



Synthesis, characterization and photovoltaic performance of novel glass-forming perylenediimide derivatives



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ABSTRACT

Novel glass-forming perylene-3,4,9,10-tetracarboxylic diimide (PDI) derivatives were synthesized from 1,7-dibromoperylene-3,4,9,10-tetracarboxylic diimides by nucleophilic substitution with a glass-forming mexylaminotriazine unit, characterized, and their performance as electron acceptors in bulk heterojunction photovoltaic cells with P3HT as donor were studied. Imide groups (octyl and 2,6-diisopropylphenyl) and bay substituents (bromo or pyrrolidinyl) were used to study the impact of sterics and electronics on device performance. The HOMO and LUMO levels of the materials were determined using cyclic voltammetry. The morphology and packing behavior of molecules in films of blends with P3HT were studied using Atomic Force Microscopy and X-ray diffraction, and in all four cases, the PDI derivatives remain in the amorphous phase, while the P3HT portion of the blends crystallizes. The devices gave photovoltaic performances ranging from 0.2 to 0.6%, and while the bay substituents showed negligible impact on device performance, switching from bulky 2,6-diisopropylphenyl imide groups to linear octyl chains improved the efficiency of the devices by 36%, current density by 66% and fill factor by 16%. The performances observed for devices incorporating these PDI glasses are comparable to that of devices with crystalline PDI acceptors.

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1. Introduction

Due to the availability of carbon feedstocks and flexible organic synthetic methodologies, organic materials have become extremely attractive for photovoltaic applications [1–3]. Depending on the solubility of organic materials, organic PV cells can be fabricated either by vacuum or by printing technologies such as spin-coating, drop-casting, doctor blading, inkjet printing, screen printing and roll-to-roll printing. Tang et al. reported in 1986 a *p*-*n* heterojunction device with a power conversion efficiency of 1% using copper phthalocyanine and a perylene-3,4,9,10-tetracarboxyl-bisbenzimidazole (PTCBI) electron donor and acceptor, respectively [4]. In recent years, great progress has been achieved in the development of solution-processed bulk heterojunction PV cells, and the technology has reached the early stages of

commercialization. Currently, organic PV cells have been demonstrated to exhibit power conversion efficiency above 9% [5,6]. The high efficiency of bulk heterojunctions is due to exciton dissociation at the interface between the electron donor and acceptor materials in the intimately mixed system and followed by efficient charge separation and transport to the electrodes by diffusion of charges in the interpenetrating donor and acceptor network, thereby facilitating an efficient charge separation due to large interfacial area [7–10]. So far, various organic materials have been developed as electron donor or *p*-type materials, which have improved properties such as high absorption, hole mobility, and adequately tuned HOMO and LUMO levels [11–13]. However, the development of electron acceptors or *n*-type materials is far behind that of donor materials. The dominant acceptors in bulk heterojunction PV cells are fullerene derivatives due to their high electron mobility, large electron affinity, and capacity to pack efficiently to form a percolated tridimensional supramolecular network. However, fullerenes absorb light only weakly in the visible region and play only a limited role in the light harvesting process. In addition, their high synthesis costs and limited tunability of energy levels hinder the commercial success of fullerene-based organic PV cells

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[9,10,14]. As the development of optimal electron acceptor materials is equally important to that of donor materials for the improvement of device performances, it is crucial to develop optimal non-fullerene acceptors for organic PV cells with improved performances [15,16].

3,4,9,10-Perylenetetracarboxylic diimide (PDI) derivatives are promising candidates as acceptors in organic photovoltaics. Not only do PDI derivatives display high electron mobilities [17], but they also possess high molar absorption coefficients in the visible range [18]. Moreover, they can be synthesized in large scale in relatively economic fashion [10]. The LUMO of parent 3,4,9,10-perylenetetracarboxylic diimide is similar to that of PCBM [19]. Their optoelectronic properties can be easily tuned by tailoring the substituents on the imide groups or on the bay positions [14,20–22]. In addition, the low-lying HOMO levels of PDI derivatives can facilitate the hole transfer process from the PDI molecules to the donor material after absorption of light [10]. All these properties make PDI derivatives an extremely attractive class of materials for use in organic photovoltaics as electron acceptor materials.

As the poly-aromatic core in PDI derivatives is planar, as opposed to spherical for fullerene derivatives, the performance of the devices is expected to depend on proper packing of the perylene moieties so that the π -orbitals can interact with each other [10]. A common problem with small molecules is their tendency to rapidly crystallize [23,24], which limits their usefulness in applications involving thin films by yielding films of poor quality, with polycrystalline topologies constituted of small domains separated by grain boundaries that limit the long-range transport of electrons by acting as electron traps [25]. Annealing conditions must thus be screened thoroughly to find the conditions that will give optimal film morphologies and limit grain boundaries.

An alternative approach consists in designing PDI derivatives (or electron acceptor materials in general) that form thin films that remain amorphous [26,27]. While amorphous solids possess no long-range periodical order, intermolecular interactions, such as the π -stacking of aromatic moieties, can nonetheless be present and regulate to a certain degree the organization at the molecular level, with a continuous material that is exempt of grain boundaries.

As with the majority of small molecules, most PDI derivatives readily crystallize [26,27]. However, it was demonstrated that strategic molecular design can hinder the process of crystallization, resulting in molecular materials that can remain in the amorphous state for extended (sometimes indefinite) periods of time. This class of materials are known as molecular glasses, or amorphous molecular materials, and combine the monodisperse nature of small molecules with the processability of polymers [28–30]. As typically, compounds designed to form glasses possess bulky, non-planar and irregular shapes, and generally interact weakly with neighbouring molecules [31], designing PDI derivatives that can form glasses despite their planar perylene core and that can interact reliably by π -stacking in the amorphous state is expected to be challenging. However, approaches where glass-forming derivatives of chromophores are synthesized by functionalization with peripheral groups have been reported in the literature [32–35]. Mexylaminotriazines are one such family of glass-forming materials that usually show outstanding glass-forming ability, high kinetic stability towards crystallization, and glass transition temperature (T_g) values that can be modulated by tuning their molecular structures [36–38]. Glass-forming mexylaminotriazine derivatives can bear functional groups that can be bonded in a covalent fashion to chromophores, thereby yielding adducts that can remain indefinitely in the amorphous state at operating temperatures, while preserving the optical and electronic properties of

the chromophore with minimal perturbation. This approach was demonstrated with a series of azobenzene dyes, with which glass-forming adducts were generated using a simple, efficient and high-yielding procedure [39,40].

In the present work, four glass-forming PDI derivatives containing mexylaminotriazine groups in the bay position were synthesized, characterized, and incorporated into organic PV cells with P3HT as donor material. The PDI glasses synthesized feature two different imide groups, 2,6-diisopropylphenyl and *n*-octyl, and two different bay substituents, bromo and pyrrolidinyl, to study the impact of steric bulk and electronics on device performance. All four acceptor materials investigated showed the ability to spontaneously form stable glasses that did not crystallize upon heating or operation of the devices, and all materials showed photovoltaic activity, with device efficiencies with P3HT as donor ranging from 0.2 to 0.6%. These values are comparable to most values previously reported for PV cells using P3HT and PDI derivatives containing a single perylene moiety [10,41], and are reasonably close to the highest values reached so far for such systems (close to 1%) [21,42]. Interestingly, the performances of the devices has been found to be independent on the electronics of the acceptor materials, with both bromo and pyrrolidinyl series giving similar results. On the other hand, the octyl imide series showed efficiency 3 times greater than their sterically hindered 2,6-diisopropylphenyl imide analogues. This is believed to be due to the 2,6-diisopropylphenyl groups shielding the perylene core and preventing efficient stacking of the perylene moieties, thereby impeding electron transport. While the P3HT portion of the bulk heterojunction is semi-crystalline, the PDI domains remain amorphous, and the results reported herein show that the electron transport over long range required for current generation is possible in the amorphous state and yields performances comparable to that of crystalline materials.

2. Experimental

2.1. Materials

2-Methylamino-4-mexylamino-6-(4-mercaptophenyl)amino-1,3,5-triazine (**1**) [37], *N,N'*-bis(2,6-diisopropylphenyl)-2,7-dibromo-3,4,9,10-perylenetetracarboxylic diimide (**2a**) [43], and *N,N'*-dioctyl-2,7-dibromo-3,4,9,10-perylenetetracarboxylic diimide (**2b**) [44], were prepared according to the literature. Pyrrolidine was purchased from Sigma-Aldrich, and all other solvents and reagents were purchased from Caledon Labs. All reagents were used without further purification. Regioregular poly(3-hexylthiophene-2,5-diyl (P3HT) used as electron donor was purchased from Rieke Metals. Molybdenum oxide used as hole transport layer was purchased from Alfa Aesar. ZnO as electron transporting material was synthesized by the sol-gel method reported in the literature [45]. The Indium tin oxide (ITO) glasses used as substrates were purchased from Luminescence Technology Corporation, which has ITO film thickness about 135 ± 15 nm, and sheet resistance is $15 \text{ } \Omega \text{sq}^{-1}$. Glass transition temperatures were determined with a TA Instruments 2010 Differential Scanning Calorimeter calibrated with indium at a heating rate of $5 \text{ } ^\circ\text{C}/\text{min}$ from 30 to $250 \text{ } ^\circ\text{C}$. Values were reported as the half-height of the heat capacity change averaged over two heating runs. For compounds **3a** and **4a**, values were averaged over heating runs on two different samples because of thermal degradation. FTIR spectra were acquired with thin films cast from CH_2Cl_2 on KBr windows using a Perkin-Elmer Spectrum 65 spectrometer. UV–visible absorption spectra were acquired using a Hewlett-Packard 8453 spectrometer or a Olid[®] HP8452 Diode Array Spectrometer. NMR spectra were acquired on either a 400 MHz Bruker AV400 or on a 300 MHz Varian Oxford spectrometer. Luminescence was measured with a USB2000-Ocean

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