Synthesis and Spectroscopic Properties of a Novel Perylenediimide Derivative

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Summary: A novel symmetric 3,4,9,10-perylenetetracarboxylic acid derivative (PDI1) dye based on thiophene donor group was synthesized and characterized by FT-IR and ^{1}H NMR. Cyclic Voltammetry analysis is performed to determine the energy levels of the perylene derivative. Optical characteristics were determined by visible absorption and fluorescence emission spectra. Spectral behavior and fluorescence quantum yield of PDI1 have been measured in different solvents. The dye exhibits high fluorescence quantum yield (Φ_F: 0.94-0.99). But the quantum yield PDI1 is very low in the *n*-butanol solution (Φ_F: 0.12). The photophysical properties have important implications for use in a variety of electroactive and photovoltaic applications. A photovoltaic device was fabricated with PDI1 as transporting material. The conversion efficiency for DSSC sensitized by PDI1 is 0.0065%. PDI1 exhibits electrochromic behavior by switching between neutral (red) and oxidized (blue) states. Electron transfer capacity of PDI to the TiO_2 was investigated by incorporation of dye as sensitizer in dye sensitized solar cell (DSSC). **Soluble dye molecules are very important to prepare dye sensitized solar cell. Solubility was increased with thiophene group.**

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Introduction

Perylene diimides (PDIs) are optoelectronic pigments **which are** highly promising materials for applications in organic solar cells, photovoltaic devices and for dye lasers as molecular semiconductor. PDI derivatives have high fluorescence quantum yields of photoluminescence, strong absorption and emission, good semi-conductivity, high molar absorptivity, high photochemical and thermal stability [1,2], which makes them ideal for many organic optoelectronic or electronic devices such as solar cells and light emitting diodes [3,4].

PDI molecules are very important in photoelectronic applications. PDIs are described as *n*-type semiconductors in which the major charge carriers are in their conduction band while most organic conducting materials can be described as *p*-type semiconductors. PDIs show two reversible electrochemical reductions. It forms stable anions and di-anions. This property of PDIs makes them attractive materials in chemiluminescence electrochromic devices [5].

In the present work, our goal was to synthesis a novel PDI molecule which may be used in photoelectronic applications as given in scheme 1. We have synthesized the PDI1 molecule with a thiophene donor group in order to increase its solubility. Furthermore, **the** thiophene group **allows for** band gap level **engineering**. Its UV/Vis absorption and steady state emission were investigated in detail by using a series of solvents which differ in polarity.

Fluorescence decay times of the synthesized compounds were calculated from the time resolved experiments. The optical, electrochemical properties and solar cell applications of perylene diimide molecules were investigated.

Scheme 1

Results and Discussion

Absorption and Emission Spectra

Normalized UV-Vis absorption spectra of the PDI1 dye in chloroform and acetonitrile solutions exhibit almost the same absorption properties of the perylene diimide. Absorption data are shown in Fig. 1 and also summarized in Table-1. The absorption and fluorescence spectra of PDI1 show consistent mirror-image behavior. Generally perylene dye display an intense absorption band in the visible spectrum located between 400-600 nm corresponding to a π- π^* singlet transition. PDI1 dye shows characteristic absorption peaks for the perylene diimide at 458, 490, and a greater shoulder peak at 526 nm, which are denoted to theirs (0,2), (0,1), and (0,0) transitions, respectively. Also, the emission spectra of the PDI dyes resemble each other. It is shown that no clear substituent effect of **the** thiophene moiety on perylene diimide emission spectra is observed, as given in Fig. 1. But the solubility of molecule increased.

Fig. 1

Table-1

Optical absorption and emission properties of PDI1 molecule in solvents having different polarities are summarized in Table 1. Fig. 1 shows the absorption and emission spectra of the dye in the most polar and the least polar solvents. It is understood that the higher the polarity of the solvents, shorter the wavelengths of absorption and emission maxima of the dye. It is seen that solute molecules have an excited state less polar than the ground state. Increase in solvent polarity will stabilize the excited state less than the ground state [11]. Therefore, a blue shift is observed for the dyes. In addition, a small increase in emission maximum of the PDI1 dye was visible in *n*-butanol solution at a wavelength of 537 nm. This different behavior is attributed to the hydrogen bonding ability of the non-bonding electrons of the sulfur atom in the thiophene ring of the PDI1 dye in the excited states.

Quantum Yield

Fluorescence quantum yields of PDI1 are measured with reference to the absorption and fluorescence emission spectra of perylene 3,4,9,10- tetracarboxylic-bis-*N,N*-dodecyl diimide (N-DODOPER)   ($Q_f = 1$ in chloroform). The calculated relative Q_f values are corrected for the index of refraction differences generated

from the solvent. All the excitations are carried out at the wavelength that is abbreviated as about $\lambda2$. Quantum yields were determined according to the equation

$Q_x = Q_{St}(A_{St} \cdot I_x \cdot n^2_x / A_x \cdot I_{St} \cdot n^2_{St})$ [12]

where Q_{St} is the quantum yield of the respective standard;

A_{St} and A_x are absorbances at the excitation wavelength of the standard (St) and the N-DODEPER (x), respectively; I_{St} and I_x are the integrated area of the corrected emission spectra of the standard (St) and the N-DODEPER (x), respectively; and n_{St} and n_x are the refractive indices of the solvent of the standard (St) and the N-DODEPER (x), respectively.

Fluorescence quantum yields and photophysical properties of the studied dye are given in Table 2. Φ_F values of the dye are high in the studied solvents, except for the n-butanol solution. In this solvent the Φ_F values were calculated to be about 0.12 for the PDI1. No clear evidence is obtained about the formation of different excited state species in n-butanol solution. The excitation spectra of the dye in the studied solvents at the emission wavelength of 535-540 nm are identical to the S_0-S_1 absorption band of the dye. One of these spectra studied in dichloromethane solution is displayed in Fig. 2 for the PDI1 dye. Also, time resolved measurements indicate that the dye give only two decay components. One of these decays corresponds to the solvent relaxation process, and the other is referred to the excited state form of the dye. In n-butanol solutions, strong hydrogen bonding ability of the solvent molecules with the non-bonding electrons of the heteroatom of thiophene moiety and carbonyl groups of the dyes accelerates the aggregation processes. Perylene rings come close to each other because of the inter- and intra-molecular hydrogen bonded forms of the dyes. As a result, emission intensities of PDI1 dye dramatically decrease in n-butanol solutions. Also, high values of non-radiative rate constants (k^{nr}) for the dyes in n-butanol solution support the aggregation tendency of the dye molecules.

Fig. 2

Table-2

We used approximately 10^{-5}M concentration of the PDI1 dye while measuring the emission and absorption spectra and calculating the photophysical properties in solution phase. The radiative lifetimes, τo, in Table 2, were calculated by the formula: $\tau o = 3.5 \times 10^8 / v^2_{max} \, \varepsilon_{max}. \, \Delta v_{1/2}$, where v_{max} is the wavenumber in cm^{-1}, ε_{max} is the molar extinction coefficient at the selected absorption wavelength, and $\Delta v_{1/2}$ is the half width of the

selected absorption in wavenumber units of cm^{-1}. Fluorescence lifetimes are estimated as $\tau_f = \tau_o \cdot Q_f$ and the rates of fluorescence as $k_f = 1/\tau_o$. τf values[14].

CV measurements and Spectroelectrochemistry

Fig. 3 shows the cyclic voltammograms at a glassy carbon electrode of PDI1 dye. HOMO and LUMO levels were calculated [15]. A reversible reduction wave showing a two electron process was observed with typical double reduction one electron process at -0.48 and -0.74 V for PDI1 dye. The two reduction peaks correspond to the mono and dianion forms of PDI dyes [16]. The cyclic voltammogram data of PDI1 is given Table-3. Cyclic Voltammetry (CV) was used to obtain information about the energetic for formation of the species radical anions, radical cation and their stability. Perylene diimide molecules accept two electrons due to the carbonyl groups and produce an anion radical and dianion forms for PDI in negative region of cyclic voltammetry. The mechanism of anion radical and dianion formation is presented in Scheme 2 [17].

Fig. 3

Table-3

Scheme 2

One reversible oxidation wave, indicating the stable radical cation, was observed for PDI dyes. Oxidation wave of PDI1 dye shifts to the higher oxidation region because of the electron donating property of thiophene moiety attached to the phenyl and perylene ring.

The cyclic voltammogram of PDI1 is given Fig. 4. PDI1 show reversible reduction and irreversible oxidation. Reversible reduction wave showing electron process was observed in the -0.74 V and -0.48 V. The anodic peak potential of PDI1 was located at 1.27 V. It is important to get information about HOMO and LUMO energy levels dye for solar cell applications. The measured redox potentials and energies of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbial (LUMO) of PDI 1 are listed in Table-3. In order to calculate the LUMO energy level of PDI1 with respect to the vacuum level, the redox data are standardized to the ferrocene/ferricenium couple which has a calculated absolute energy of -4.8 eV. Taking the reduction onsets into account, the LUMO energy levels have been calculated and listed in Table 3. The HOMO energy level of PDI1 containing thiophene ring is calculated to be about -5.62 eV. The corresponding LUMO

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energy level is found to be –3.87 eV with the formula $E_{HOMO} = E_{LUMO} - E_{gap}$. The optical band gap values (E_g) was calculated as 2.01 eV.

Fig. 4

Spectroelectrochemistry of the compounds PDI1 was studied to determine the change of the color of the said compounds between reduced and neutral state with applied voltage. nc-TiO$_2$ / FTO / glass was chosen as an electrode and the thickness of TiO$_2$ layer is around 6 μm. TiO$_2$ is a *n*-type semiconductor and nanoporous TiO$_2$ electrode is a good adsorbent for perylene diimides [18-19]. A color change from red to blue and from blue to violet is observed when the potential decreases from 0 to -1.5 V. The blue color appears at the first reduction potential which corresponds to the monoanion. The color change from blue to violet (dianion) appears down to -1.1V. Figure 4 shows the absorption spectra PDI/TiO$_2$ films with respect to the applied voltage conditions. The peak at 567 nm disappears and peak at 700 nm starts to appear with applied voltage. The peak at 700 nm is a characteristic peak of the monoanion. The formation of dianion wasn't shown in the Fig. 4 because the degradation of PDI starts by the formation of dianion. The response time and stability of the change of the color between red (neutral) and blue (monoanion) is fast and stable.

HOMO-LUMO energy densities of PDI1 dye are calculated at the ZINDO/S (Single Point/CI) using Hyperchem Package Version 8.0 computational software. The geometry optimization of the compound in the ground state is realized with the MM+ force field function. Fig. 5 shows the optimized structure and HOMO-LUMO orbital separation of PDI1 dye. HOMO is surrounded totally on the thiophene moiety, while LUMO is surrounded totally on the perylene core. Also, there is a twist angle between the thiophene moiety and perylene ring. These LUMO orbitals show that the electron density is predominantly distributed in the π bonds of the core region. In photovoltaic process, possible charge transfer process from dye to the TiO$_2$ surface occurs at the perylene core region when it is photo-excited. Similar observations with perylene core and HOMO-LUMO orbital partitioning are given in the literature [20].

Fig. 5

Photovoltaic Performance

Fig. 6 and Table-4 show the I-V graphs and photovoltaic performances of DSSCs sensitized by PDI1. The conversion efficiency for DSSC sensitized by PDI1 is 0.0065%. The results show that PDI 1 is not suitable as a sensitizer for TiO$_2$ based DSSC because of low energy conversion efficiency. From the previous studies with

PDIs, it is known that PDIs were adsorbed onto TiO$_2$ surface via four carboxyl groups and this kind of adsorption allows to other PDI molecules to stack on the adsorbed molecule and forms multi layer aggregates [19]. Fig. 7 shows schematic energy diagram for a DSSC based on PDI nanocrystalline TiO$_2$ electrode and I$^-$/ I^{3-} redox couple. Aggregates increase the charge recombination and lower the charge injection to the TiO$_2$ conduction band. On the other hand, the LUMO level of the PDIs is very close to the conduction band of TiO$_2$. The LUMO level of PDI1 is at 3 .87 eV. The thiophene group is known as a strong electron donor which increases the LUMO level and the donor property of the molecule.

Fig. 6

Fig. 7

Table-4

Experimental

Perylene-3,4:9,10-tetracarboxylic bisanhydride was purchased from Merck. 2-(3-thienyl)ethanol being the starting material, triphenylphosphine dibromide, 3-aminophenylboronic acid hemisulfate were purchased from Aldrich company. Chloroform, tetrahydrofuran, toluene were received from Merck. Imidazole was received from Fluka. However, all the solvents (chloroform, dichloromethane, n-butanol, acetonitrile) used in spectroscopic and fluorimetric studies were of spectrophotometric grade. All the other chemicals (hydrochloric acid, sodium carbonate) were purchased from domestic chemical suppliers.

^{1}H NMR spectra was measured on a 500 MHz Varian Inova NMR. The FT-IR spectra were determined on a Perkin-Elmer model Spectrum BX spectrophotometer by dispersing samples in KBr disks. UV-Vis spectra were recorded by Analytic Jena Speedcord S-600 diod-array spectrophotometer and emission spectra measurements were taken on a PTI QM1 fluorescence spectrophotometer.

Fluorescence quantum yields were determined with respect to perylene-3,4,9,10-tetracarboxylic-bis-N,N′-dodecyldiimide (N-DODEPER) (Φ_F = 1.0 in chloroform), which was synthesized before, at an excitation wavelength of 485 nm [6]. The fluorescence decay times were taken on a sub-nanosecond pulsed LEDs. The system consists of a pulsed laser driver and interchangeable LED heads. LED heads with center wavelengths of 460 nm are available and can be provided with optional spectral band pass filters to excite samples with a narrow spectral range. The fluorescence decay histograms were recorded in 2893 channels and the fluorescence decays were analyzed by using a Marquardt Algorithm [7] with a multiexponential fluorescence decay fit (FluoFit)

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software. The quality of the fits has been judged by the fitting parameters such as $\chi^2 < 1.2$ as well as by the visual inspection of the residuals and autocorrelation function [8]. The instrument response function (IRF) has been measured using a ludox scattering solution. All the experiments were carried out at 25 $^\circ$C, and all the compounds were analyzed at an optical density below 0.1 to prevent self quenching.

Synthesis

*Synthesis of 3-(2-Bromoethyl)thiophene **(1)**:*

The synthesis of this initial compound was performed according to a published procedure [9]. Triphenylphosphine dibromide (20.05 g, 48.6 mmoL) was added to solution of 2-(3-thienyl)ethanol (4.60 g, 35.9 mmoL) in dry acetonitrile (75 mL), with the temperature being kept below 8 $^\circ$C. After stirring at room temperature for 20 h, the reaction mixture was filtered and concentrated. The residue was purified by column chromatography (silica gel, *n*-hexane) yielding a colorless oil. (4.64 g, 68%). ^{1}H NMR (CDCl$_3$): (C$_6$H$_7$SBr) δ 7.27 (m, 1H, Th-**H**), 7.01 (m, 2H, Th-**H**), 3.55 (t, 2H, **-CH$_2$**), 3.18 (t, 2H, **-CH$_2$**) ppm.

*Synthesis of 3-[2-(3-thienyl)ethyl]aniline **(2)**:*

A similar synthetic procedure given in the literature was followed for the synthesis of 3-(2-Bromoethyl)thiophene [10]. A 100-mL three-necked round-bottom flask equipped a nitrogen inlet–outlet was charged with 1 M Na$_2$CO$_3$ (10 mL) and THF (15 mL). The mixture of the solvents had previously been bubbled with nitrogen over a period of 1 hour and refluxed under nitrogen for 4 hours. A 20 mL three-necked round-bottom flask was charged under an inert atmosphere with 0.62 mmol of 3-(2-bromoethyl)thiophene (0.1191 g), 3 mmol (0.579 g) of 3-aminophenylboronic acid hemisulfate, and 0.02 mmol (0.0276 g) of Pd(PPh$_3$)$_4$. The solvent mixture (12 mL) was introduced. The mixture was refluxed under nitrogen for 5 days. The mixture was cooled till room temperature and then extracted with chloroform. The organic phase was dried over the MgSO$_4$ was filtrated and the solvent was evaporated. Purification was performed by passing the product through a silica gel column using chloroform as eluent. (0.127 g, 23%). ^{1}H NMR (CDCl$_3$; δ, ppm): 7.60-6.95 (m, 4H, Ar-**H**), 6.7 (m, 3H, Th-**H**), 3.5 (t, 2H, **-CH$_2$**), 2.9 (t, 2H, **-CH$_2$**), 2.8 (s, 2H, **-NH$_2$**). C$_{12}$H$_{13}$NS.

Synthesis of N,N'-Di-[3-[2-(3-thienyl)ethyl]phenyl]perylene-3,4,9,10-bis(dicarboximide) **(PDI1)**:

Perylene-3,4:9,10- tetracarboxylic acid bisanhydride (0.49 mmol, 192 mg) 3-[2-(3-thienyl)ethyl]aniline (0.98 mmol, 200 mg) and imidazole (3.5 g) were heated at 140 °C for 4.5 hours under Ar atmosphere. Then 2N HCl (200 mL) was added to the reaction solution and the resulting mixture was stirred for 1 h at room temperature then extracted with chloroform (600 mL). The organic phase was evaporated under vacuum and the crude product was purified by column chromatography (silica gel; CH_2Cl_2-MeOH, 12:1). Yield: 60%. FT–IR (KBr cm^{-1}): 2928, 2841, 1702 and 1649 (imide group), 1587 (aromatic C=C), 1404, 1346 (C-N), 1250, 1173. ^{1}H NMR ($CDCl_3$; δ, ppm): 8.65 (dd, 8H, perylene-**H**), 7.8-7.42 (m, 8H, Ar-**H**), 7.3 (m, 6H, Th-**H**), 1.6 (t, 4H, -**CH₂**), 1.3 (t, 4H, -**CH₂**). $C_{48}H_{30}N_2O_4S_2$.

Synthesis of TiO₂ Nanoparticles and Electrode Preparation

TiO₂ nano-particles were synthesized by sol-gel method and grown to a size of the 20-25 nm by Ostwald ripening in autoclave. Titanium tetra isopropoxide $Ti(OPr^i)_4$ (58.6 g) was injected into glacial acetic acid (12 g). The solution was added drop wise into cool deionized water (290 mL) with vigorous stirring. Nitric acid (65% HNO_3, 5.4 mL) was added to the colloidal suspension to adjust the pH till 1-2. The sol was waited at 78 °C for 75 minutes in the oven. The volume of the resulting transparent colloidal sol was adjusted to 370 mL by adding water and transferred to the teflon baker equipped autoclave. The autoclave was placed in the oven at 235 °C for 12 hours for hydrothermal growth of the particles. Nitric acid (65% HNO_3, 2.4 mL) was added to the autoclaved suspension and then concentrated to 16.5% (w/w) TiO_2. The remaining water was exchanged with ethanol by centrifuging and 40% (w/w) TiO_2 paste was obtained. Ethyl cellulose (4.5%) in ethanol and anhydrous α-terpineol (79 g) were added and the paste was sonicated by ultrasonic horn at a power of 200W power for 10 minutes. The obtained homogeneous paste was placed in the rotary evaporator to remove all ethanol.

The TiO_2 paste was coated on transparent conductive oxide coated glass electrodes (SnO_2:F, TEC15, R_{sheet}: 15 ohm/) by doctor blade technique. Before coating with the TiO_2 paste, FTO electrodes were treated with 50 mM $TiCl_4$ for 30 min at 70 °C to have better contact with TiO_2 nano-particles. TiO_2 electrodes were first dried at room temperature and then sintered at 450 °C for 1 hour with 10 °C/min heating rate. After sintering, again $TiCl_4$ solution was applied on the TiO_2 film by Pasteur pipette and left under water vapor for 30 min at

room temperature to prevent the electrical contact between the nano-particles. Finally the TiO$_2$ electrodes were sintered again at 500 °C for 30 minutes with 10 °C/min heating rate.

Sensitization with Dye and DSSC Assembly

The sintered electrodes were allowed to cool down slowly. While the electrode temperature was around 100 °C, the TiO$_2$ electrodes were immersed for 3 hours in the dye solution containing 0.3 mM perylene diimide dye in acetonitrile:*tert*-butanol (1:1). Sensitized TiO$_2$ electrodes were rinsed with acetonitrile and kept in desiccators. The counter electrode was prepared by thermal reduction of hexachloroplatinic acid by platinum. 1% (v/v) solution in 2-propanol was used for platinization of the FTO coated electrode. Drop casted electrodes were annealed at 400 °C for 20 minutes.

The DSSC was prepared by placing the electrodes on top of each other in a sandwich geometry, with in the middle a 50 µm thick thermoplastic polymer frame Surlyn® 1702 (DuPont). The electrodes were sealed by heating around 100 °C and simultaneous pressing together slightly. Prepared electrolyte was filled into the cell via a pre-drilled small hole by using vacuum. The electrolyte consisted of 0.6 M *N*-methyl-*N*-butyl imidazolium iodide (BMII) + 0.1 M LiI +0.05M I$_2$ in 3methoxypropyonitrile. Finally the small hole was sealed with a piece of Surlyn and a cover glass. The active areas of the prepared solar cells were 1.0 cm^2.

Photovoltaic characteristicproperty of the DSSC was determined under dark and standard conditions by illumination of AM1.5 global radiation with 100 mW/cm^2 light intensity. I-V data collection was made by using Keithley 2400 Source-Meter and LabView data acquisition software.

The overall energy conversion efficiency, η, has been calculated using the equation, $\eta = P_{max} / P_{light} = (V_{mpp} \cdot I_{mpp}) / P_{light} = (V_{oc} \cdot I_{sc} \cdot FF) / P_{light}$, where V_{oc} (V) is the open circuit voltage, I_{sc} (mA/cm^2) is the short circuit current, FF is the fill factor, P_{max} (mW/cm^2) is the maximum power point, P_{light} (mW/cm^2) is the incident light power, V_{mpp} and I_{mpp} are the voltage and current at the point of maximum power output of the cell, respectively.

Electrochemistry and Spectroelectrochemistry Studies

The electrochemical properties of PDI 1 were studied by cyclic voltammetry (CV). These measurements were recorded using a CH 660B model potentiostate form CH Instruments in a three electrode cell consisting of

a platinum wire as counter electrode (CE), a glassy carbon electrode used as a working electrode (WE) and a Ag/AgCl electrode in 3M KCl (aq) used as a reference electrode (RE). Measurements were carried out in the 0.1 M TBAPF$_6$ as supporting electrolyte in acetonitrile. Sweep rate was kept constant at 0.1V/s. The oxidation potential of Ferrocene/ Ferrocenium couple at about +0.45V was used as an internal reference.

The data obtained from UV-Vis spectra and cyclic voltammetry were used for spectro-electrochemical measurements of PDI/TiO$_2$/FTO/glass transparent films. These measurements were carried out to consider absorption spectra of this polymer film under applied voltage. The spectro-electrochemical cell includes a quartz cuvette, an Ag wire (RE), Pt wire counter electrode (CE) and ITO/glass as transparent working electrode (WE). Measurements were carried out in the 0.1 M TBAPF$_6$ as supporting electrolyte in acetonitrile.

Conclusions

We have synthesized new perylene diimide molecule containing thiophene donor group as a side chain to fabricate the DSSC. Also, we have studied the optical and electrochemical properties of the dye to evaluate the photovoltaic performance. Steady-state spectroscopic measurements were carried out in solvents with increasing polarities.

Perylene diimides are excellent materials for solar photovoltaic applications as such *n*-type semiconductors. However, the aggregation tendency of PDI molecules decreases the photovoltaic performance by increasing the charge of recombination process. The conversion efficiency for DSSC sensitized by PDI1 is very low. However, the remarkable color change from red to blue and from blue to violet when the applied potential values were changed gives potential usage toward the preparation of electrochromic devices.

References

1.   Y. Feng and W. Feng, Opt.Mater., **30**, 876 (2008).

2.   Y. Chen, Y. Konga, Y. Wang , P. Mab, M. Baoa and X. Li, J. Coll. and Int. Sci. **330**, 421 (2009).

3.   B. Liang, Y. Zhang, Y. Wang, W. Xu, and X. Li, J. Mol. Struct., **917**, 133 (2009).

4.   Y. Zhang, Z. Xu, L.Cai, G. Lai, H. Qiu and Y. Shen, J..Photochem. and Photobiolog. A: Chem. **200**, 334 (2008)

5.   M. Kus, O. Hakli, C. Zafer, C. Varlikli, S. Demic, S. Ozcelik and S. Icli, Org. Elect., **9**, 757 (2008).

6.   S. Icli and H. Icil, Spect. Lett., **29**, 1253 (1996).

7.   JR. Knutson, JM. Beechem and L. Brand, Chem. Phys. Lett., **102**, 501 (1983).

8.   O.D.V.Connor and D. Phillips, Time-correlated Single Photon Counting, Academic Press, London

Solvent	ε^a	Compound	λ_1	λ_2	λ_3	$\lambda_{em(max)}$	$\Delta\lambda$

(1984).

9.   C. Della-Casa, P. Costa-Bizzari, M. Lanzi, L. Paganin, F. Bertinelli, R. Pizzoferrato, F. Sarcinelli and M. Casalboni, Synt. Met., **138**, 409 (2003).

10.   B. Kiskan, D. Colak, A.E. Muftuoglu, I. Cianga and Y. Yagci, Macromol. Rapid Commun., **26** , 819 (2005).

11.   P. Suppan, Chemistry and Light the Royal Society of Chemistry, London (1994).

12.   Tomeckova, V. Poskrobova, M., Stefanisinova, M. and Perjesi, P., Spectrochim. Acta A., **74**, 1442 (2009).

13.   JC.Scaino, CRC Handbook of Organic Photochemistry, Vol II. Florida, CRC Pres (1989).

14.   P. Suppan, Chemistry and Light the Royal Society of Chemistry London (1994).

15.   NJ. Turro, Molecular Photochemistry London, Benjamin (1965).

16.   J. Cremer, E. Mena-Osteritz, NG. Pschierer, K. Müllen and P. B¨auerle, Org. Biomol. Chem,, **3**, 985 (2005)**.**

17.   G.Türkmen, S.Erten-Ela and S. Icli, Dyes Pigments **83**, 297 (2009).

18.   C. Karapire, C. Zafer, S.Icli, Synth. Met., **145**, 51 (2004).

19.   C. Zafer, C. Karapire, NS. Sariciftci and S. Icli, Solar Energy Mat. Solar Cells, **288**, 11 (2005) .

20.   C. Li, J.Schöneboom, Z.Liu, N.G.,Pschirer and P.Erk, A.Herrmann and K.Mullen, Chem.Eur.J., **15**, 878 (2009).

Chloroform	4.8	PDI1	458	490	526	535	50
Dichloromethane	8.9	PDI1	457	489	525	534	49
n-Butanol	17.8	PDI1	456	487	523	537	52
Acetonitrile	35.9	PDI1	454	484	518	530	45

Table-1: The visible absorptions, fluorescence emissions, and Stokes shifts ($\Delta\lambda$) data of PDI dye in solvents of different polarity (λ / nm, ε / l.mol^{-1}.cm^{-1}) (λ_{exc} = 485 nm)

[a] Dielectric constant, ε, is taken from reference [13].

Table-2: Fluorescence emission data, fluorescence quantum yields (Φ_F), fluorescence decay times (τ_f / ns), fluorescence lifetimes (τ_f / ns), radiative lifetimes (τ_0 / ns), fluorescence rate constants (k_f^r x 10^8 / s^{-1}), non-

radiative rate constants (k^{nr} x 10^8 / s^{-1}), and singlet energies (E_s / kcal.mol^{-1}) of PDI1 dye in solvents of different polarity (λ_{exc} = 485 nm)

Solvent	Compound	Φ_f	$\tau_{f(1)}$	$\tau_{f(2)}$	τ_f	τ_0	k_f^{r}	k^{nr}	E_s
Chloroform	PDI1	0.94	3.6	0.4	2.0	2.1	4.7	0.3	55.1
Dichloromethane	PDI1	0.75	3.8	0.4	2.1	2.8	3.6	1.2	55.2
n-Butanol	PDI1	0.12	0.3	3.9	2.1	17.3	0.6	4.2	55.4
Acetonitrile	PDI1	0.99	0.3	4.0	2.1	2.2	4.6	0.05	56.0

Table-3: Cyclic voltammetry data for PDI1 dye

Dye	E^0_{red2} (V)	E^0_{red1} (V)	E^0_{ox1} (V)	LUMO (eV)	HOMO (eV)	E_g (eV)
PDI1	-0.74	-0.48	1.27	-3.87	-5.62	2.01

Table-4: The photovoltaic performances of DSSCs sensitized with **PDI1** under illumination with 100 mW/cm^2

light intensity by AM 1.5 solar simulator.

	PDI1
V_{oc} [V]	0.140
I_{sc} [mA/cm^2]	0.102
V_{mpp} [V]	0. 90
I_{mpp} [mA/cm^2]	0.072
MPP [mW]	0.0065
FF	0.45
η [%]	0.0065
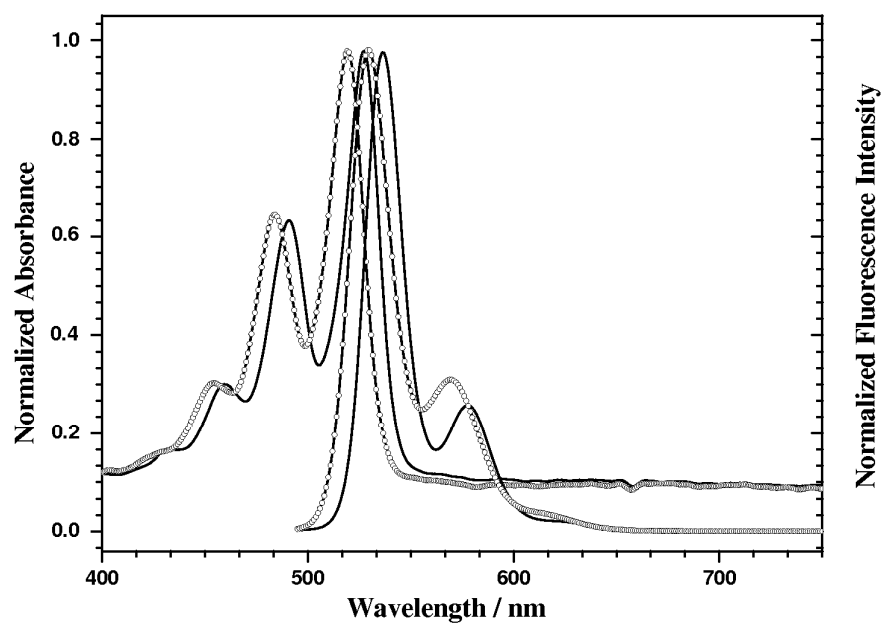
Fig. 1: Comparison of UV-vis absorption and normalized fluorescence spectra of **PDI1** dye in chloroform (straight line) and acetonitrile (ball symbol) solutions $(\lambda_{exc} = 485$ nm).
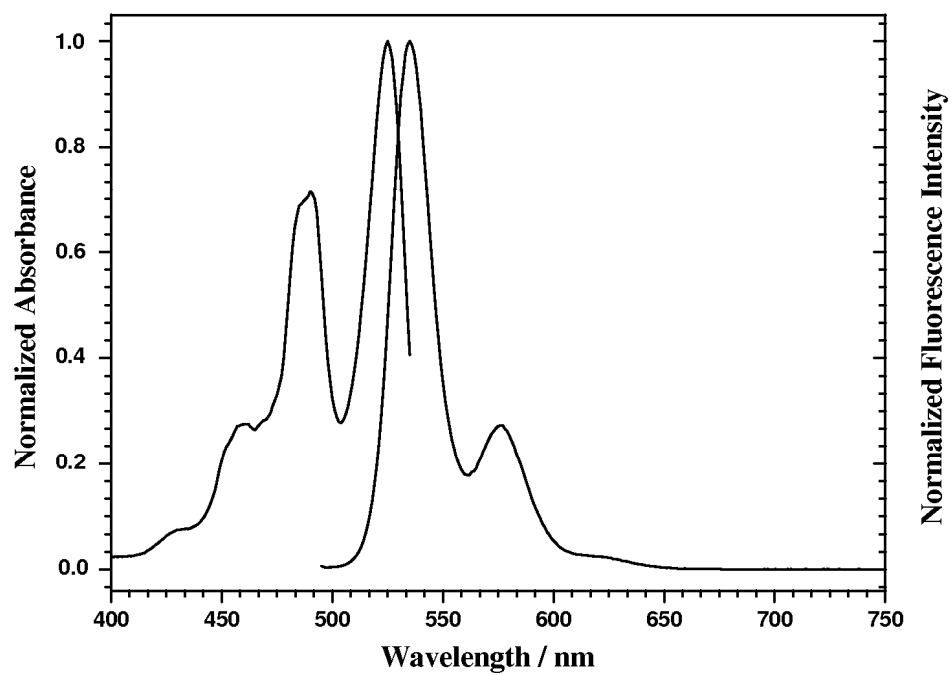
Fig. 2: Comparison of fluorescence and excitation spectra of **PDI1** in dichloromethane $(\lambda_{exc} = 485$ nm, $\lambda_{em} = 535$ nm).
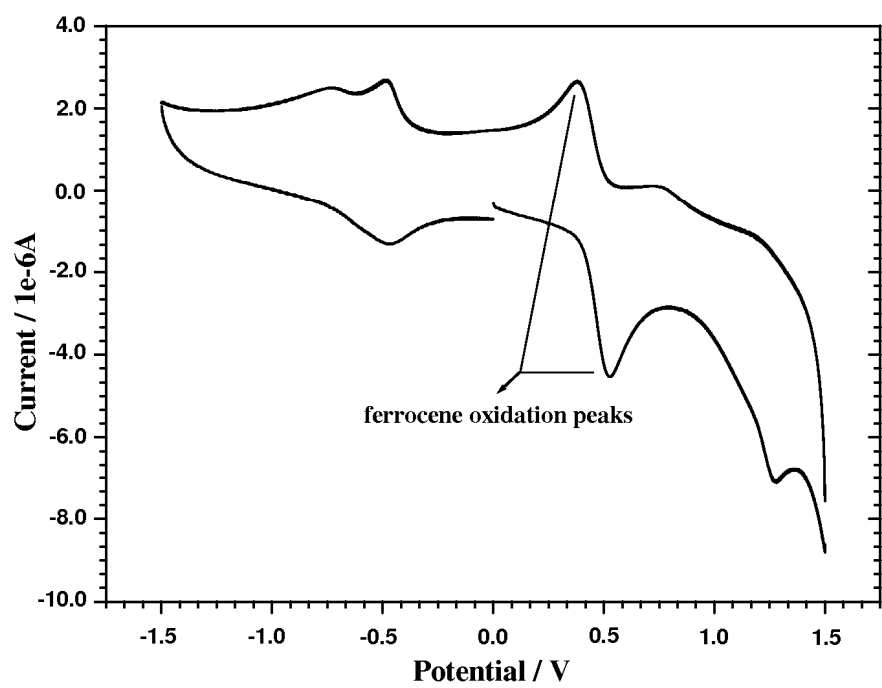
Fig. 3: Cyclic voltammogram at a glassy carbon electrode of PDI1 dye (1 mM) in MeCN containing 100 mM [TBA][PF6] and ferrocene as an internal electrode (E = 0.45 V).
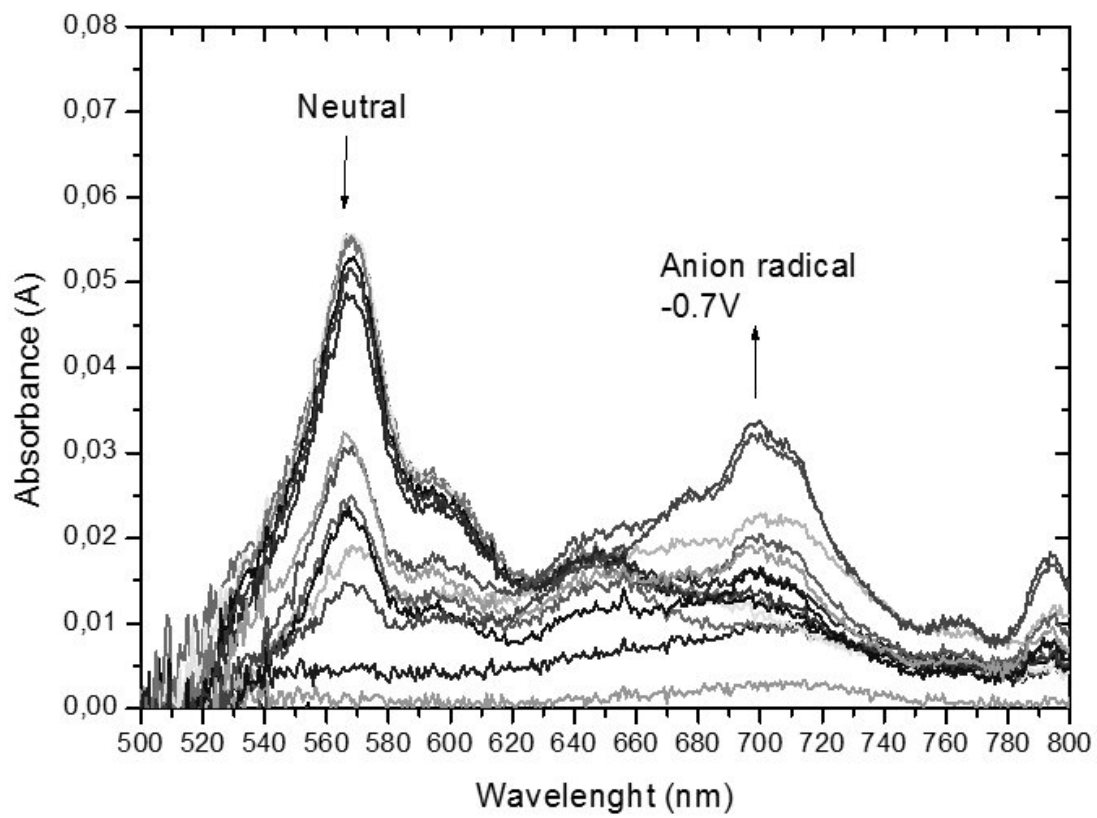
Fig. 4: UV-Vis absorption spectra change of PDI1 with applied voltage
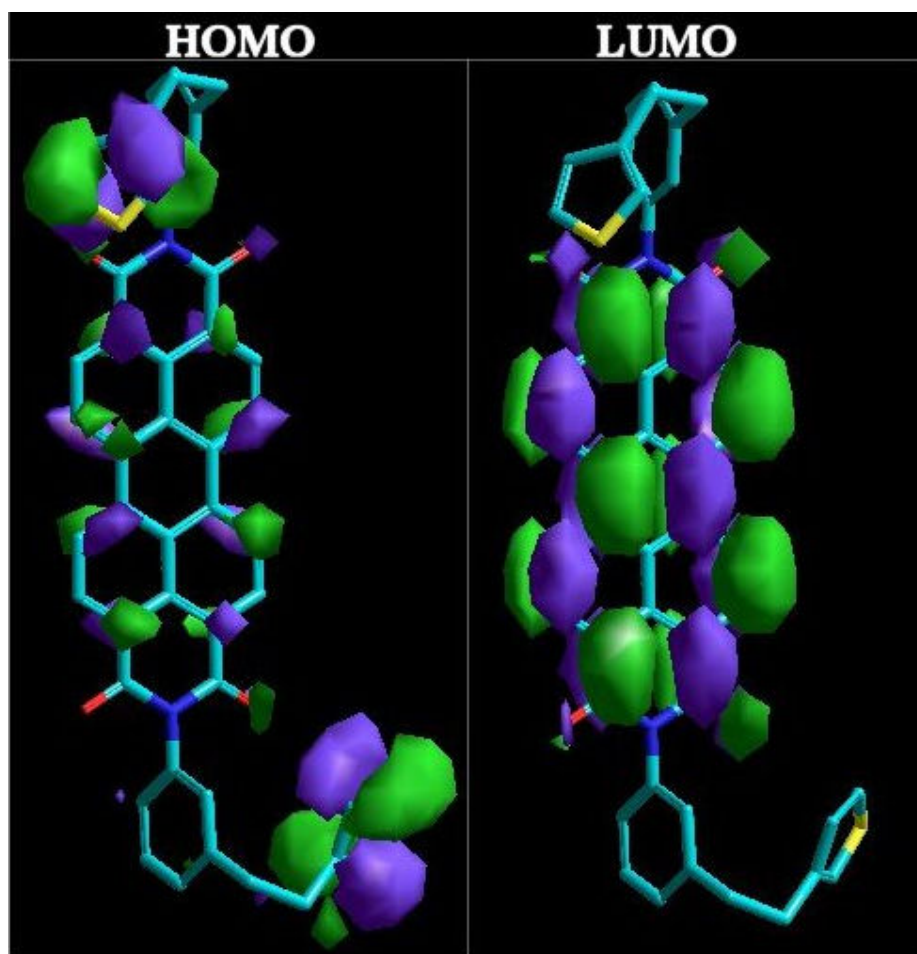
Fig. 5: Schematic representation of the HOMOs and LUMOs of PDI1
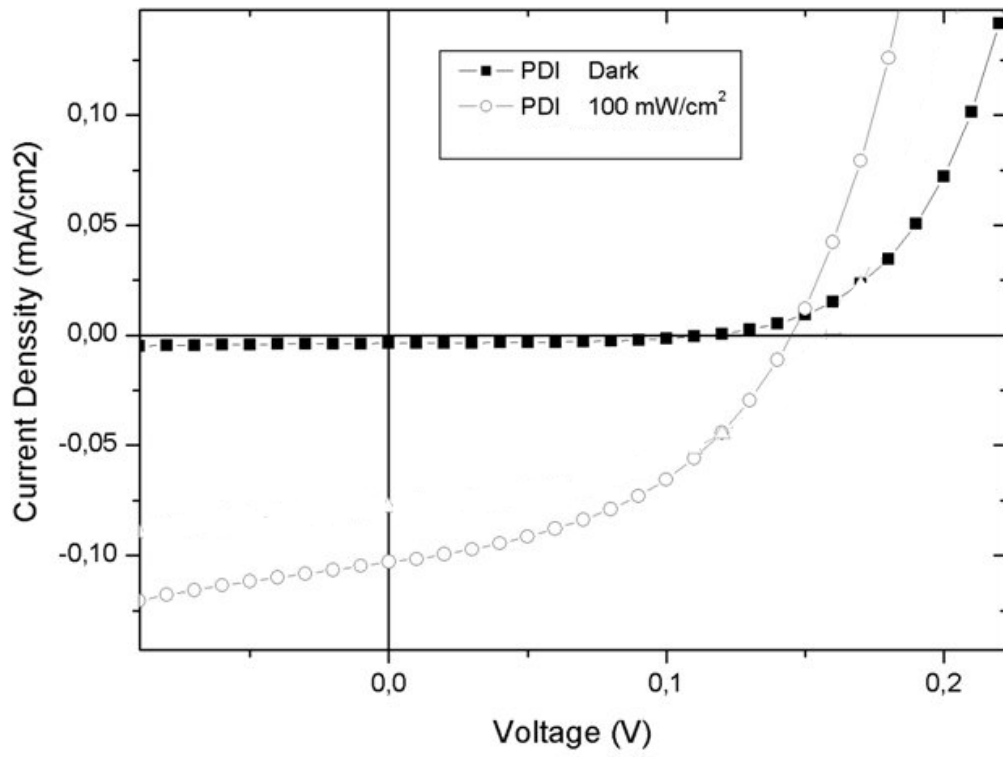
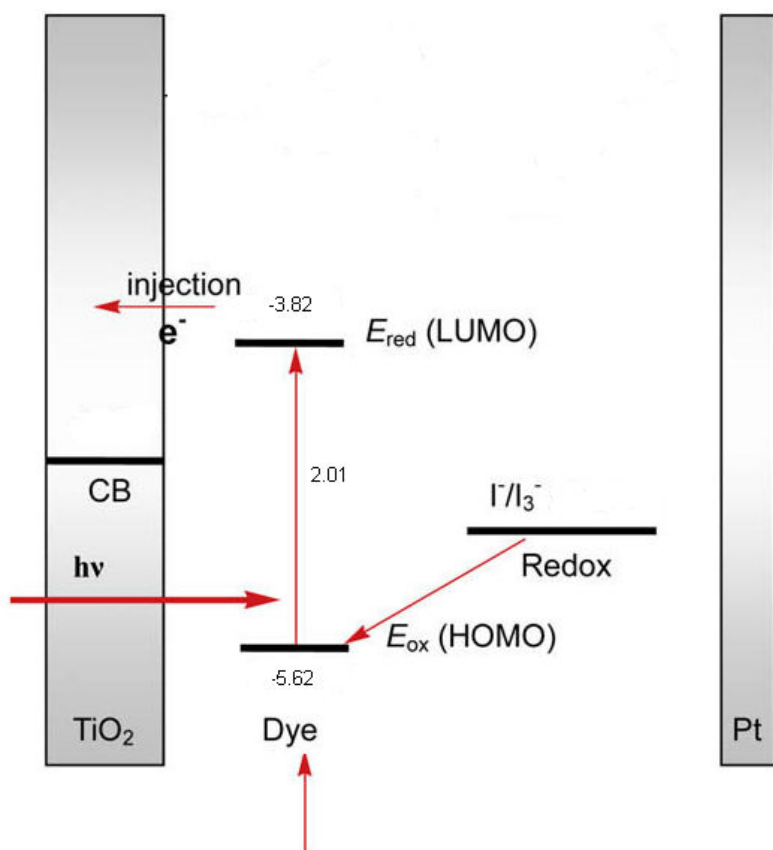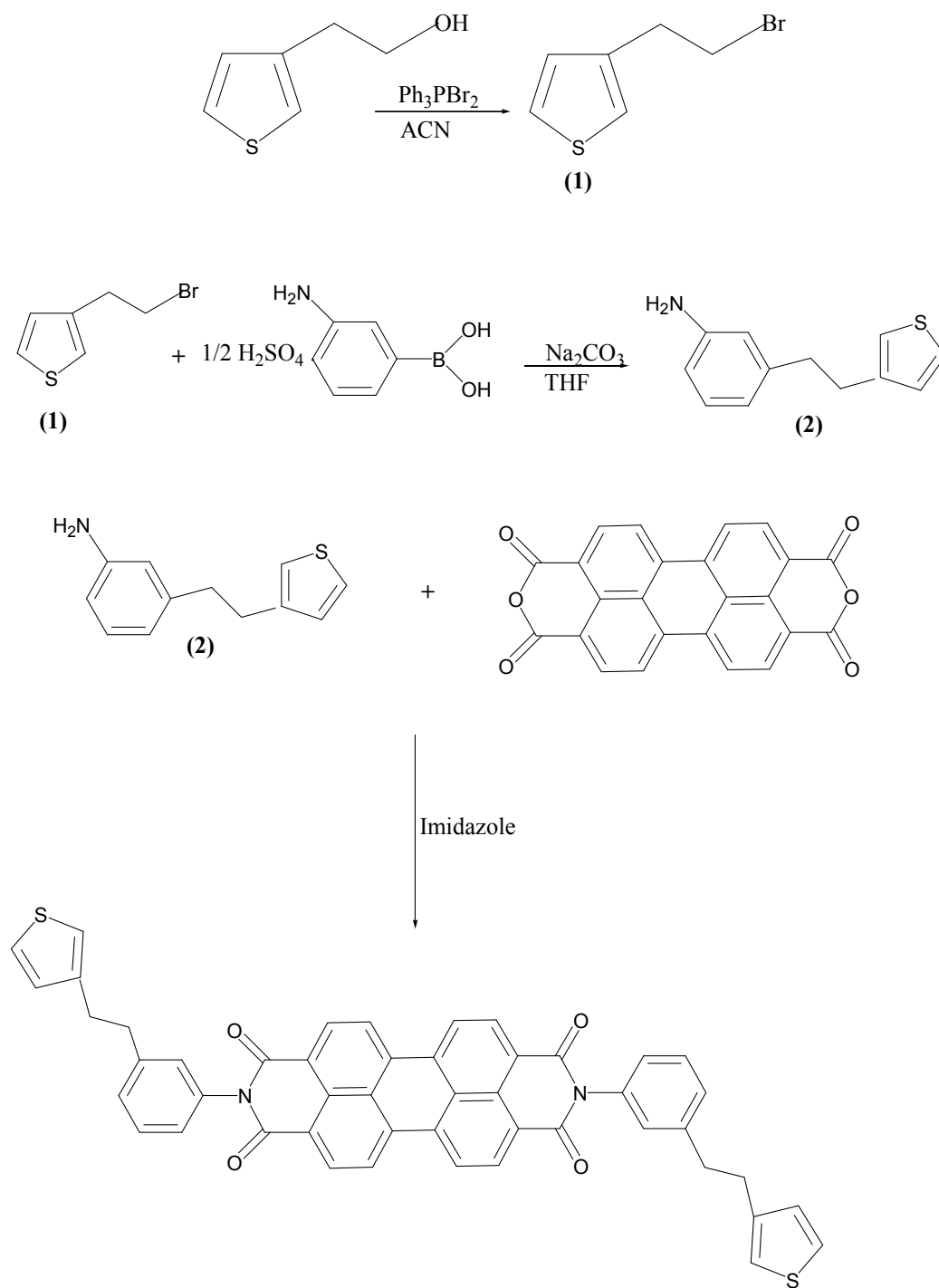**Fig. 6:** I-V curves of PDI1 in dark and under 100 mW/cm^2 AM1.5 global illumination.
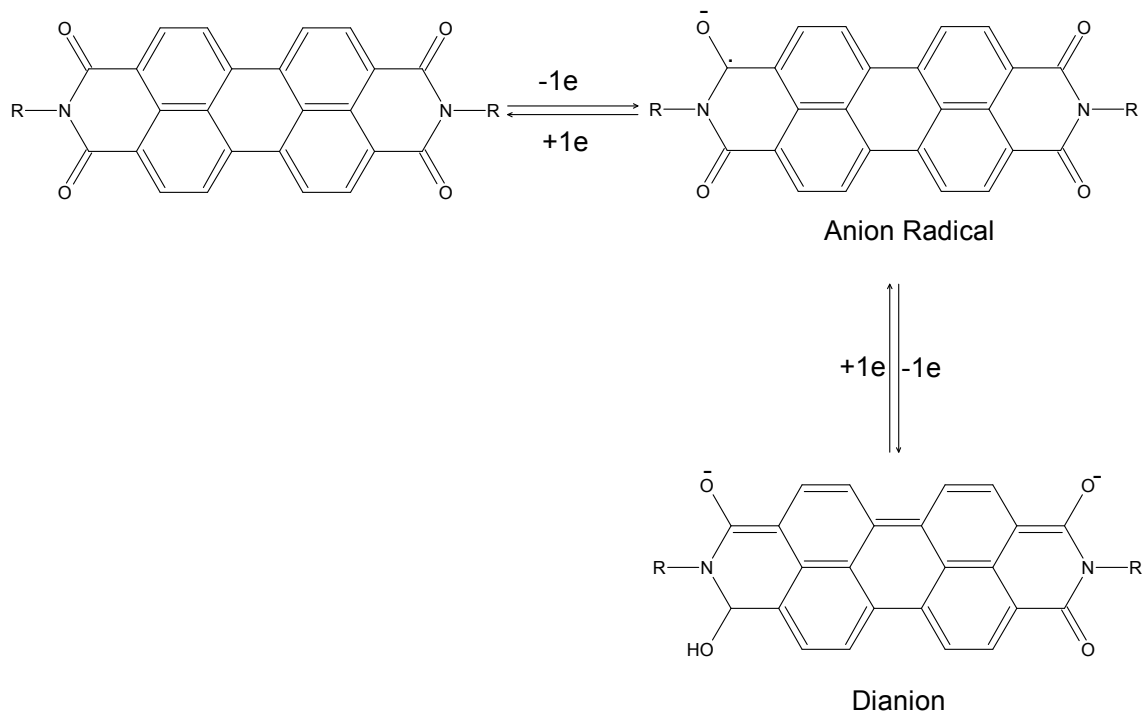
Fig. 7: Schematic energy diagram for a DSSC based on PDI nanocrystalline TiO$_2$ electrode, and I$^-$/I^{3-} redox couple.

Scheme 1: The synthesis of N,N´-Di-[3-[2-(3-thienyl)ethyl]phenyl]perylene-3,4,9,10-bis(dicarboximide) (PDI1)

Scheme 2: Anion, Dianion formation for perylene diimide dyes