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## SOME PERYLENE MOLECULES FOR SOLAR CELLS: THEIR STRUCTURE AND POWER CONVERSION EFFICIENCY

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### ABSTRACT

The aim of this article is, first, to summarize the literature of the perylene used in dye-sensitized solar cells (DSSC), and second, to give in brief the results of certain experimental studies about perylene in this literature.

**Keywords:** perylene diimide, solar cells

## INTRODUCTION

The sun light being renewable energy is the abundant source of clean and cheap energy [1]. Photovoltaic cells have a widespread application as a source of clean and renewable energy [2]. Solar cells, also called photovoltaic cells, are an electronic device used to generate electricity directly from sunlight. Dye-sensitized solar cells (DSSCs) have some advantages due to low-cost electricity production from sun light, high power conversion efficiency for solar energy. DSSCs are composed of four parts: (1) the electrode film layer ( $\text{TiO}_2$ ), (2) dye, (3) electrolyte (4) counter electrolyte (Fig.1) [3]. The typical DSSC is a sandwich structure device consisting of two electrodes: photoelectrode and counter electrode.

Metal oxides semiconductor is used material for the photoelectrode which is onto deposited some substrate such as indium-doped  $\text{SnO}_2$  (ITO), fluorine-doped  $\text{SnO}_2$  (FTO), aluminum-doped  $\text{ZnO}$  (AZO) [4]. A commonly used semiconductor material in cells is wide bandgap titanium dioxide ( $\text{TiO}_2$ ).  $\text{TiO}_2$  that is n-type semiconductor has some advantages such as non-toxic, biocompatible, cheap and abundant material.  $\text{TiO}_2$  occurs in three crystal structure: rutile, anatase and brookite. The nanocrystalline  $\text{TiO}_2$  film used in DSSCs is made of anatase due to its larger bandgap (3.2 eV) compared to rutile (3.0 eV) [5].  $\text{TiO}_2$  film is used as a photoanode. That is, semiconductor materials act as electron acceptor from photoexcited electrons of sensitizer [4]. It is a pathway for electrical current [6]. The high dielectric constant of  $\text{TiO}_2$  ( $\epsilon = 80$  for anatase) provides good electrostatic shielding of the injected electrons from the oxidized dye molecule attached to the  $\text{TiO}_2$  surface, thus reduced their combination before reduction of the dye by the redox electrolyte [4].

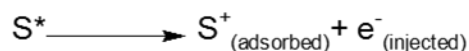
The role of the dye in DSSC is electron pump. It absorbs the visible light, pumps an electron into the semiconductor and accepts an electron from the redox couple in the solution and then repeats the cycle. Dye for DSSC must have some properties such as a strong absorption in the visible range, high stability, rapidly regenerated by the mediator layer in order to avoid electron recombination, no toxicity [6,7]. The sensitizers used in dye based solar cell are divided into two types according to their structure: the organic and inorganic dye. Organic dyes are inexpensive, easy to synthesize with molar extinction coefficients, their tunable absorption and electrochemical properties through suitable structure design [3]. Generally, organic dye has

the general structure of Donor (D)- $\pi$  conjugation bridge-Acceptor (A). Structure of dye is important to improve the light harvesting, absorption and photovoltaic performance [8]. Also, the functional groups are preferred for DSSC efficiency. For example; the carboxylate groups confer a strong bonding to the TiO<sub>2</sub> surface, while the NCS groups enhance its visible absorption [6]. The immobilization of the sensitizer is achieved by attaching anchoring groups such as carboxylate, phosphonate, salicylate, sulfonate, acetyl acetate and catechol groups to the surfaces of the mesoporous TiO<sub>2</sub> nanoparticles [5]. In the DSSC, it is used dye molecules such as coumarin, perylene, porphyrin, phenothiazine.

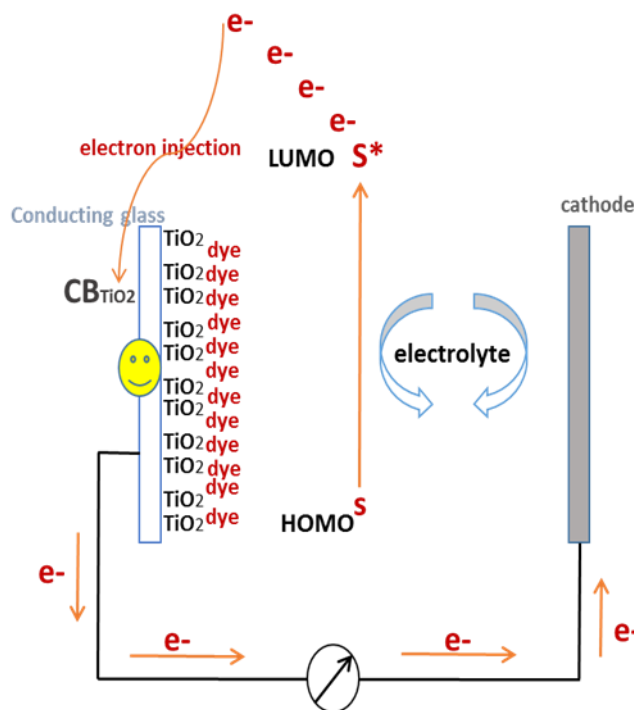
Generally, it is used iodide/triiodide-based redox electrolyte as electrolyte. Electrolyte acts as charge carrier between the photoanode and the counter electrode for regeneration of the dye. After electron injection, the electron donor in the electrolyte must reduce the oxidized dye to the ground state as rapidly as possible [6].

Counter electrode is important for electrons transfer. There are several types of counter electrodes such as platinum, carbon based materials, conducting polymer, nitrides and sulfides based materials. Platinum (Pt) is the most common counter electrode used due to its high catalytic activity and high power conversion efficiency. Pt nanoparticles have some properties such as high surface area, high transmittance, low charge transfer resistance, high electrical conductivity, corrosion resistance [4]. It is explained that dye-sensitized solar cell consists of nanocrystalline semiconductor oxide film electrode, dye sensitizer, electrolyte, counter electrode and transparent conducting substrate. Thus, the sandwiched solar cell is formed. Photovoltaic cell is illuminated through TiO<sub>2</sub> side [7].

Under the irradiation of sun light;



1. The dye sensitizer on metal oxide semiconductor absorbs the sun light. It is excited from ground state at HOMO (High Occupied Molecular Orbital) to the excited state at the LUMO (Lowest unoccupied Molecular Orbital). It became photo-excited.
2. The electrons from photoexcited dye are injected into the conduction band of the  $\text{TiO}_2$  from LUMO level of dye. The electron flows through the outer electrical circuit.
3. The oxidized dye is regenerated to its neutral state by accepting electron from electron.
4. The iodide is regenerated by reduction of triiodide at the counter electrode.
5. The circuit is completed [8].



**Fig.1.** Working Principle of DSSC

This work will give short information about some properties and the structure of perylene dyes used in DSSC.

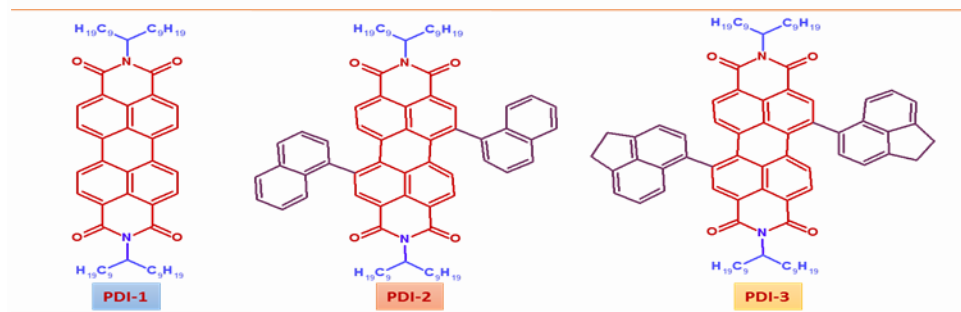
## 1. Some Perylene Diimide Dyes used in Dye-Based Solar Cells

Perylene-3,4,9,10-tetracarboxylic diimide (PDI) is highly conjugated molecule. It has some properties such as high electron affinity, large electron mobility, excellent thermal and oxidative stability, high molar absorptivity and quantum yield of fluorescence [9-15]. It is widely used used n-type materials [16,17] for organic electronic devices [18,19] such as solar cells, field-effect transistors [20-22], light-emitting diodes [23,24]. It exhibits strong visible absorptions in the 400–450 nm (B band) and 500–700 nm (Q band) range [25,26]. PDI are good electron acceptors. Several PDI probes should be promising candidates for fluorophores in fluorescent probes based on photoinduced electron transfer (PET) [27]. The electrical characteristic of the derivative of PDI have been investigated for different heterojunction structures. Perylene diimide derivatives are promising class of n-type organic semiconductors [28].

Organic solar cells are particularly attractive because of their easy processing, mechanical flexibility and low fabrication cost [29]. The optical properties and solubility of PDI molecules are tuned by introducing of some substituents at the bay or N-imide positions. Dye is key for DSSC. The role of the dye in DSSC consists in acting as a molecular electron pump. It is responsible for absorbing the visible light, generating excited electrons and pumping them into the semiconductor. The dye must have some properties such as strong absorption in the visible range, high photo and thermal stability, good adsorption to the semiconductor's surface, no toxicity, have a broad absorption spectrum in the visible range.

As an electron acceptor PDI molecules have been linked to some molecules such as fullerene, pyrenes, phthalocynines, porphyrins or tetrathiafulvalene [30].

PDI-2 and PDI-3 synthesized were used as acceptor in P3HT (Poly(3-hexylthiophene-2,5-diyl) /PDI (perylene dimide) bulk heterojunction solar cell application. The introduction of aromatic rings into the bay positions form a steric hindrance. For PDI-2 and PDI-3, the long alkyl branched chains at the imide positions increases solubility of molecule. Also, fused aromatic rings at the bay positions lead to a twisted perylene plane and create a strong steric hindrance.



**Fig.2.** Molecular structure of PDI derivatives synthesized by Kozma et al.

PDI-2 and PDI-3 are thermally stable up to 400 °C. The HOMO and LUMO energy levels of PDI-2 are -5.79 eV and -3.73 eV. The HOMO and LUMO energy levels of PDI-3 are -5.55 eV and -3.63 eV. The HOMO and LUMO energy levels of P3HT are -5.00 eV and -3.00 eV.

**Table 1.** HOMO and LUMO energy levels of PDI-2, PDI-3 and P3HT

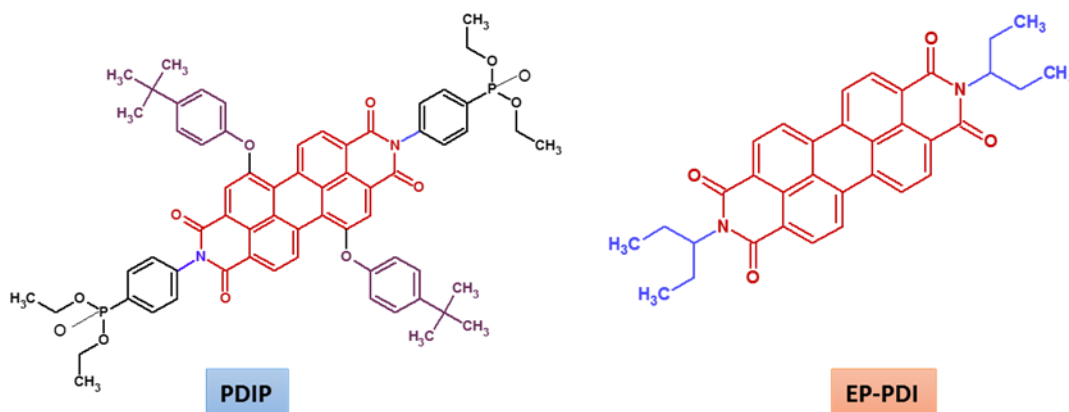
Material	HOMO (eV)	LUMO (eV)	It is clear that the HOMO and LUMO energy levels of PDIs are suitable.
PD-2	-5.79	-3.73	
PDI-3	-5.55	-3.63	
P3HT	-5.00	-3.0	

PDI-1 is nearly planar. The optical properties are significantly different in solution and in solid state. Generally, the PDIs have two absorption bands. The absorption peaks of PDI-2 and PDI-3 in chloroform solvent are at the 542 nm and 558 nm. The author investigated that the photovoltaic properties of PDI-1, PDI-2 and PDI-3 in bulk heterojunction solar cells. P3HT is donor [29]

**Table 2.** Power Conversion Efficiency of PDI-2, PDI-3 and PDI-3 [29]

Molecule	P3HT:PDI (w:w)	PCE(%) (Power Conversion Efficiency)	The best performances were obtained with 1:2 weight ratio blend. It is well known that the polymer solar cells containing P3HT as donor component improve their efficiencies upon thermal and solvent annealing
PD-1	1:1	0.03	
	1:2	0.04	
PDI-2	1:1	0.35	
	1:2	0.42	
	2:1	0.22	
PDI-3	1:1	0.28	
	1:2	0.33	
	2:1	0.20	

Li et al. have fabricated an organic photovoltaic device based on N,N'-bis(1-ethylpropyl)-perylene-3,4,9,10-tetracarboxylic diimide (EP-PDI) and phosphate group-containing perylene diimide derivative (PDIP). PDIP has alcohol-soluble phosphate group at N-imide position. It plays role as a cathode interfacial layer.



**Fig.3.** Molecular structure of PDI derivatives synthesized by Liet et al.

**Table 3.** LUMO energy levels of PDIP and EP-PDI

Material	LUMO	The LUMO level of PDIP is lower than that EP-PDI. PDIP would be suitable electron transport material for PDI-based solar cells.
PDIP	-3.90 eV	
EP-PDI	-3.74 eV	

The PDI-based organic photovoltaics with Ca/Al electrode showed a PCE value of 0.29 %.

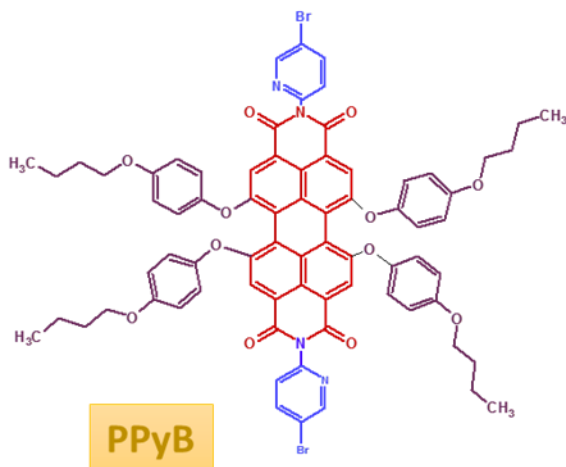
**Table 4.** Photovoltaic properties of PCDTB:EP-PDI (1:1) blend solar cells fabricated different cathodes

Cathode	PCE (%)
Ca/Al	0.292
PDIP/Al (1000r 60s)	0.404
PDIP/Ca/Al(1000r 60s)	0.522

PDIP was used as an interfacial layer between organic active layer and metal electrode for efficient device performance. The active layer covered by PDIP layer exhibited much smoother and more hydrophilic surface, thus reducing contact resistance and easing inherent incompatibility at the metal/organic layer interface. Introduction of alcohol soluble PDI material as a cathode interfacial layer should be promising candidates for interfacial modification in PDI-based OPV devices [31].



Polymer solar cell was fabricated by using N,N'-bis-(5-bromopyridine-2yl)-1,6,7,12-tetrakis(4-n-butoxyphenoxy)-3,4,9,10-perylene tetracarboxydiimide (PPyB) by Jeong et al. PPyB molecule has pyridine derivative at N-imide position and 4-n-butoxyphenol at bay position.



**Fig.4.** Molecular structure of PPyB derivatives synthesized by Jeong et al.

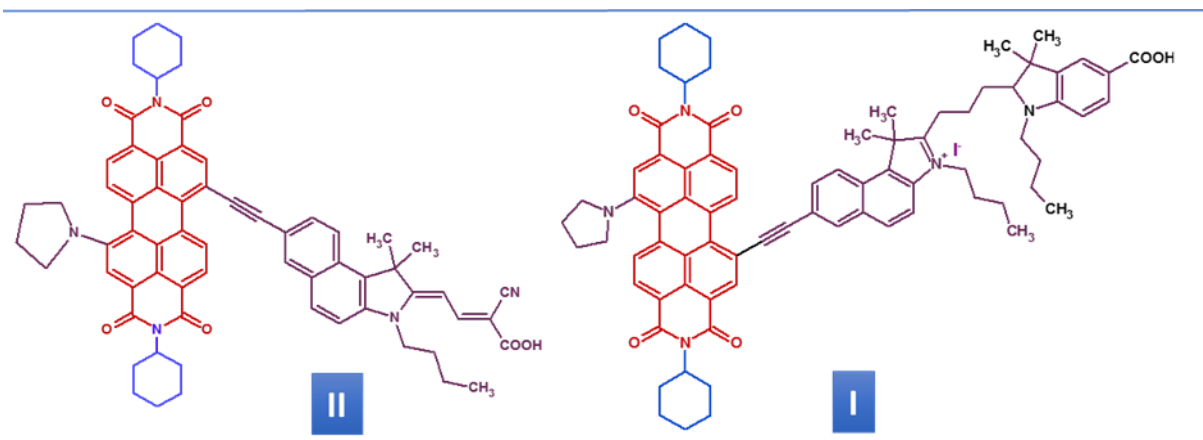
The PPyB film showed two absorption peaks at 563 nm and 602 nm. The absorption coefficient of the perylene film recorded as  $1-4 \times 10^5 \text{ cm}^{-1}$  in the visible region. These absorption properties of PPyB in the visible region may be favorable for improving the PCE. The photovoltaic properties of the devices with and without PPyB were investigated. Devices containing 1 wt% of the additive showed the best performance.

**Table 5.** Photovoltaic characteristics of non-annealed devices

Devices	Content of additive	PCE %
PSCo	0 wt%	1.4
PSC1	1 wt% of PPyB	2.5

The control device (PCS0) without any additive presented relatively poor photovoltaic characteristics, with a PCE of 1.4 %. But the device with 1 wt% exhibited an improved performance with a PCE of 2.5% [32].

Two perylene derivatives were synthesized as sensitizers for dye-sensitized solar cells. molecule I and II have cyclohexyl at N-imide position and pyrrolidine derivative at the bay position at the one side.

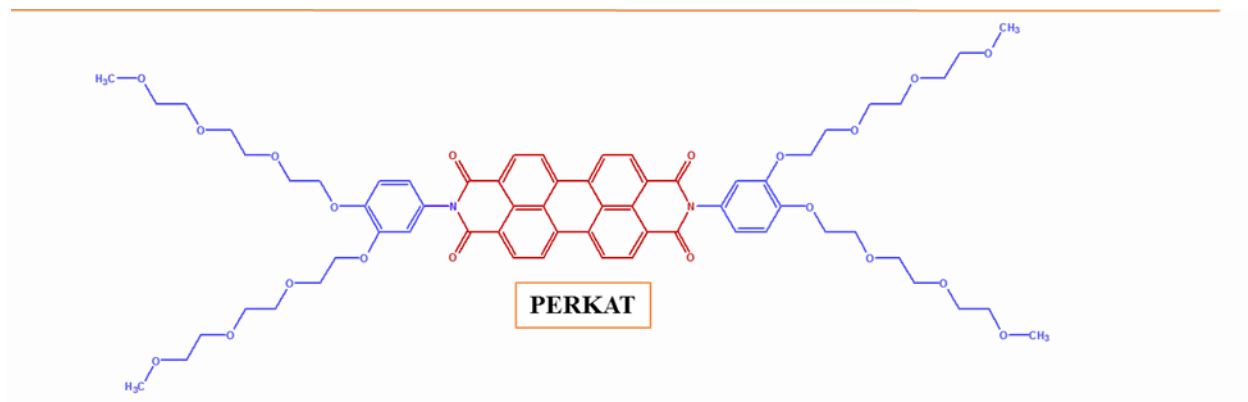


**Fig.5.** Molecular structure of I and II derivatives synthesized by Jin et al.

The absorption spectra of I contain two bands located at 589 and 680 nm, which are corresponding to the transitions of cyanine unit and 7-pyrrolidinylperylene unit. Molecule II exhibits also two bands located at 464 and 680 nm, which are attributed to the transitions of  $\pi$ -conjugation unit between condensation reaction of benzo[e]indole and cyanoacetic acid and 7-pyrrolidinylperylene imide unit, respectively. The corresponding maximum extinction coefficient of I and II were  $8.2 \times 10^4 \text{ cm}^{-1}$  and  $7.5 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ , respectively. The dyes can be adsorbed on  $\text{TiO}_2$  films from the variety of solutions because of the presence of a carboxylic group in the molecules.

The value of DSSC based on I and II is 0.34 % and 1.38%, respectively. As shown, their conversion efficiency is low. The lower conversion efficiency may be because the perylene imide group, which contains strong electron-withdrawing nature has effect on the polarity of the whole molecule, resulting in the unbeneficially transferring direction of photo-generated electrons, which decreases the overall photocurrent performance [33].

Perylene derivative containing the polyoxy group at the imide positions has been synthesized by Birel et al. These groups increase solubility of perylene molecule.



Perylene diimide dyes show generally characteristic absorption peaks for the perylene diimide at 458, 490, 526 nm, which are denoted to their (0,2), (0,1), and (0,0) electronic transitions, respectively. These absorption peaks are matched by the corresponding emission peaks at 540, 576, 624 nm, respectively. used as reference. The  $\Phi$  Values are low (0.0041 in toluene, 0.0027 in chloroform, 0.0016 in tetrahydrofuran, 0.014 in benzonitrile, 0.0014 in methanol). The low fluorescence quantum yields in various solvents can be attributed to the re-absorption of emitted photons and the self-quenching due to the intra and intermolecular interactions. Also, the polyoxychains may be quench the fluorescence intensity. As the dielectric constant increases, the fluorescence quantum yield decreases.

The LUMO energy level was calculated as 3.98 eV. HOMO energy level have been found as -6.35

The power conversion efficiency ( $\eta$ ) is 0.038 % [34].

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