



# Influence of *para*-alkyl chain length of the *bay*-phenyl unit on properties and photovoltaic performance of asymmetrical perylenediimide derivatives



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## ABSTRACT

In this report, three asymmetrical perylenediimide derivatives (PDI) substituted on the *bay*-position with *para*-alkylphenyl groups were synthesized, on which the substituted alkyl side chain was *n*-propyl (**4-PP-PDI**), *n*-hexyl (**4-HP-PDI**), or *n*-nonyl (**4-NP-PDI**) group. The effect of alkyl chain length on the optical and electrochemical properties, thermal behavior, as well as the photovoltaic performance of these materials in solution processed polymer solar cells were systematically studied. Results indicated that the *para*-alkyl side chain length showed negligible influence on the spectroscopy and redox behaviors of the materials, but significant influence on the photovoltaic performance. The propyl substituted compound **4-PP-PDI** showed the best photovoltaic performance of  $V_{OC} = 0.63$  V,  $J_{SC} = 1.93$  mA cm<sup>-2</sup>, FF = 0.63 and a power conversion efficiency of 0.77%, which was attributed to the balanced intermolecular interaction of PDI molecules and the donor-acceptor phase separation of the blend films.

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## 1. Introduction

Perylenediimide derivatives (PDI) have been extensively used in car and textile industry owing to their particular features such as excellent chemical and thermal stability, high absorption coefficient, high fluorescence quantum yield, and good solubility [1,2]. In recent years, PDIs were also used in optoelectronic devices [3], especially as *n*-type organic semiconductor in organic field-effect transistors (OFET) [4,5] and bulk heterojunction (BHJ) solar cells [6–8]. In comparison with the most widely used fullerene electron acceptor [6,6],-phenyl-C<sub>61</sub>-butyric acid methyl ester (PC<sub>61</sub>BM) [9], PDI derivatives have similar lowest unoccupied molecular orbital level (LUMO, around -4.0 eV) [10], but higher charge carrier mobility [10<sup>1</sup>–10<sup>-3</sup> cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>] [11] and more intensive light

absorption ability in visible light range [12]. The first solution processed BHJ solar cells using a PDI derivative (PPEI) as the electron acceptor was reported by Friend et al. in year 1999 [13]. In this pioneer work, a conjugated polymer poly[2-methoxy-5-(2'-ethylhexyloxy)-*p*-phenylenevinylene] (MEH-PPV) was used as the electron donor, and low external quantum efficiency (EQE) of 0.25% was obtained for this kind of device. Morphology studies showed that large PDI crystalline domains (around 1 μm in size) were formed in blend films [14–16], which was speculated to be the reason for the poor charge separation and low exciton splitting efficiency [16].

Knowing that nano-scale phase separation of the donor and acceptor in the blend film is a prerequisite for achieving high performance solar cells [17,18], introducing bulky group on the PDI molecule to reduce the intermolecular interactions has therefore been considered as the effective way to develop high performance PDI acceptors. In this respect, chemical modifications of PDI core on the N-position [8,19], the *bay*- (1,6,7,12-) [20–23] and the *ortho*- (2,5,8,11-) position(s) [6,10,24] have been reported. Among these three chemical modification possibilities, functionalization on the

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bay-position(s) has been proved to be the most efficient and feasible way to achieve high performance PDI acceptors [7,20,22]. To date, PDIs functionalized at 1,7-positions [25–28] and PDI oligomers with increased molecular dimensionalities, such as PDI dimers [29–36], star-shaped trimer [37], as well as four-wing propeller-shaped tetramers [38–40] have been developed, and high power conversion efficiency (PCE) was achieved by carefully tuning the thin film formation processing [22,38].

Interestingly, although 1,7-*bis*-aryl-substituted PDIs and aryl-cored PDI oligomers have been reported as excellent electron acceptors in organic solar cells [26,28], very few *mono*-aryl-substituted PDI molecules were reported in the literature [28,39,41,42], and only two of them were reported for use in organic solar cell [28,39]. It should be noted that the *bis*-substituted PDI derivatives are usually composed of 1,6- and 1,7- isomers [43], which might lead to a batch-to-batch variation due to the different properties of these two isomers. Taking it into account that the *mono*-substituted compounds are easy to synthesize and purify, it is therefore highly interesting to investigate the structure-property relationships of the *bay-mono*-substituted PDI derivatives, which will provide useful guidelines for the development of PDI based acceptor materials.

In this article, we will describe the synthesis of three asymmetric *bay-mono*-functionalized PDI derivatives, on which *para*-alkylphenyl group with different alkyl chain length was introduced to reduce the planarity of the PDI molecules. It is also known that alkyl side chain of conjugated small molecules or polymers plays a critical role in influencing the materials performance [44–49]. Therefore, the influence of the alkyl chain length on the optical and electrochemical properties, as well as the photovoltaic performance are investigated in detail in this article. The results indicate that the *bay*-substituted PDIs showed improved photovoltaic performances in comparison with that of non-substituted PDI compound, which was attributed to the decreased planarity of the PDI molecules.

## 2. Experimental section

### 2.1. Materials

All of the reagents and chemicals were purchased from commercial sources and used without further purification unless stated otherwise. *para*-Propylphenylboronic acid, *para*-hexylphenylboronic acid and *para*-nonylphenylboronic acid were purchased from J&K Chemical Ltd. (Shanghai). 2-Enthylhexylamine was purchased from Alfa Aesar, and 3,4,9,10-perylenetetracarboxylic dianhydride was purchased from Energy Chemical. Anhydrous dichlorobenzene and chlorobenzene were purchased from Sigma-Aldrich and used as received. Anhydrous trichloromethane and dichloromethane were purchased from Sinopharm Chemical Reagent Co., Ltd, and were dried by distillation over calcium hydride before use. Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS Heraeus Clevios PVP AI 4083) was purchased from Heraeus Precious Metals GmbH & Co. KG. Regioregular poly(3-hexylthiophene) (SMI-P3HT,  $M_n = 5.0 \times 10^4 \text{ g mol}^{-1}$ , PDI = 1.7, regioregularity Rr = 95%) was purchased from Solarmer Energy, Inc. (Beijing). ZnO nanoparticles were synthesized according to literature procedures [50], and were dispersed in acetone with a concentration of  $10 \text{ mg mL}^{-1}$  before use.

### 2.2. General methods

The  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra of the synthesized chemicals were recorded on a Varian MR 400 spectrometer (400 MHz), and on a Bruker Avance III 400 MHz NMR spectrometer, respectively.

Chemical shifts are reported in  $\delta$  (ppm), referenced to solvent residual peak (7.26 ppm for  $^1\text{H}$  NMR and 77.0 ppm for  $^{13}\text{C}$  NMR in chloroform-*d*) as internal standard. Matrix assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MS) was performed on a Bruker Autoflex Speed using *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene] malononitrile (DCTB) as the matrix. High resolution mass spectrometry (HRMS) was performed on a Thermo Fisher Scientific LTQ FT Ultra (operation mode: MALDI; matrix: 2,5-dihydroxybenzoic acid). Thermogravimetric analysis (TGA) was performed on a Perkin Elmer TGA 4000 instrument at a heating rate of  $10 \text{ }^\circ\text{C min}^{-1}$  under  $\text{N}_2$  atmosphere. Differential scanning calorimetry (DSC) measurements were carried out on a DSC 200 F3 Maia instrument under  $\text{N}_2$  atmosphere using heating and cooling rates of  $10 \text{ }^\circ\text{C min}^{-1}$ . UV-vis spectra of the PDIs in chloroform solution and thin film were recorded on a Perkin Elmer Lambda 750 UV-vis spectrophotometer. For UV-vis absorption spectrum measurement of each compound in solution, three solutions with different concentrations (around  $10^{-3} \text{ mol L}^{-1}$ ) were prepared independently. Each of them was further diluted to three solutions with different concentrations (around  $10^{-6}$ – $10^{-5} \text{ mol L}^{-1}$ ). The absorption spectra of the diluted solutions were measured. By plotting the absorbance at a certain wavelength versus concentration, a straight line should be obtained and the molar extinction coefficient ( $\epsilon$ ) can be derived from the slope according to the Beer–Lambert's Law equation ( $A = \epsilon \cdot L \cdot c$ ). The photoluminescence (PL) spectra of the PDIs in thin film state were obtained with an F-4600 FL spectrophotometer. Thin film samples for fluorescence measurement were prepared by spin-casting a chloroform solution (around  $1.0 \times 10^{-3} \text{ mol L}^{-1}$ ) on quartz glasses. Cyclic voltammetry (CV) experiments were performed with a RST-3000 Electrochemistry Workstation (Suzhou Risetech Instruments Co., Ltd.). All CV measurements were carried out at room temperature with a conventional three-electrode configuration under nitrogen atmosphere. The electrochemical cyclic voltammetry was performed in a  $0.1 \text{ mol L}^{-1}$  tetrabutylammonium hexafluorophosphate ( $\text{Bu}_4\text{NPF}_6$ )/dichloromethane (DCM) solution with a scan speed of  $0.1 \text{ V s}^{-1}$ . A Pt wire ( $\phi = 1 \text{ mm}$ ) embedded in Teflon was used as the working electrode. The surface was polished before use. A Pt sheet ( $\sim 1 \text{ cm}^2$ ) and Ag/AgCl electrode were used as the counter and reference electrodes, respectively. After the measurement, small amount of ferrocene was added in the solution and the ferrocene/ferrocenium ( $\text{Fc}/\text{Fc}^+$ ) redox couple was measured as an internal standard. The concentration of PDI solution was  $1.0 \times 10^{-3} \text{ mol L}^{-1}$  in DCM for CV measurement. AFM measurements were performed by using a Scanning Probe Microscope-Dimension 3100 in tapping mode. Thin film samples for AFM measurement were deposited on ITO/ZnO substrates following the same procedures as used for OPV devices fabrication (*vide infra*). Transmission electron microscopy (TEM) tests were performed on a Tecnai G2 F20 S-Twin 200 kV field-emission electron microscope (FEI). Specimens for the TEM experiments were obtained by transferring the floated blend films from the water onto the 200 mesh copper grid.

### 2.3. Fabrication and characterization of OPV cells

ITO-coated glass substrates were cleaned with detergent, deionized water, acetone, and isopropyl alcohol in turn by ultrasonic-wave cleaner, and then dried with a flow of nitrogen. After that, the substrates were treated in UV-ozone for 30 min to eliminate any remaining organic components.

For conventional devices, a thin layer (ca. 35 nm) of PEDOT:PSS (Clevios P VP AI 4083, H.C. Stark, filtered through a PTFE syringe filter,  $0.45 \text{ }\mu\text{m}$ ) was first spin-coated on the pre-cleaned ITO-coated glass substrates at 3500 rpm for 1 min and then annealed at  $120 \text{ }^\circ\text{C}$

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