitions of PDI derivatives. The absorption and fluorescence spectra of PDIs show consistent mirror-image behavior.

PDIs behave as electron acceptors toward  $\pi$ -electron rich electron donors, but behave as an electron donor toward strong acceptors such a Co<sup>2+</sup> ions. These properties of PDIs were determined by fluorescence quenching experiments by Icli et al. [12].

The cyclic voltametric measurements done in a previous study shows that the LUMO energy level of HMPER is 3.7 eV (vs. vacuum) [13]. The energy gap ( $E_G$ ) for HMPER differs between 2 and 2.3 eV depending on the solvent and/or matrix it is placed (Fig. 2).  $E_G$  for HMPER adsorbed on nc-TiO<sub>2</sub> film and in acetonitrile solution is  $\sim$ 2.1 and 2.3 eV, respectively. Therefore, the HOMO energy level of HMPER is  $\sim$ 6 eV. Fig. 3 presents the cyclic voltammogram of HMPER in acetonitrile. The reference electrode is Ag/AgCl. Tetrabutyl ammoniumhexfluorophosphate [(TBA)<sup>+</sup> (PF<sub>6</sub>)<sup>-</sup>] is used as supporting electrolyte and the scan rate is 100 mV/s. Two electron transfer processes of PDIs are known in literature [13] and two electron transfer reduction potentials of HMPER are seen in Fig. 3. The first reduction potential obtained was used for the calculation of LUMO energy level (Ferrocene is the reference).

Table 1

Absorption, fluorescence spectroscopy data of the HMPER: absorption wavelengths ( $\lambda$ /nm), molar extinction coefficients ( $\epsilon$ /mol<sup>-1</sup> cm<sup>-1</sup>), excitation wavelengths ( $\lambda_{\text{ext}}$ /nm), fluorescence quantum yields ( $\Phi_f$ ), radiative lifetimes ( $\tau_o$ /ns), fluorescence life times ( $\tau_f$ /ns, experimental values are given in brackets), fluorescence rate constants ( $k_f \times 10^8$  s<sup>-1</sup>)

Solvent	$\lambda_1$	$\epsilon_1$	$\lambda_2$ $\lambda_{\text{ext}}$	$\epsilon_2$	$\lambda_3$	$\epsilon_3$	$\Phi_f$	$\tau_o$	$\tau_f$	$k_f$
AcCN	524	97 200	489	67 638	457	24 800	0.96	4.48	4.30 (4.5)	2.3
TiO <sub>2</sub>	541	112 009	489	154096	480	145 855	0.76	4.3	3.3 (3.3)	3.0

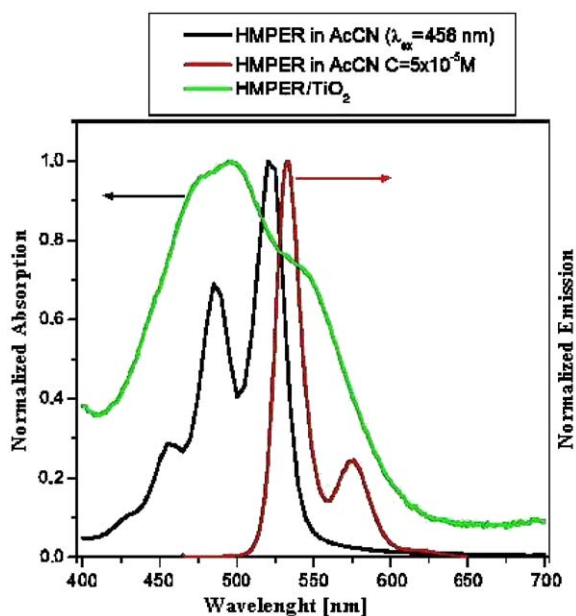


Fig. 2. Absorption spectrum of HMPER in acetonitrile (AcCN) (black line), fluorescence emission spectrum of HMPER in AcCN (red line) and absorption spectrum of HMPER adsorbed onto nc-TiO<sub>2</sub> film (green line).

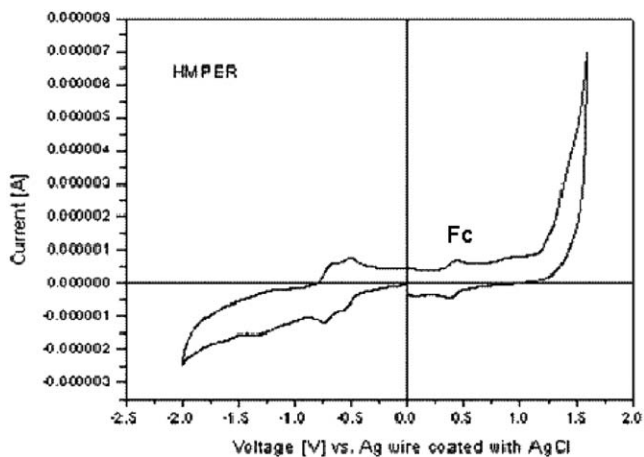


Fig. 3. Cyclic voltammogram of HMPER in acetonitrile. The reference electrode is Ag/AgCl. Tetrabutyl ammoniumhexfluorophosphate [(TBA)<sup>+</sup>(PF<sub>6</sub>)<sup>-</sup>] was used as supporting electrolyte and the scan rate is 100 mV/s. Fc denotes the ferrocene reference.

The oxidation potential of HMPER could not be obtained, since perylene derivatives had high positive oxidation potentials [18], (the oxidative electrochemical data of commercially available N,N'-di(2,5-ditert-butylphenyl)-3,4,9,10-perylene-

carboximide in  $\text{CH}_2\text{Cl}_2$  is reported as +1.66 V vs. SCE [19]) and the electrolyte,  $(\text{TBA})^+(\text{PF}_6)^-$ , used was not working beyond +1.55 (Fig. 3). For Ru 535 TBA LUMO energy level is  $-1$  V vs. SCE (3.74 eV vs. vacuum) and HOMO energy level is 0.85 V vs. SCE (5.59 eV vs. vacuum) [2].

Fig. 4 shows an energy level diagram of ITO/TiO<sub>2</sub>/PDI/P3OT/LiF/Al and ITO/TiO<sub>2</sub>/PDI/P3HT/LiF/Al devices. In this configuration short-circuit conditions require the injection of electrons from the excited state of TiO<sub>2</sub> and transfer of the hole to conjugated polymer, P3OT or P3HT and then subsequently to the metal back contact electrode (Al, Ag, Au). The energy levels are as follows: work function of ITO ( $\Phi_{\text{ITO}} \sim 4.7$  eV), conduction band edge of TiO<sub>2</sub> ( $E_{\text{CB}} \sim 4$  eV), excited and ground state energy levels of HMPER (3.7 and  $\sim 6$  eV), LUMO and HOMO energy levels of P3OT (3 and  $\sim 5$  eV), and the work function of Al ( $\Phi_{\text{Al}} \sim 4.3$  eV) and Au ( $\Phi_{\text{Au}} \sim 5.1$  eV) (Table 2).

Therefore, it appears that the charge transfer process is energetically favorable. The open circuit voltage ( $V_{\text{oc}}$ ) is determined by the difference between the quasi-Fermi level of the TiO<sub>2</sub> under illumination ( $\sim 4.2$  eV) and the HOMO level of the conjugated polymers [10].

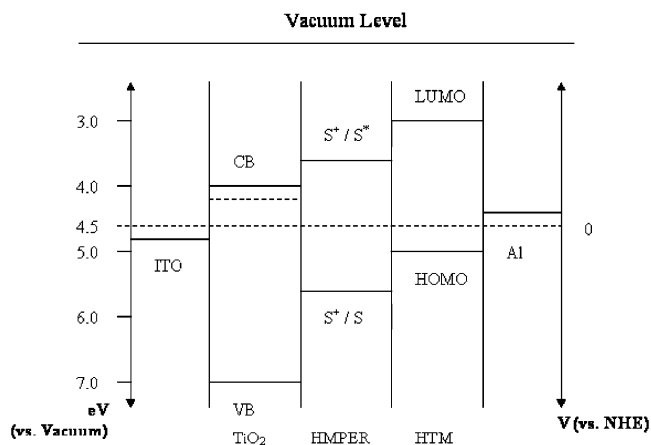


Fig. 4. Schematic potential energy level diagram ITO/TiO<sub>2</sub>/PDI/P3OT/Al and ITO/TiO<sub>2</sub>/PDI/P3HT/Al devices.  $E_{\text{CB}}(\text{TiO}_2) \sim 4$  eV,  $E_{\text{LUMO}}(\text{HMPER}) = 3.7$  eV,  $E_{\text{HOMO}}(\text{HMPER}) = 6$  eV,  $E_{\text{LUMO}}(\text{P3HT or P3OT}) = 3$  eV,  $E_{\text{HOMO}}(\text{P3HT or P3OT}) = 5$  eV,  $\Phi_{\text{Al}} = 4.3$  eV,  $\Phi_{\text{Au}} = 5.1$  eV.

Table 2  
CV data of HMPER in  $\text{CH}_3\text{CN}$  ( $E_{\text{red } 1-2}$ /V vs. Ag/AgCl)

Comp.	$E_{\text{red } 1-2}$ (V)	$E_{\text{Fc}}$ (V)	$E_{1/2}$ (V)	LUMO (eV)
HMPER	-0.70 -0.50	0.40	-1.1	-3.7

### 3.2. Photovoltaic performance of the DSSC based on HMPER and conjugated polythiophenes P3OT and P3HT:

Figs. 5 and 6 show the current–voltage characteristics obtained with solar cells produced in a sandwich geometry between two electrodes with different work functions.

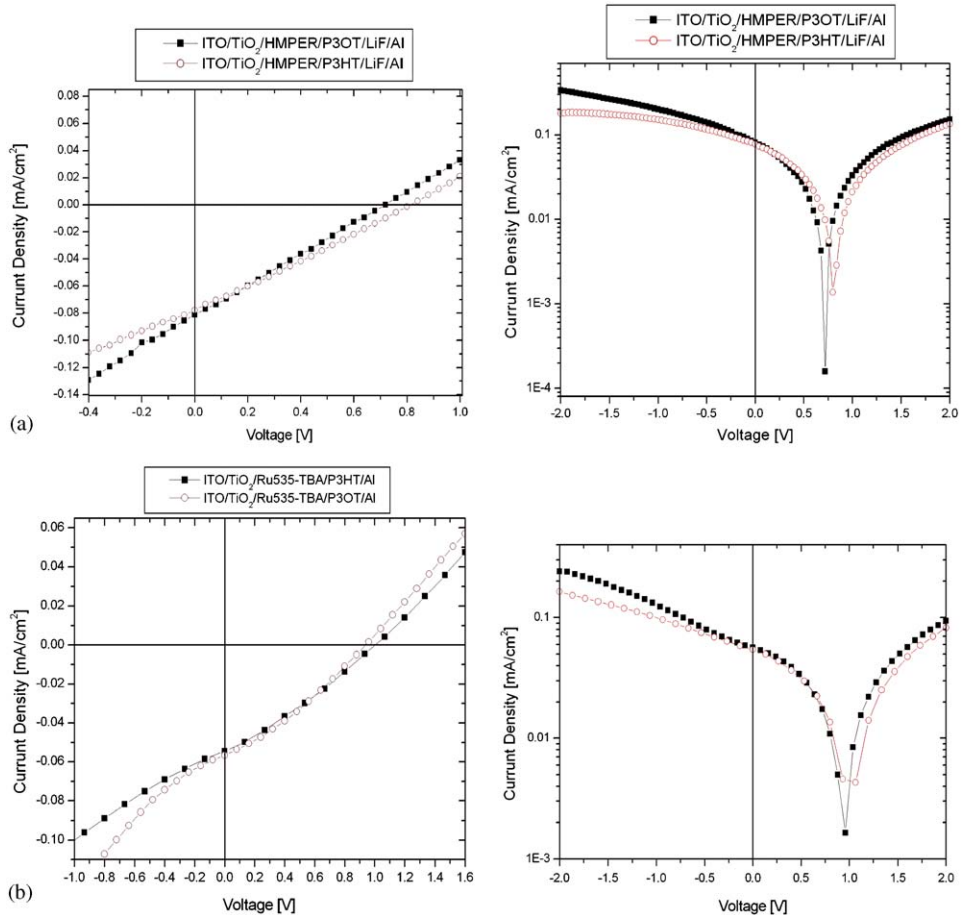


Fig. 5. I–V characteristics comparison of (a) ITO/TiO<sub>2</sub>/HMPER/P3OT/Al :  $V_{oc} = 0.82$  V,  $I_{sc} = 0.0759$  mA/cm<sup>2</sup>,  $V_{mpp} = 0.44$  V,  $I_{mpp} = 0.038$  mA/cm<sup>2</sup>, FF = 0.26,  $\eta$  (%) = 0.020 and ITO/TiO<sub>2</sub>/HMPER/P3HT/Al:  $V_{oc} = 0.7$  V,  $I_{sc} = 0.0815$  mA/cm<sup>2</sup>,  $V_{mpp} = 0.36$  V,  $I_{mpp} = 0.040$  mA/cm<sup>2</sup>, FF = 0.26,  $\eta$  (%) = 0.020. (b) ITO/TiO<sub>2</sub>/Ru535TBA/P3HT/Al:  $V_{oc} = 0.93$  V,  $I_{sc} = 0.054$  mA/cm<sup>2</sup>,  $V_{mpp} = 0.53$  V,  $I_{mpp} = 0.03$  mA/cm<sup>2</sup>, FF = 0.31,  $\eta$  (%) = 0.019 and ITO/TiO<sub>2</sub>/Ru535TBA/P3OT/Al:  $V_{oc} = 0.88$  V,  $I_{sc} = 0.056$  mA/cm<sup>2</sup>,  $V_{mpp} = 0.48$  V,  $I_{mpp} = 0.039$  mA/cm<sup>2</sup>, FF = 0.37,  $\eta$  (%) = 0.019 under illumination with 80 mW/cm<sup>2</sup> light sources and AM 1.5 conditions.

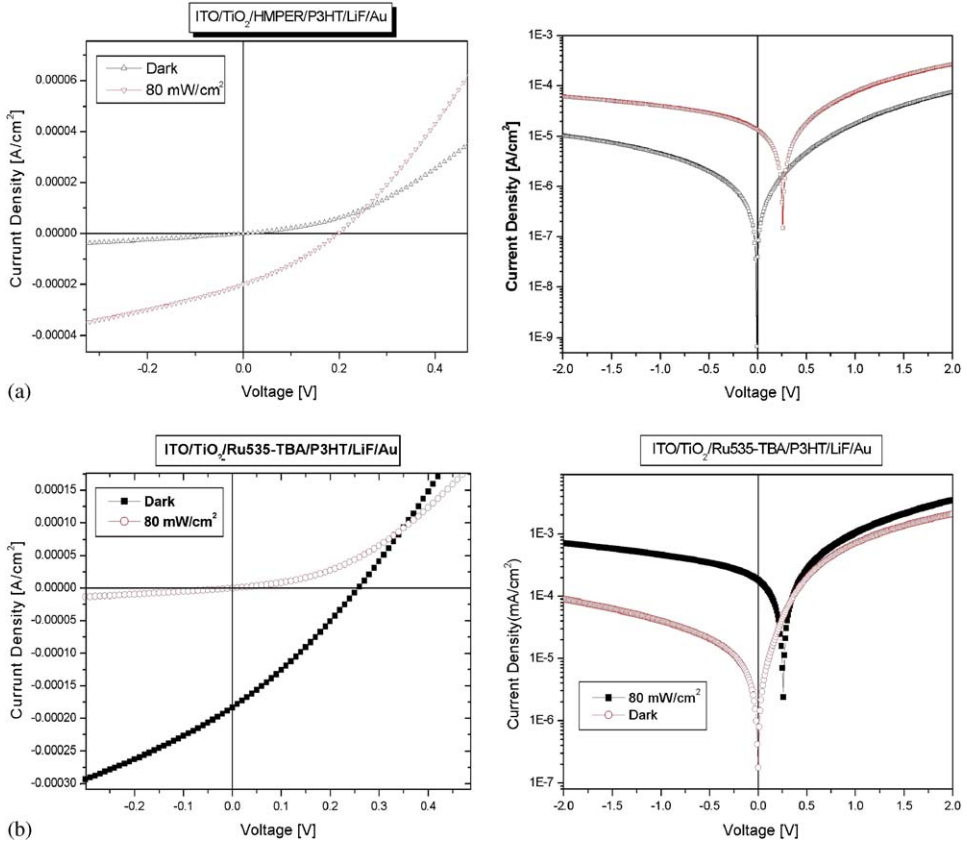


Fig. 6. I–V characteristics comparison of (a) ITO/TiO<sub>2</sub>/PDI/P3HT/LiF/Au:  $V_{oc} = 0.200$  V,  $I_{sc} = 0.0199$  mA/cm<sup>2</sup>, FF = 0.30,  $\eta$  (%) = 0.0015 and (b) ITO/TiO<sub>2</sub>/ Ru 535 TBA/ P3HT/LiF/Au:  $V_{oc} = 0.261$  V,  $I_{sc} = 0.182$  mA/cm<sup>2</sup>,  $V_{mpp} = 0.140$  V,  $I_{mpp} = 0.098$  mA/cm<sup>2</sup>, FF = 0.29,  $\eta$  (%) = 0.017.

The overall energy conversion efficiency under lumination,  $\eta$ , has been calculated using the equation.

$$\eta = (V_{oc} I_{sc} FF / P_{light}),$$

where  $V_{oc}$  (V) is open-circuit voltage,  $I_{sc}$  (mA/cm<sup>2</sup>) is short-circuit current, FF is fill factor and  $P_{light}$  (mW/cm<sup>2</sup>) is incident light power. FF was calculated by the formula given below,

$$FF = V_{max} I_{max} / V_{oc} I_{sc},$$

where  $V_{max}$  and  $I_{max}$  are voltage and current at the point of maximum power output of cell.

The measured short-circuit current and open-circuit voltage for the device with ITO/TiO<sub>2</sub> /PDI/P3OT/LiF/Al configuration under illumination with 80 mW cm<sup>-2</sup> light intensity are  $I_{sc} = 80 \mu\text{A cm}^{-2}$  and  $V_{oc} = 0.7 \text{ V}$ . The FF is quite low, being 0.25.

For the device with ITO/TiO<sub>2</sub>/PDI/P3HT/LiF/Al configuration,  $I_{sc} = 75 \mu\text{A cm}^{-2}$  and  $V_{oc} = 0.8 \text{ V}$ . The fill factor for this device is also fairly low, FF = 0.26. The overall energy conversion efficiency ( $\eta$ ) for both P3OT and P3HT cells is 0.02% under illumination with 80 mW/cm<sup>2</sup> light intensity under AM 1.5 conditions.

#### 4. Conclusion

N, N'-bis-2-(1-hydroxy-4-methylpentyl)-3,4,9,10-perylene bis (dicarboximide) (HMPER) sensitized nanocrystalline TiO<sub>2</sub> solar cells with P3HT and P3OT hole conductors were investigated. Under illumination by 80 mW/cm<sup>2</sup> light intensity, the device with ITO/TiO<sub>2</sub> /HMPER/P3OT/LiF/Al and ITO/TiO<sub>2</sub> /PDI/P3HT/LiF/Al configurations give  $\sim 80 \mu\text{A cm}^{-2}$  short-circuit current and  $\sim 0.7 \text{ V}$  open-circuit voltage. The FF is  $\sim 0.26$ . The overall energy conversion efficiency ( $\eta$ ) is  $\sim 0.02\%$ . These values are quite low in comparison with DSSCs with liquid electrolyte. This may arise basically from, (i) a low contact area of hole conductor polymer and electron conductor nanocrystalline TiO<sub>2</sub> particles and/or, (ii) HMPER may be a poor sensitizer. Preliminary results of wet cell experiments give  $\sim 0.03\%$  of conversion efficiency. Further optimization of morphologies of layers and investigation of different perylene derivative dyes with increased electron donor properties in both wet and solid state cells are going to be performed in future studies.

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