

1 ***Bis-lactam-based donor polymers for organic solar***  
2 **cells: evolution by design**

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

20

21 **Keywords: organic photovoltaics – solution processed – semiconducting polymers –**  
22 **lactam - morphology – bulk heterojunction**

23

24 Organic electronic materials have potential as thin, lightweight, flexible, large-area and  
25 crucially inexpensive solar cells, fabricated by printing techniques [1-4]. In contrast,  
26 inorganic cells have historically been cut from silicon as expensive, rigid, small-scale

1 devices. With rising atmospheric carbon dioxide levels and a shortage of fossil fuels,  
2 coupled with increasing global energy demand, the flourishing field of organic solar cells is  
3 thus well justified, as a currently under-exploited but renewable, green energy source,  
4 which could find widespread application in textiles, vehicles and construction [5].

5  
6 On a molecular design level,  $\pi$ -conjugated polymers, and more recently small-molecules,  
7 routinely exhibit the required solubility for use in solution-processed bulk heterojunction  
8 organic photovoltaic (OPV) devices [6]. While much studied homo-polymer/fullerene  
9 systems such as poly(3-hexylthiophene) (**P3HT**) and [6,6]-phenyl C71-butyric acid methyl  
10 ester (**PC<sub>71</sub>BM**) have now reached ~5% efficiency [7-9], the recent record of 10.6% was set  
11 with **PDPDT-DFBT**, a donor-acceptor type polymer comprising poly(cyclopentadithiophene)  
12 and difluorobenzothiadiazole [10]. Fullerenes such as **PC<sub>71</sub>BM** are the most common  
13 acceptor materials, as alternatives such as perylene derivatives and porphyrin type metal  
14 complexes have been widely studied but are uncommon due to their typically lower  
15 performance [11-14]. However, it is the class of donor polymer materials with a push-pull  
16 donor-acceptor hybridization that give some of the highest power conversion efficiencies,  
17 such as **PMDPP3T** (Figure 1), affording almost 9% [15]. While obtained with varied device  
18 architectures, this high-performance is due in-part to their readily tuneable optical and  
19 electronic properties and alkyl side-chains to afford the required solubility and processability  
20 [16].

21

## 22 **Device structure and operation**

23 Solar cells operate by absorbing light in a photoactive layer, such as a blend of donor  
24 polymer and fullerene based acceptor (Figure 2). Valence electrons in a donor material are  
25 promoted from the Highest Occupied Molecular Orbital (HOMO) to the conduction band, or

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

16  
17 The OPV device efficiency (PCE) may be limited by several factors, in both a molecular  
18 design and device structure sense. The molecular design of the photoactive layer can be  
19 tailored to (a) light absorption and the generation of charge, by ensuring a sufficient HOMO-  
20 LUMO bandgap to coincide with photon energy in the solar spectrum; (b) having a potential  
21 difference (voltage) that drives the flow of current, originating from the LUMO-LUMO offset  
22 of the donor and acceptor; (d) planarity for enhanced charge mobility; (c) solubility for  
23 solution processing; and (e) bringing intrinsic stability [18]. Subsequently the donor and  
24 acceptor will have different molecular structures and most likely need additives to enhance  
25 their stability (thermal, optical and chemical) and morphology, such as generating a  
26 percolating structure of both materials between the electrodes to carry charges away. An

1 intuitive solution is the bilayer device, layering the donor above the acceptor, though this  
2 limits the interface for charge separation, reducing efficiencies. The device structure also  
3 bears several considerations: (d) the percolated structure of donor and acceptor materials  
4 should have domain sizes no greater than the exciton diffusion length, and be stable over a  
5 long lifetime; (e) the electrodes need appropriate energy levels for charge extraction, and  
6 adhesion to the active materials; (f) the active layer could be sandwiched between electron  
7 and hole transport and blocking layers to avoid charge recombination and expedite  
8 extraction. Lastly the device may be encapsulated from atmospheric dopants (oxygen and  
9 water) to aid stability. This is a complex optimisation process, for example even just in  
10 controlling polymer morphology device efficiency is enhanced by choice of solvent,  
11 evaporation rate, the blend composition, thermal treatment and cross-linking. Finally the  
12 method of device manufacture should be considered, solution processing is advantageous  
13 as it allows for the large-scale and inexpensive production of devices by printing techniques  
14 such as ink-jet, gravure or roll-to-roll [19].

15

## 16 **Evolution of the *bis*-lactam motif for acceptor units**

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

1  
2 Leaving the lactam core intact, conjugated polymer backbones are often judiciously tailored  
3 to fine-tune their energy levels; for example the flanking thiophenes of **DPP** have been  
4 switched for furans and thienothiophenes, with PCE rising from 4.7% to 5.0% and 5.4%,  
5 respectively, echoing the increasingly electron-rich nature of these units (Figure 3) [30-32].  
6 In addition, their planarity and ability to hydrogen-bond similarly encourages  $\pi$ - $\pi$  stacking  
7 facilitating charge transport and leading to high performing organic solar cells [33]. The  
8 effect of varying the chalcogen atom from sulfur to selenium has also been investigated:  
9 while PCEs over 5% have been observed these are lower than their sulfur analogues, as  
10 selenium lowers the LUMO, reducing the bandgap to the extent that the open-circuit voltage  
11 may be compromised [34]. Flanking thienothiophenes afford greater planarity and electron-  
12 donating character, improving performance in sufficiently soluble and high molecular weight  
13 polymers.

14  
15 More recently, **DPP**'s structural isomer, **isoDPP**, has also been synthesized (Figure 4),  
16 providing an interesting comparison whereby the ketone and *N*-alkyl positions are  
17 interchanged, moving the electron-withdrawing functional groups closer to the conjugation  
18 pathway and lowering the HOMO level, which may improve device stability [34-36]. Notably  
19 from the crystal structure, the thieno sulfur atom now points towards the carbonyl. However,  
20 **isoDPP**-based polymers retain their planarity, giving ~5% PCE in unoptimized cells.

21  
22 The resurgence of interest in colorant-based materials has included work on the "stretched  
23 **isoDPP**", benzodipyrrolidone (**BP**) [37-39], which has been used to construct low-bandgap  
24 polymers containing the *bis*-lactam molecular architecture (Figure 4). The **BP** core is larger  
25 than **DPP**, being tricyclic with a central six-membered ring, increasing planarity and the

1 delocalization of electrons. When flanked with phenyl moieties torsional twisting is induced,  
2 reducing  $\pi$  orbital overlap along the conjugated backbone and limiting charge transport.  
3 However, when the phenyls are changed for planar flanking thiophenes (**BPT**), the  
4 delocalization of the LUMO is extended in particular, leading to high electron affinities, and  
5 low bandgaps, resulting in well balanced ambipolarity in organic field-effect transistors [40].

6  
7 A recent extension of the **BP** core was dihydropyrroloindoleione (**DPID**) [41-42],  
8 introducing a vinyl group either side of the *bis*-lactam core similar to polycroconaines [43]:  
9 this extends the backbone donor-acceptor aspect ratio, which has been shown to reduce  
10 steric hindrance between polymer chains and enhance solid-state packing [44]. In addition,  
11 an extraordinary S-O planarization is believed to reduce backbone twisting, in contrast to  
12 the hydrogen bonding in **DPP**. However, the **DPID** core features an aromatic central ring  
13 (making the *bis*-lactam a *bis*-oxindole), while in **BPT** this is quinoidal, which imparts greater  
14 planarity on the polymer backbone, resulting in higher charge mobility. The deep HOMO  
15 levels of both materials confer stability and a high open-circuit voltage but encumber solar  
16 cell performance, due to a poor LUMO-LUMO offset with common fullerene acceptors,  
17 resulting in a low current. Typically an offset of  $>0.3$  eV is thought to be desired, depending  
18 on the polymer system [45]. However, the improved solubility induced by the **DPID** vinyl  
19 groups allows for processing of these polymers from printing friendly solvents such as *m*-  
20 xylene with modest PCEs of  $\sim 2\%$ .

21

22 The well known *bis*-oxindole pigment indigo has also been studied, and most pertinently its  
23 structural isomer isoindigo, which is comparative to **DPID** containing a vinyl linkage, the  
24 lactam motif and aromatic phenyl rings in the core. However, the torsional twisting induced  
25 by the phenyl moieties has led to these being replaced with thiophene-based derivatives

1 (IGTs) [46]. Isoindigo reiterates many familiar design rules in this respect: *N*-alkylation  
2 brings solubility and planarity to an electron-deficient core where an orthogonal dipole,  
3 resulting from a carbonyl which forms the lactam functionality, enhances solid-state packing  
4 effects and charge transport along the conjugated polymer backbone. When copolymerized  
5 with benzothiadiazole (IGT-BT) (Figure 5), HOMO levels are below -5 eV, conferring  
6 stability to atmospheric dopants [47], and low bandgaps of ~1.3 eV overlap well with the  
7 solar emission spectrum. Copolymers with alkylated terthiophene and isoindigo have  
8 achieved PCEs as high as 6.2% in bulk heterojunction OPVs with **PC<sub>71</sub>BM** [48].

9

## 10 Solubilizing alkyl side-chain influence

11 In exploring various chromophores the exact structure of the solubilizing chain is often  
12 overshadowed by energetic contributions influencing the frontier orbital bandgap, despite  
13 evidence that side chain spacing and whether to use branched or straight chain groups can  
14 prove vital [49-50]. The size of the solubilizing chain is also a key factor to consider during  
15 polymer synthesis: with a longer alkyl chain solubility is generally gained, though other  
16 factors such as packing, blend morphology and fullerene miscibility may be perturbed [51-  
17 52]. Typically linear chains have been preferred for transistor applications compared to  
18 branched chains for OPV, with the optimum side-chain structure being highly dependent on  
19 the exact polymer system. Recent efforts have turned to the effects of overall steric bulk,  
20 such as shifting the branching-point of the alkyl chain further from the conjugated polymer  
21 backbone to improve performance and developing hybrid siloxane side-chain dynamics for  
22 high mobilities [53].

23

24 The *N*-alkylation of lactam containing units imparts greater solubility allowing for a wider  
25 range of donor comonomers to be exploited. An additional benefit of **DPP** units is the ability

1 to produce high molecular-weight polymers, which can lead to improved performance [54-  
2 55]. Typically number-average molecular weights above 25 kDa are considered optimal,  
3 while particularly high molecular weight chains can bring problems of solubility, depending  
4 on the polymer. Moreover, purification by size exclusion gel permeation chromatography to  
5 give narrow polydispersity fractions, which most likely affords consistent ordering, and  
6 improved PCE [56].

7

## 8 **Challenges and prospects**

9 In conclusion, we have outlined a number of rational design rules for the development of  
10 next generation semiconducting donor polymers for high efficiency OPV applications. These  
11 include the basic requirements of sufficient molecular weight and solubility, typically gained  
12 from branched alkyl-side chains with minimal steric effects, tailored to each polymer and  
13 readily affixed to nitrogen atoms in a lactam motif. The backbone may be substituted to fine-  
14 tune energy levels for stability, bandgap and LUMO-LUMO offset optimization, while  
15 typically being rigid and planar, incorporating fused, conjugated heterocycles such as  
16 thienothiophene, where a quinoidal character enhances charge mobility. An electron rich-  
17 poor donor-acceptor hybridization extends the delocalization of electrons, aiding  
18 planarization, solid-state packing and lowering the bandgap to give improved efficiencies.  
19 Hybrid structures that challenge the current plethora of building blocks can be envisaged  
20 with tailored alkyl side-chains for optimal performance. In particular, careful choice of co-  
21 monomers can build polymers that not only meet these criteria but also challenge  
22 conventional matching of donor-acceptor units to give improved performance, for example  
23 weak donors with strong acceptors [57].

24

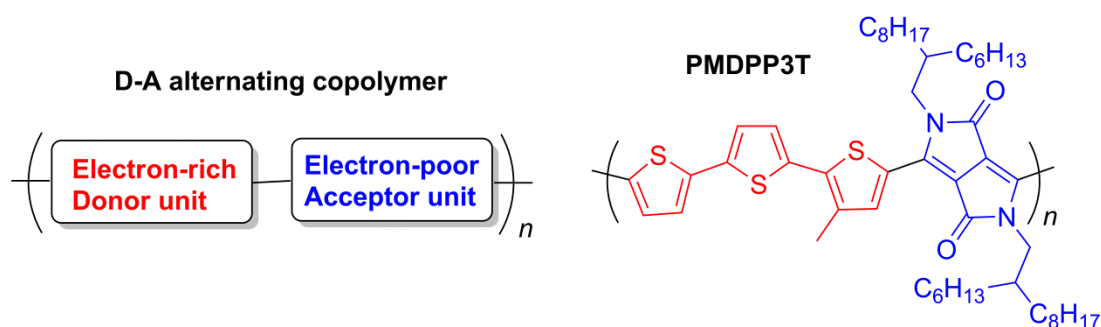


1 The use of computational models to accurately predict trends in properties such as HOMO  
 2 energy levels and bandgaps has recently been evaluated, identifying quantum-chemical  
 3 models as a useful tool for pre-screening and structure-optimization [58-59]. Structures are  
 4 required that maintain high efficiencies (>10% PCE) in simple solution processed devices  
 5 with long-term stability.

6

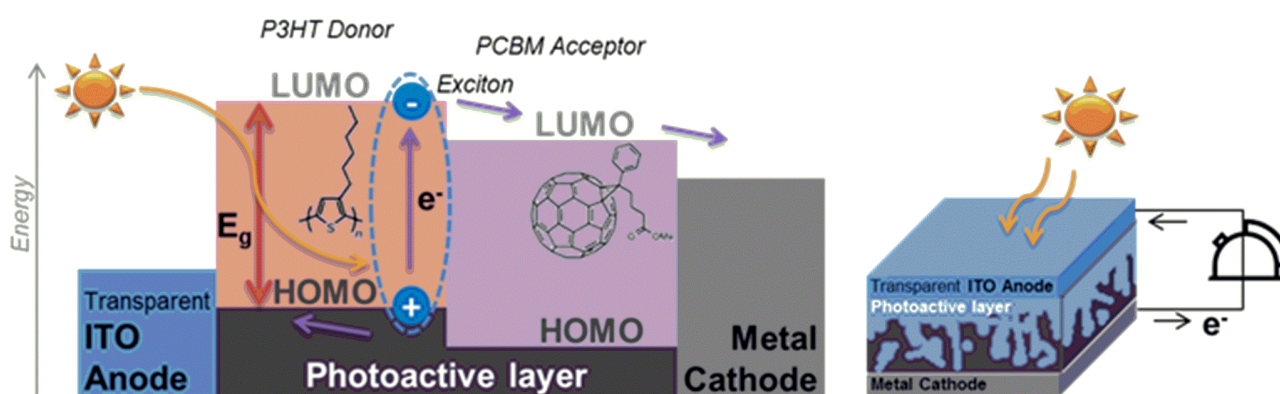
7 **LIST OF FIGURE CAPTIONS**

8 **Note: figures supplied in colour for use on the web but to be printed in black and**  
 9 **white**



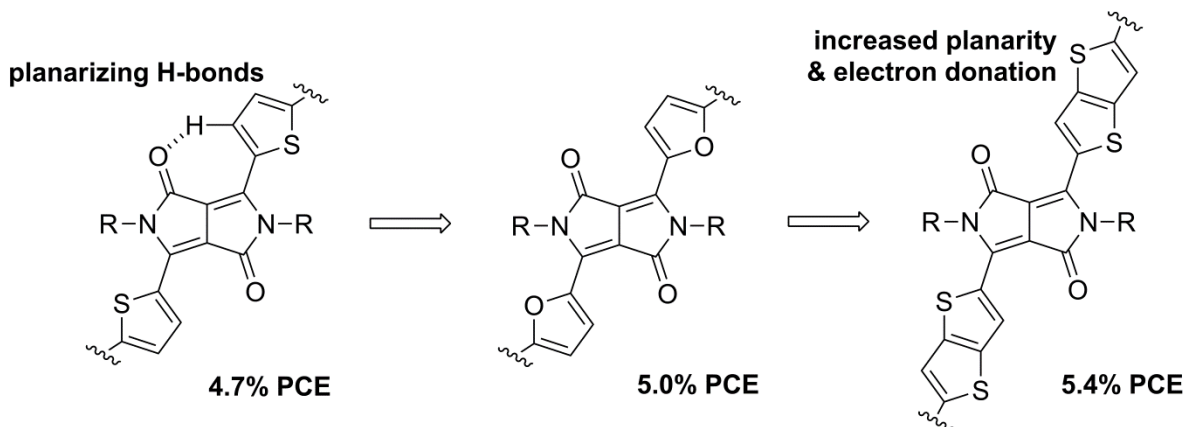
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11 **Figure 1.** A schematic of the donor-acceptor alternating copolymer structure used in high-  
 12 performance donor materials and in example **PMDPP3T**.



13

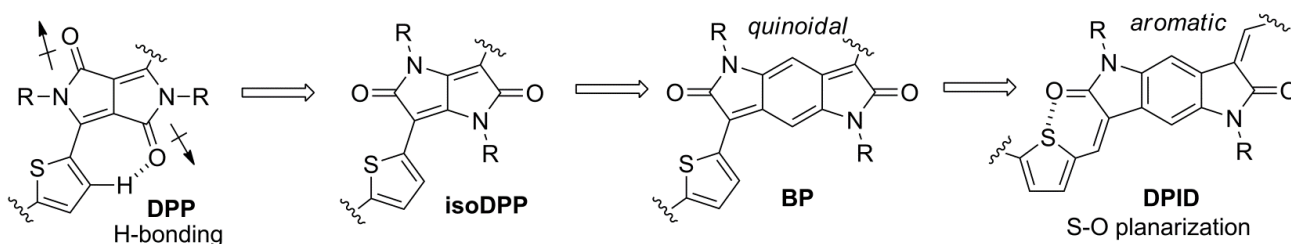
14 **Figure 2.** Bulk heterojunction photovoltaic cell operation: (left) a schematic of the energy  
 15 levels illustrating exciton formation, splitting and charge transport; and, (right) a simple  
 16 device architecture; ITO = indium tin oxide.



1

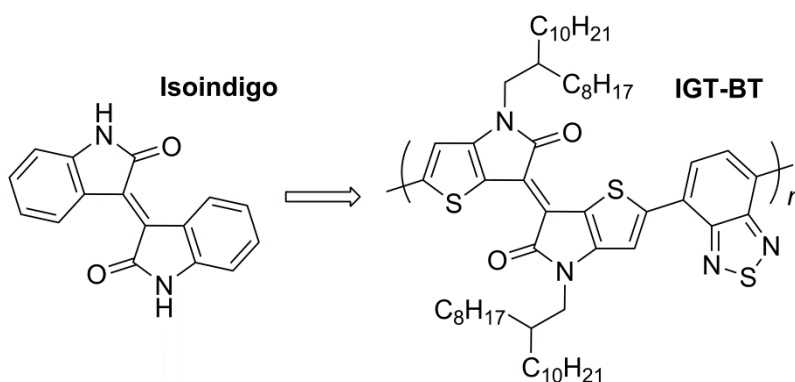
2 **Figure 3.** Varying the flanking aromatics on the **DPP** bis-lactam core: aromatic, fused  
 3 thienothiophene is more electron rich and induces greater planarity along the conjugated  
 4 polymer backbone, resulting in improved photovoltaic performance.

5



6 **Figure 4.** The development of *N*-alkylated, planar electron-deficient acceptor units for  
 7 donor-acceptor copolymers: the quinoidal form enhances charge transport when used in  
 8 the photoactive layer of organic bulk heterojunction photovoltaic cells.

9



10 **Figure 5.** Isoindigo and its thiophene analogue polymerized with benzothiadiazole to give  
 11 **IGT-BT.**

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## 1 REFERENCES

- 2 [1] Zhou, H.; Yang, L.; You, W. *Macromolecules* 45 (2012) 607.
- 3 [2] Facchetti, A. *Chem. Mater.* 23 (2011) 733.
- 4 [3] Beaujuge, P. M.; Fréchet, J. M. J. *J. Am. Chem. Soc.* 133 (2011) 20009.
- 5 [4] Yan, H.; Chen, Z. H.; Zheng, Y.; Newman, C.; Quinn, J. R.; Dötz, F.; Kastler, M.;  
6 Facchetti, A. *Nature* 457 (2009) 679.
- 7 [5] M. Pagliaro, G. Palmisano, R. Ciriminna, *Flexible Solar Cells*; Wiley-VCH: Weinheim,  
8 2008.
- 9 [6] T. A. Skotheim, J. R. Reynolds, Eds; *Handbook of Conducting Polymers*, 3<sup>rd</sup> ed.; CRC  
10 Press: Boca Raton, Florida, USA, 2007.
- 11 [7] Dang, M. T.; Hirsch, L.; Wantz, G.; Wuest, J. D. *Chem. Rev.* 133 (2013) 3734.
- 12 [8] Khlyabich, P. P.; Burkhart, B.; Rudenko, A. E.; Thompson, B. C. *Polymer* 54 (2013)  
13 5267.
- 14 [9] Ma, W.; Yang, C.; Gong, X.; Lee, K.; Heeger, J. A. *Adv. Funct. Mater.* 15 (2005) 1617.
- 15 [10] You, J.; Dou, L.; Yoshimura, K.; Kato, T.; Ohya, K.; Moriarty, T.; Emery, K.; Chen,  
16 CC.; Gao, J.; Li, G.; Yang, Y. *Nature Communications* 4 (2013) 1446.
- 17 [11] Brabec, C. J.; Gowrisanker, S.; Halls, J. J. M.; Laird, D.; Jia, S.; Williams, S. P. *Adv.*  
18 *Mater.* 22 (2010) 3839.
- 19 [12] Guldi, D. N.; Illescas, B. M.; Atienza, C. M.; Wielopolski, M.; Martin, N. *Chem. Soc.*  
20 *Rev.* 38 (2009) 1587.
- 21 [13] (Non-fullerene acceptors) Sonar, P.; Lim, J. P. F.; Chan, K. L. *Energy Environ. Sci.* 4  
22 (2011) 1558.
- 23 [14] (Polymeric acceptors) Facchetti, A. *Materials Today* 16 (2013) 123.
- 24 [15] Li, W.; Furlan, A.; Hendriks, K. H.; Wienk, M. M.; Janssen, R. A. J.; *J. Am Chem. Soc.*  
25 135 (2013) 5529.

- 1 [16] Zhicai, H.; Zhong, C.; Su, S.; Xu, M.; Wu, H.; Cao, Y. *Nature Photonics* 6 (2012) 591.
- 2 [17] Janssen, R. A. J.; Nelson, J. *Adv. Mater.* 25 (2013) 1847.
- 3 [18] Chocos, C. L.; Choulis, S. A. *Prog. Polym. Sci.* 36 (2011) 1326.
- 4 [19] Brabec, C. J.; Heeney, M.; McCulloch, I.; Nelson, J. *Chem. Soc. Rev.* 40 (2011) 1185.
- 5 [20] Nielsen, C. B.; Turbiez, M.; McCulloch, I. *Adv. Mater* 25 (2013) 1859.
- 6 [21] Robb, M. J.; Ku, S-Y.; Brunetti, F. G.; Hawker, C. J. *J. Polym. Sci. Pol. Chem*, 51  
7 (2013) 1263.
- 8 [22] Li, Y.; Sonar, P.; Murphy, L.; Hong, W. *Energy Environ. Sci.* 6 (2013) 1684.
- 9 [23] Chandran, D.; Lee, K-S. *Macromol. Res.* 21 (2013) 272.
- 10 [24] Chen, Z.; Lee, M. J.; Ashraf, R. S.; Gu, Y.; Albert-Seifried, S.; Meedom Nielsen, M.;  
11 Schroeder, B.; Anthopoulos, T. D.; Heeney, M.; McCulloch I.; Siringhaus, H. *Adv.*  
12 *Mater.* 24 (2012) 647.
- 13 [25] Bronstein, H.; Chen, Z.; Ashraf, R. S.; Zhang, W.; Du, J.; Durrant, J. R.; Shakya  
14 Tuladhar, P.; Song, K.; Watkins, S. E.; Geerts, Y.; Wienk, M. M.; Janssen, R. A.;  
15 Anthopoulos, T.; Siringhaus, H.; Heeney, M.; McCulloch, I. *J. Am. Chem. Soc.* 133  
16 (2011) 3272.
- 17 [26] Zhang, X.; Richter, L. J.; DeLongchamp, D. M.; Kline, R. J.; Hammond, M. R.;  
18 McCulloch, I.; Heeney, M.; Ashraf, R. S.; Smith, J. N.; Anthopoulos, T.; Schroeder, B.;  
19 Geerts, Y. H.; Fischer, D. A.; Toney, M. F. *J. Am. Chem. Soc.* 133 (2011) 15073.
- 20 [27] Yiu, A. T.; Beaujuge, P. M.; Lee, O. P.; Woo, C. H.; Toney, M. F.; Fréchet, J. M. J. *J.*  
21 *Am. Chem. Soc.* 134 (2012) 2180.
- 22 [28] Kanimozhi, C.; Yaacobi-Gross, N.; Chou, K. W.; Amassian, A.; Anthopoulos, T. D.;  
23 Patil, S. *J. Am. Chem. Soc.* 134 (2012) 16532.
- 24 [29] Guo, X.; Zhang, M.; Huo, L.; Cui, C.; Wu, Y.; Hou, J.; Li, Y. *Macromolecules* 45 (2012)  
25 6930.

- 1 [30] Bijleveld, J. C.; Zoombelt, A. P.; Mathijssen, S. G. J.; Wienk, M. M.; Turbiez, M.; de  
2 Leeuw, D. M.; Janssen, R. A. J. *J. Am. Chem. Soc.* 131 (2009) 16616.
- 3 [31] Woo, C. H.; Beaujuge, P. M.; Holcombe, T. W.; Lee, O. P.; Frechet, J. M. J. *J. Am.*  
4 *Chem. Soc.* 132 (2010) 15547.
- 5 [32] Bronstein, H.; Chen, Z.; Ashraf, R. S.; Zhang, W.; Du, J.; Durrant, J. R.; Tuladhar, P.  
6 S.; Song, K.; Watkins, S. E.; Geerts, Y.; Wienk, M. M.; Janssen, R. A. J.; Anthopoulos,  
7 T.; Siringhaus, H.; Heeney, M.; McCulloch, I. *J. Am. Chem. Soc.* 133 (2011) 3272.
- 8 [33] Li, W.; Roelofs, W. S. C.; Wienk, M. M.; Janssen, R. A. J. *J. Am. Chem. Soc.* 134  
9 (2012) 13787.
- 10 [34] Shahid, M.; Ashraf, R. S.; Huang, Z.; Kronemeijer, A. J.; McCarthy-Ward, T.;  
11 McCulloch, I.; Durrant, J. R.; Siringhaus, H.; Heeney, M. *J. Mater. Chem.* 22 (2012)  
12 12817.
- 13 [35] Welterlich, I.; Charov, O.; Tieke, B. *Macromolecules* 45 (2012) 4511.
- 14 [36] Lu, S.; Drees, M.; Yao, Y.; Boudinet, D.; Yan, H.; Pan, H.; Wang, J.; Li, Y.; Usta, H.;  
15 Facchetti, A. *Macromolecules* 46 (2013) 3895.
- 16 [37] Weibin, C.; Yuen, J.; Wudl, F. *Macromolecules* 44 (2011) 7869.
- 17 [38] Deng, P.; Liu, L.; Ren, S.; Li, H.; Zhang, Q. *Chem. Commun.* 48 (2012) 6960.
- 18 [39] Hong, W.; Guo, C.; Li, Y.; Zheng, Y.; Huang, C.; Lu, S.; Facchetti, A. *J. Mater. Chem.*  
19 22 (2012) 22282.
- 20 [40] J. W. Rumer; S-Y. Dai; M. Levick; S. Rossbauer; Z. Huang; L. Biniek; T. Anthopoulos;  
21 J. R. Durrant; D. J. Procter; I. McCulloch, I. *Chem. Commun.* 49 (2013) 4465.
- 22 [41] Rumer, J. W.; Dai, S-Y.; Levick, M.; Biniek, L.; Procter, D. J.; McCulloch, I. *J. Polym.*  
23 *Sci. Pol. Chem.* 51 (2013) 1285.

- 1 [42] Rumer, J. W.; Dai, S-Y.; Levick, M.; Kim, Y.; Madec, M-B.; Ashraf, R. S.; Huang, Z.;  
2 Rossbauer, S.; Schroeder, B.; Biniek, L.; Watkins, S.; Anthopoulos, T.; Janssen, R. A.  
3 J.; Durrant, J. R.; Procter, D. J.; McCulloch, I. J. *Mat. Chem. C* 1 (2013) 2711.
- 4 [43] Havinga, E. E.; Hoeve, W. T.; Wynberg, H. *Synth. Met.* 55 (1993) 299.
- 5 [44] Chen, H.; Guo, Y.; Yu, G.; Zhao, Y.; Zhang, J.; Gao, D.; Liu, H.; Liu, Y. *Adv. Mater.* 24  
6 (2012) 4618.
- 7 [45] Shoaee, S.; Clarke, T. M.; Huang, C.; Barlow, S.; Marder, S. R.; Heeney, M.;  
8 McCulloch, I.; Durrant, J. R. *J. Am. Chem. Soc.* 132 (2010) 12919.
- 9 [46] Ashraf, R. S.; Kronemeijer, A. J.; James, D. I.; Siringhaus, H.; McCulloch I., *Chem.*  
10 *Commun.* 48 (2012) 3939.
- 11 [47] de Leeuw, D. M.; Simenon, M. M. J.; Brown, A. R.; Einerhand, R. E. F. *Synth. Met.* 87  
12 (1997) 53.
- 13 [48] E. Wang, Z. Ma, Z. Zhang, K. Vandewal, P. Henriksson, O. Inganäs, F. Zhang, M. R.  
14 Andersson, *J. Am. Chem. Soc.* 133 (2011) 14244.
- 15 [49] Mayer, A. C.; Toney, M. F.; Scully, S. R.; Rivnay, J.; Brabec, C. J.; Scharber, M.;  
16 Koppe, M.; Heeney, M.; McCulloch, I.; McGehee, M. D. *Adv. Funct. Mater.* 19 (2009)  
17 1173.
- 18 [50] Piliago, C.; Holcombe, T. W.; Douglas, J. D.; Woo, C. H.; Beaujuge, P. M.; Frechet, J.  
19 M. J. *J. Am. Chem. Soc.* 132 (2010) 7595.
- 20 [51] Yang, L. Q.; Zhou, H. X.; You, W. J. *Phys. Chem. C* 114 (2010) 16793.
- 21 [52] Bronstein, H.; Leem, D. S.; Hamilton, R.; Woebkenberg, P.; King, S.; Zhang, W.;  
22 Ashraf, R. S.; Heeney, M.; Anthopoulos, T. D.; de Mello, J.; McCulloch, I.  
23 *Macromolecules* 44 (2011) 6649.
- 24 [53] Lee, J.; Han, A-R.; Kim, J.; Kim, Y.; Oh, J. H.; Yang, C. *J. Am. Chem. Soc.* 134 (2012)  
25 20713.

- 1 [54] Schilinsky, P.; Asawapirom, U.; Scherf, U.; Biele, M.; Brabec, C. J. Chem. Mater. 17  
2 (2005) 2175.
- 3 [55] Kline, R. J.; McGehee, M. D.; Kadnikova, E. N.; Liu, J.; Frechet, J. M J.; Toney, M. F.  
4 Macromolecules 38 (2005) 3312.
- 5 [56] Ashraf, R. S., Schroeder, B. C., Bronstein, H. A., Huang, Z., Thomas, S., Kline, R. J.,  
6 Brabec, C. J., Rannou, P., Anthopoulos, T. D., Durrant, J. R.; McCulloch, I. Adv.  
7 Mater. 25 (2013) 2029.
- 8 [57] Price, C. J.; Stuart, A. C.; Yang, L.; Zhou, H.; You, W. J. Am. Chem. Soc. 133 (2011)  
9 4625.
- 10 [58] McCormick, T. M.; Bridges, C. R.; Carrera, E. I.; DiCarmine, P. M.; Gibson, G. L.;  
11 Hollinger, J.; Kozycz, L. M.; Seferos, D. S. Macromolecules 46 (2013) 3879.
- 12 [59] Kirkpatrick, J.; Nielsen, C. B.; Zhang, W.; Bronstein, H.; Ashraf, R. S.; Heeney, M.;  
13 McCulloch, I. Adv. Energy Mater. 2 (2012) 260.
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