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Special feature

Bis-lactam-based donor polymers for organic solar cells: Evolution by design

Joseph W. Rumer *, Bob C. Schroeder, Christian B. Nielsen, Raja S. Ashraf, Daniel Beatrup, Hugo Bronstein, Samuel J. Cryer, Jenny E. Donaghey, Sarah Holliday, Michael Hurhangee, David I. James, Stefanie Lim, Iain Meager, Weimin Zhang, Iain McCulloch

Department of Chemistry, Imperial College London, London SW7 2AZ, UK
Centre for Plastic Electronics, Imperial College London, London SW7 2AZ, UK

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ABSTRACT

Lactam-based semiconducting donor polymer materials often exhibit high performance in the photoactive layer of solution processed organic solar cells. In this review we focus on the structure–property–device performance relationships, offering a set of rational design rules for next generation materials from a chemical structure perspective.

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1. Introduction

Organic electronic materials have potential as thin, lightweight, flexible, large-area and crucially inexpensive solar cells, fabricated by printing techniques [1–4]. In contrast, inorganic cells have historically been cut from silicon as expensive, rigid, small-scale devices. With rising atmospheric carbon dioxide levels and a shortage of fossil fuels, coupled with increasing global energy demand, the flourishing field of organic solar cells is thus well justified, as a currently under-exploited but renewable, green energy source, which could find widespread application in textiles, vehicles and construction [5].

On a molecular design level, π-conjugated polymers, and more recently small-molecules, routinely exhibit the required solubility for use in solution-processed bulk heterojunction organic photovoltaic (OPV) devices [6]. While much studied homo-polymer/fullerene systems such as poly(3-hexylthiophene) (**P3HT**) and [6,6]-phenyl C71-butyric acid methyl ester (**PC$_{71}$BM**) have now reached ~5% efficiency [7–9], the recent record of 10.6% was set with **PDPDT–DFBT**, a donor–acceptor type polymer comprising poly(cyclopentadithiophene) and difluorobenzothiadiazole [10]. Fullerenes such as **PC$_{71}$BM** are the most common acceptor materials, as alternatives such as perylene derivatives and porphyrin type metal complexes have been widely studied but are uncommon due to their typically lower performance [11–14]. However, it is the class of donor polymer materials with a push–pull donor–acceptor hybridization that gives some of the highest power conversion efficiencies, such as **PMDPP3T** (Fig. 1), affording almost 9% [15]. While obtained with varied device architectures, this high-performance is due in-part to their readily tuneable optical and electronic properties and alkyl side-chains to afford the required solubility and processability [16].

2. Device structure and operation

Solar cells operate by absorbing light in a photoactive layer, such as a blend of donor polymer and fullerene based acceptor (Fig. 2). Valence electrons in a donor material are promoted from the Highest Occupied Molecular Orbital (HOMO) to the conduction band, or Lowest Unoccupied Molecular Orbital (LUMO), generating positively charged holes, which together form coulombically bound excitons (electron–hole pairs). Before decay to the ground state, excitons can diffuse ~5–10 nm through a structure where the HOMO is delocalised. If the exciton meets the interface with the acceptor material within this diffusion length, then charge separation can occur: the electron transfers to the lower energy LUMO of the acceptor. The exciton can then dissociate into free charge carriers which are able to flow towards their respective electrodes, generating a current. The efficiency of a solar cell may be quantified by the ratio of power out to power in, or rather the ratio of electricity generated to photons absorbed, termed power conversion efficiency (PCE); this is a useful number being the product of short-circuit current, open-circuit voltage (derived from the potential difference of the donor HOMO and acceptor LUMO), and the fill factor (describing internal losses). A recent overview of OPV cell operation mechanisms has highlighted that while empirical formulations suggest upper limits of 10–12% PCE, more fundamental descriptions raise this to 20–24% for single junction devices, becoming competitive with crystalline p–n junction photovoltaic cells [17].

The OPV device efficiency (PCE) may be limited by several factors, in both a molecular design and device structure sense. The molecular design of the photoactive layer can be tailored to (a) light absorption and the

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* Corresponding author.
E-mail address: jwrumer@imperial.ac.uk (J.W. Rumer).

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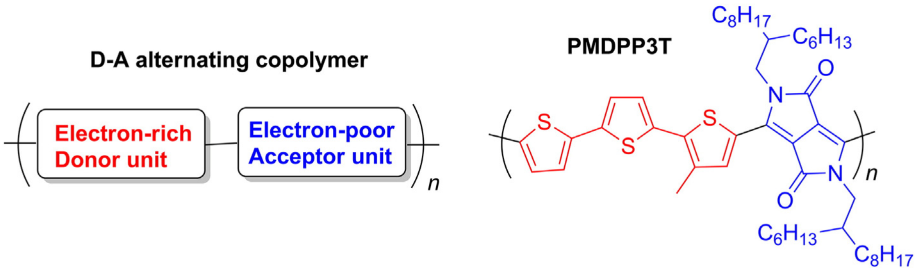

Fig. 1. A schematic diagram of the donor–acceptor alternating copolymer structure used in high-performance donor materials and in example **PMDPP3T**.

generation of charge, by ensuring a sufficient HOMO–LUMO bandgap to coincide with photon energy in the solar spectrum; (b) having a potential difference (voltage) that drives the flow of current, originating from the LUMO–LUMO offset of the donor and acceptor; (c) planarity for enhanced charge mobility; (d) solubility for solution processing; and (e) bringing intrinsic stability [18]. Subsequently the donor and acceptor will have different molecular structures and most likely need additives to enhance their stability (thermal, optical and chemical) and morphology, such as generating a percolating structure of both materials between the electrodes to carry charges away. An intuitive solution is the bilayer device, layering the donor above the acceptor, though this limits the interface for charge separation, reducing efficiencies. The device structure also bears several considerations: (a) the percolated structure of donor and acceptor materials should have domain sizes no greater than the exciton diffusion length, and be stable over a long lifetime; (b) the electrodes need appropriate energy levels for charge extraction, and adhesion to the active materials; (c) the active layer could be sandwiched between electron and hole transport and blocking layers to avoid charge recombination and expedite extraction. Lastly the device may be encapsulated from atmospheric dopants (oxygen and water) to aid stability. This is a complex optimisation process, for example even just in controlling polymer morphology device efficiency is enhanced by choice of solvent, evaporation rate, the blend composition, thermal treatment and cross-linking. Finally the method of device manufacture should be considered, solution processing is advantageous as it allows for the large-scale and inexpensive production of devices by printing techniques such as ink-jet, gravure or roll-to-roll [19].

3. Evolution of the *bis*-lactam motif for acceptor units

Organic semiconducting polymers based on dye pigment chromophores, such as 2,5-diketopyrrolo[3,4-*c*]pyrrole (**DPP**), have recently attracted much attention, delivering impressive device performances [20–23]. The **DPP** *bis*-lactam unit is a commonly used *N*-alkylated acceptor: the electron-deficient nature of the **DPP** core lowers the HOMO levels of donor–acceptor copolymers and promotes intramolecular charge transfer, while exhibiting a quinoidal form in the excited state, lowering the bandgap. In addition, the planarity and ability to hydrogen-bond through the carbonyl groups encourages intermolecular interactions such as π–π stacking. Flanking the electron-deficient *bis*-lactam core with electronically-coupled electron-rich units, such as [3,2-*b*]thienothiophene, renders these excellent building blocks for donor polymers [24–29].

Leaving the lactam core intact, conjugated polymer backbones are often judiciously tailored to fine-tune their energy levels; for example the flanking thiophenes of **DPP** have been switched for furans and thienothiophenes, with PCE rising from 4.7% to 5.0% and 5.4%, respectively, echoing the increasingly electron-rich nature of these units (Fig. 3) [25,30,31]. In addition, their planarity and ability to hydrogen-bond similarly encourages π–π stacking facilitating charge transport and leading to high performing organic solar cells [32]. The effect of varying the chalcogen atom from sulfur to selenium has also been investigated: while PCEs over 5% have been observed these are lower than their sulfur analogues, as selenium lowers the LUMO, reducing the bandgap to the extent that the open-circuit voltage may be compromised [33]. Flanking thienothiophenes afford greater planarity and electron-donating character, improving performance in sufficiently soluble and high molecular weight polymers.

More recently, **DPP**'s structural isomer, **isoDPP**, has also been synthesized (Fig. 4), providing an interesting comparison whereby the ketone and *N*-alkyl positions are interchanged, moving the electron-withdrawing functional groups closer to the conjugation pathway and lowering the HOMO level, which may improve device stability [33–35]. Notably from the crystal structure, the thieno sulfur atom now points towards the carbonyl. However, **isoDPP**-based polymers retain their planarity, giving ~5% PCE in unoptimized cells.

The resurgence of interest in colourant-based materials has included work on the "stretched **isoDPP**", benzodipyrrolidone (**BP**) [36–38], which has been used to construct low-bandgap polymers containing the *bis*-lactam molecular architecture (Fig. 4). The **BP** core is larger than **DPP**, being tricyclic with a central six-membered ring, increasing planarity and the delocalization of electrons. When flanked with phenyl moieties torsional twisting is induced, reducing π orbital overlap along the conjugated backbone and limiting charge transport. However, when the phenyls are changed for planar flanking thiophenes (**BPT**), the delocalization of the LUMO is extended in particular, leading to high electron

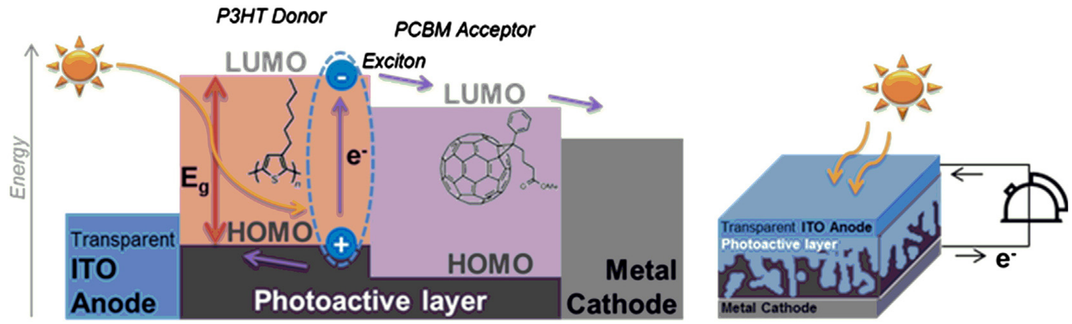

Fig. 2. Bulk heterojunction photovoltaic cell operation: (left) a schematic diagram of the energy levels illustrating exciton formation, splitting and charge transport; and, (right) a simple device architecture; ITO = indium tin oxide.

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