



# Molecular geometry regulation of *bay*-phenyl substituted perylenediimide derivatives with bulky alkyl chain for use in organic solar cells as the electron acceptor



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## ABSTRACT

Perylenediimide derivatives (PDI) are among the most promising non-fullerene electron acceptor materials for use in organic solar cells. However, owing to the intensive intermolecular interactions, the non-functionalized PDI molecules showed high tendency of aggregation in solid film, which leads to poor device performance. In this paper molecular geometry of PDI derivatives was finely tuned by introducing a bulky isopropyl group on the *bay*-phenyl unit, and influences of such a bulky alkyl group on the optical and electrochemical properties were systematically studied. Results indicated that the bulky isopropyl group on the *para*- and *meta*-position of the *bay*-phenyl group has negligible influence on the twist angle between the PDI core and the *bay*-phenyl unit, and these two compounds (**4-iPP-PDI** and **3-iPP-PDI**) have similar molecular properties. However, large steric hindrance of the *ortho*-isopropyl group causes a large twist between the PDI core and the *bay*-phenyl unit, which leads to conjugation break, and consequently to a blue-shifted absorption spectrum and an increased optical band gap for the final PDI compound (**2-iPP-PDI**). Polymer solar cells using these *bay*-phenyl functionalized PDIs as the electron acceptor were fabricated and tested. And the *meta*-substituted PDI compound **3-iPP-PDI** show the better device performance than the *para*- and *ortho*-substituted compounds (**4-iPP-PDI** and **2-iPP-PDI**), which was ascribed to the proper nano-scale phase separation and high electron mobility of the blended film. The current results proved that molecular geometry of PDI derivatives can be finely regulated through introducing bulky alkyl side chain on the *bay*-substitution group to achieve a balanced property of crystallinity and electron mobility.

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## 1. Introduction

The field of solution-processed bulk heterojunction organic solar cells (BHJ-OSCs) has seen steady growth in efficiencies over the past decades [1,2]. To date, the power conversion efficiencies (PCEs) based on single-junction polymer:fullerene [3–6] or small molecule:fullerene [7,8] blend OSCs have already exceeded 10%. Such

high efficiencies are mainly attributed to the development of new photoactive materials [2,9–11]. Fullerenes and their derivatives are the most used electron acceptor materials in OSCs, while they have some inevitable disadvantages [12,13] that limited further improving the PCEs, including low light absorption in visible light range, high cost and difficulty of structure modification. High performance non-fullerene electron acceptor alternatives are therefore high interesting for OSCs, both in academy research and industrial application [13–20]. Till now, various non-fullerene acceptors, including A- $\pi$ -D- $\pi$ -A type small molecules [21–27], bifluorenylidene derivatives [28], heterocyclic diimide derivatives [29–31], diketopyrrolopyrrole derivatives [32–34], naphthalene diimide derivatives [35–37], perylene diimide derivatives [17,38],

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and other types electron acceptor materials [39–43] have been developed and applied in BHJ-OSCs, and high power conversion efficiencies (PCEs) exceeding 11% have been achieved very recently [21].

Among these non-fullerene acceptor materials exploited so far for OSCs, perylene-3,4,9,10-tetracarboxylic diimide derivatives (PDIs) are the mostly frequently developed ones [13,14,17,38,44]. Advantages of PDIs as electron acceptors in OSCs are mainly including their strong absorption in the visible region between 400 nm and 650 nm, high electron mobilities ( $10^{-3}$ – $10^1$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>), low-lying LUMO levels (about –4.0 eV), simplicity in synthesis and purification, as well as chemically, thermally, and environmentally robust [45]. However, because of the large planar structure of the perylene core, the non-functionalized PDI molecules typically showed high aggregation tendency in thin film, leading to large crystallization domains over 20 nm [46,47]. This may limit the exciton diffusion [48], and consequently decrease device performance. To reduce the aggregation tendency of PDIs, strategy of introducing bulky substitution groups onto the *N*- [49,50], *bay*- [51,52] and/or *ortho*-position [53,54] of PDI core has been proved to be the most effective way in developing high performance PDI acceptors for use in organic solar cells. Among which, *bay*-functionalization is the most widely used chemical modification way, since the *bay*-position can be easily activated by bromination. With that, PDI oligomers, including dimers [55–58], trimers [59] and tetramers [60,61] have been developed, where the multiple PDI units were connected via C–C bond [57,58,62], alkyl chain [53,63] or aromatic unit [59,64], and high power conversion efficiency of more than 8% has been achieved for these PDI oligomers based solar cells [58,62,63]. Understanding the effect of the *bay*-substitution group on the property and performance of the PDI molecules is therefore highly important for further development of new PDI molecules. However, most of the reported *bay*-functionalized PDI derivatives are *bis*-substituted compounds [51,65], which are typically comprised of 1,6- and 1,7-isomers [66], making them not ideal compounds for such structure-property-performance relationship study. In contrast, *mono*-substituted compounds are better model molecules for this purpose. However, there was no systematic study on such a fundamental relationship, until very recently we reported the effect alkyl chain length on the property and performance the *mono-bay*-alkylphenyl substituted PDI derivatives [67]. 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 [67]. These results confirmed that it is possible to finely tune the molecular packing behavior of the PDI molecules by varying the position of the alkyl chain on the *bay*-substituent.

In this article, we report our efforts on regulating the structure

and property of *mono-bay*-substituted PDI derivatives with bulky isopropyl group. By introducing the isopropyl group on the *para*-, *meta*-, and *ortho*-position of the *bay*-phenyl unit, we are able to finely tune the molecular geometry of these compounds, and consequently tune the optical and electrochemical properties. The molecular packing behaviors as well as the photovoltaic performance of these compounds in polymer solar cells are also studied, and a highest device performance was obtained for the *meta*-isopropyl-phenyl substituted compound. This result demonstrates that substitution position plays also an important role in determine the property and performance of the PDI derivatives.

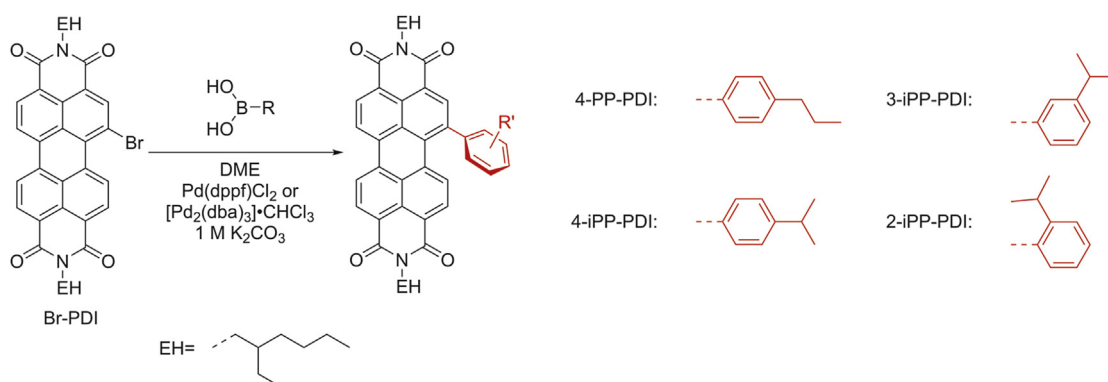
## 2. Results and discussion

### 2.1. Synthesis and characterization

The synthetic route to the target PDI derivatives is shown in Scheme 1. The key starting material **Br-PDI** was synthesized using literature reported method [68]. The detailed synthetic process of **4-PP-PDI** can be found in our previous report [67]. Three final compounds of **4-iPP-PDI**, **3-iPP-PDI** and **2-iPP-PDI** were synthesized through Suzuki coupling reactions of **Br-PDI** with corresponding phenylboronic acid (for **4-iPP-PDI** and **3-iPP-PDI**) or ester (for **2-iPP-PDI**) catalyzed with Pd(dppf)Cl<sub>2</sub> (for **4-iPP-PDI** and **3-iPP-PDI**) or [Pd<sub>2</sub>(dba)<sub>3</sub>]·CHCl<sub>3</sub> (**2-iPP-PDI**) in high yields of 92%, 80% and 72%, respectively. Synthesis of **2-iPP-PDI** catalyzed with Pd(dppf)Cl<sub>2</sub> was not successful, which could be due to the high steric hindrance of the 2-isopropylphenyl group, and less reactivity of Pd(dppf)Cl<sub>2</sub>. The decreased coupling yield from **4-iPP-PDI**, **3-iPP-PDI** to **2-iPP-PDI** could be also explained by the gradually increased steric hindrance between isopropyl substituted phenyl-unit and PDI-core (*vide infra*). All compounds have been fully characterized by <sup>1</sup>H NMR, <sup>13</sup>C NMR, MALDI-TOF-MS, and HRMS. These three PDI derivatives were found to be soluble in most common organic solvents, such as chloroform, dichloromethane, dichlorobenzene, and chlorobenzene at ambient temperature, making them suitable for use in solution-processed BHJ solar cells.

### 2.2. DFT calculations

Density functional theory (DFT) calculations were performed using the Gaussian 09 program with B3LYP/6-31G approach to investigate the molecular geometry and electronic structures of **4-iPP-PDI**, **3-iPP-PDI** and **2-iPP-PDI**. Calculated optimal molecular conformations and molecular orbital surfaces of the frontier molecular orbitals (FMOs) highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are shown in Fig. 1 and the related data are listed in Table 1. As shown in Fig. 1, the



Scheme 1. The synthetic routes for **4-PP-PDI**, **4-iPP-PDI**, **3-iPP-PDI** and **2-iPP-PDI**.

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