

# Efficient Small Molecule Bulk Heterojunction Solar Cells with High Fill Factors via Pyrene-Directed Molecular Self-Assembly

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Organic photovoltaics (OPVs) are a promising technology for cost-effective and scalable production of renewable energy.<sup>[1]</sup> Current research in OPV materials focuses primarily on the design and synthesis of semiconducting polymers capable of both light absorption and charge transport. In OPV cells utilizing a bulk heterojunction (BHJ) architecture, conjugated polymers have demonstrated promising device efficiency; however, they can suffer from drawbacks such as batch-to-batch variation and chain-end contamination, which can reduce overall performance and device consistency.<sup>[2a,3]</sup>

In order to develop OPV materials that exhibit not only favorable electronic properties but also batch-to-batch consistency, electroactive small molecules have recently received attention as alternatives to polymers.<sup>[2]</sup> While small molecules can be synthesized and solution-processed into devices just like polymers, they do not suffer from the inherent polydispersity of polymeric materials. They can be synthesized and purified as single molecular entities, thus eliminating the sort of device variability that can arise from material inhomogeneity. Despite these potential advantages, current data shows that the photovoltaic efficiencies of small molecules lag behind those of the highest-performing polymers.<sup>[3,4]</sup>

The relatively low performance of small molecules may be attributed to their limited interconnectivity through the active layer, resulting in low device fill factors. Earlier studies<sup>[5,6]</sup> have shown that polymers with higher molecular weight ( $M_n$ ) perform better in BHJ solar cells than lower  $M_n$  polymers. In low  $M_n$  polymers, charge transport is limited by the short chain length.<sup>[5a]</sup> By extension, as small molecules represent the lower limit of  $M_n$ , their device performance can suffer from inadequate

interconnectivity and inefficient charge extraction. Herein, we demonstrate that the interconnectivity of small molecule semiconductors can be greatly improved by directed molecular self-assembly. Small molecules designed with this principle are shown to form highly ordered and interconnected domains and exhibit large fill factors and efficiencies in OPV devices.

We postulated that the introduction of  $\pi$ -stacking moieties onto the ends of small molecules would facilitate favorable end-to-end  $\pi$ - $\pi$  interactions, leading to enhanced charge transport between adjacent molecules. To investigate this approach, a series of small molecules was synthesized, each with different electron-rich end-groups (**Figure 1**). End-groups were selected for their varying degrees of planarity, which can affect their tendency to  $\pi$ -stack. Triphenylamine (TPA) has a non-planar structure with its phenyl groups twisting into a propeller motif.<sup>[7]</sup> Benzo[1,2-*b*;4,5-*b'*]dithiophene (BDT) contains a planar fused ring but has non-coplanar alkoxy substituents. Pyrene is a completely planar moiety and has a strong propensity to  $\pi$ -stack. In addition, the regio-connectivity between pyrene and the chromophoric core was varied in order to study the effect of end-group symmetry. As a platform for investigating the effects of these end-groups, diketopyrrolopyrrole (DPP) was chosen to be the electron-deficient core, since this moiety allows for control of small molecule solution-processability and solid-state molecular ordering through modulation of the *N*-alkyl substituents.<sup>[8]</sup> The DPP core has also demonstrated promising optical properties, charge carrier mobility, and photovoltaic performance in numerous small molecule and polymeric materials;<sup>[3,9,10]</sup> in particular, Nguyen et al. have reported a DPP-containing small molecule donor that achieved 4.4% efficiency with phenyl-C<sub>71</sub>-butyric acid methyl ester (PC<sub>71</sub>BM) in BHJ devices.<sup>[3]</sup>

Syntheses of the small molecules were achieved through Suzuki or Stille cross-coupling reactions to append the end-groups to the DPP core (see Supporting Information, SI).<sup>[3,11]</sup> Notably, the C2-pyrene boronate ester was obtained by Ir(I)-catalyzed C-H functionalization for selective access to the C2 position.<sup>[12]</sup> All four molecules have comparable absorption profiles (**Figure 1**) and HOMO/LUMO energy levels (SI) that are suitable for OPV applications.

To determine the OPV performance of the small molecule materials, thin-film BHJ devices were prepared with the following architecture: ITO/PEDOT:PSS/small molecule:PC<sub>71</sub>BM/Al. Upon extensive device optimization, small molecule **4a** exhibits a notable maximum power conversion efficiency (PCE) of 2.7%, whereas **1**, **2** and **3** exhibit lower device PCEs of 1.3%, 1.7% and 0.7%, respectively (**Table 1**, **Figure 2**). While **1**, **2** and **4a**

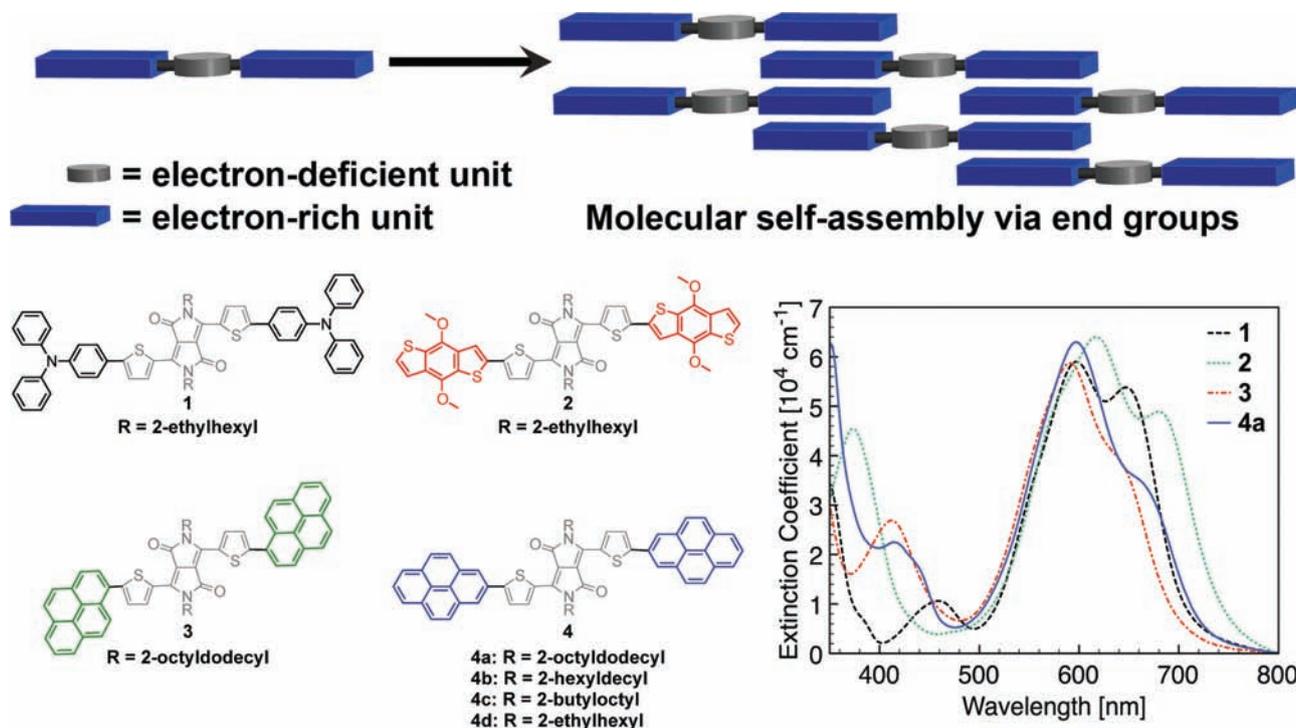
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**Figure 1.** Donor-acceptor small molecules are designed to self-assemble through the electron-rich  $\pi$ -stacking units (top). Molecules **1**, **2**, **3**, and **4** are based on a DPP core moiety flanked by electron-rich end-groups (bottom left). The UV-vis absorption spectra of **1**, **2**, **3**, and **4a** were obtained as thin films (bottom right).

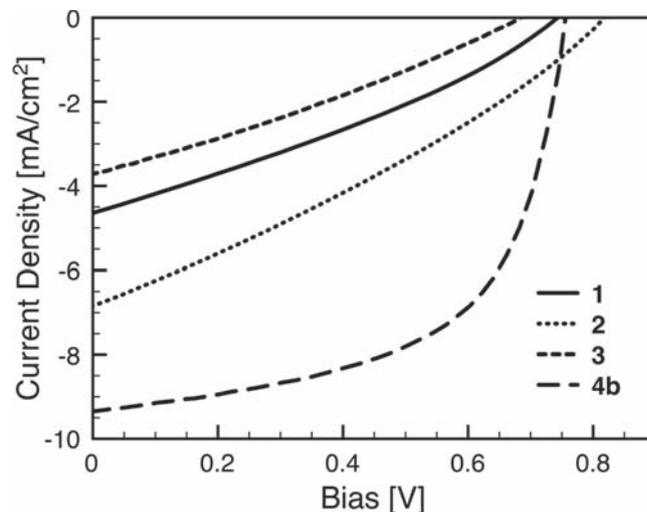
possess similar optoelectronic properties, their varying device performances suggest that PCE is highly dependent on end-group planarity. However, end-group planarity alone does not ensure high device efficiency, as demonstrated by the low PCE of **3**. Changing the site of pyrene substitution from C1 (**3**) to C2 (**4a**) led to an enhancement of device performance, indicating that end-group symmetry can also have a dramatic influence on PCE. Further structural optimization of the C2-pyrene-based molecules was achieved by varying the *N*-alkyl solubilizing side-chains on the core moiety. Previous studies have shown that side-chains can affect crystallinity, intermolecular spacing, and OPV device performance.<sup>[13]</sup> To determine whether shorter alkyl chains could tighten molecular packing and improve OPV

performance, the 2-octyl-dodecyl groups on **4a** were replaced with 2-hexyl-dodecyl (**4b**), 2-butyloctyl (**4c**), and 2-ethylhexyl (**4d**) groups. Molecule **4b** exhibits the highest PCE (4.1% max.) in this series and has the one of the highest fill factors (0.58) for a solution-processed small molecule OPV system.<sup>[14]</sup> Further decreasing the size of the alkyl groups resulted in limited solubility and processing challenges, giving **4c** a lower device performance than **4b**. Molecule **4d** lacked sufficient solubility to be processed into a functional device.

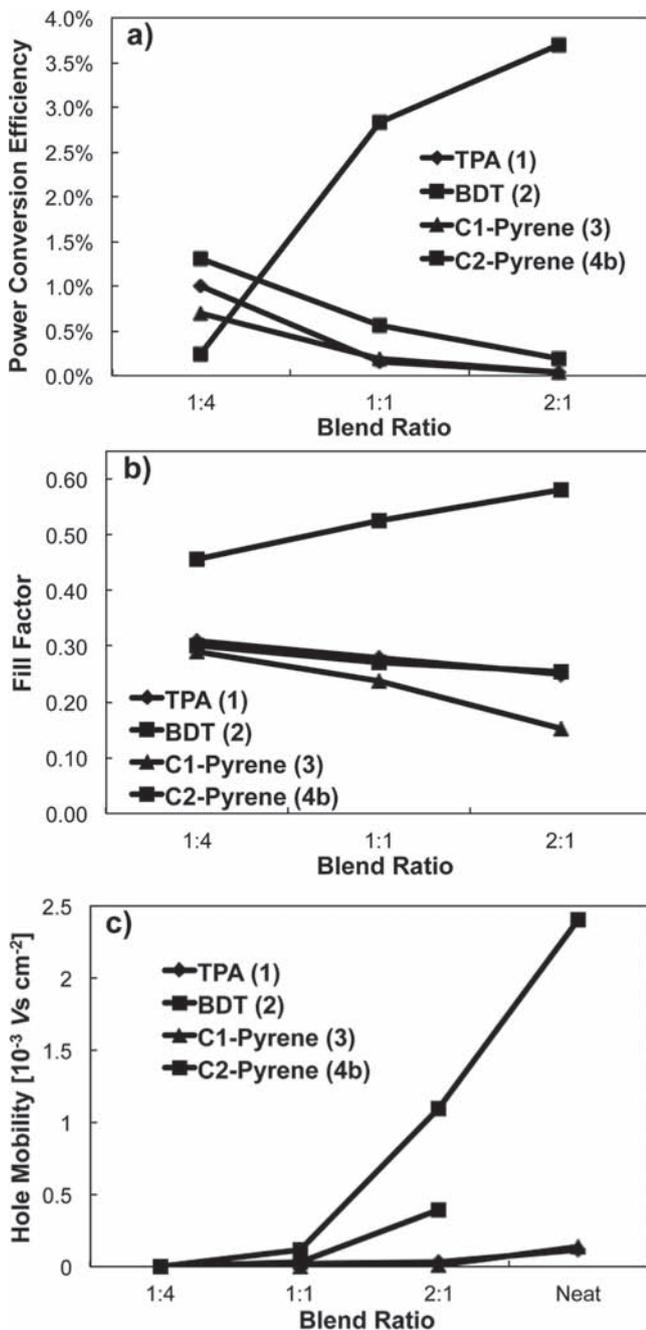
**Table 1.** Average PV performance of 1–4 blended with PC<sub>71</sub>BM.

Blend	Ratio <sup>a)</sup>	$J_{sc}$ <sup>e)</sup> [mA cm <sup>-2</sup> ]	$V_{oc}$ <sup>f)</sup> [V]	FF <sup>g)</sup>	PCE [%]	Max. PCE [%]
<b>1</b>	1:4 <sup>b)</sup>	-4.3	0.73	0.31	1.0	1.3
<b>2</b>	1:4 <sup>c)</sup>	-6.2	0.81	0.30	1.3	1.7
<b>3</b>	1:4 <sup>b)</sup>	-3.2	0.73	0.29	0.7	0.7
<b>4a</b>	2:1 <sup>b)</sup>	-5.7	0.77	0.55	2.4	2.7
<b>4b</b>	2:1 <sup>b)</sup>	-8.3	0.76	0.58	3.7	4.1
<b>4c</b>	2:1 <sup>d)</sup>	-6.6	0.78	0.48	2.4	3.0

<sup>a)</sup>Mass ratio of small molecule donor to PC<sub>71</sub>BM; <sup>b)</sup>Devices prepared from solution in chloroform; <sup>c,d)</sup>Devices prepared from solution in mixed solvent: chlorobenzene/1,2-dichlorobenzene ([c] 66.7/ 33.3 v/v; [d] 75/ 25 v/v); <sup>e)</sup> $J_{sc}$  = short-circuit current density; <sup>f)</sup> $V_{oc}$  = open-circuit voltage; <sup>g)</sup>FF = fill factor.

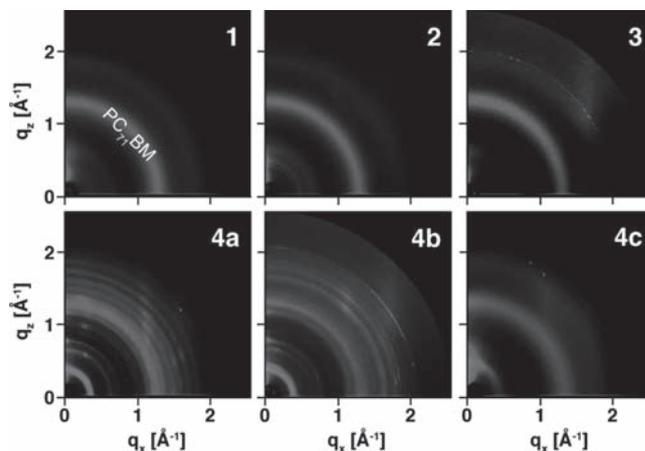


**Figure 2.** Characteristic  $J$ - $V$  curves of solar cells fabricated from **1**, **2**, **3** and **4b** illuminated under AM 1.5 G, 100 mW cm<sup>-2</sup>.



**Figure 3.** Effects of different blend ratios (small molecule:PC<sub>71</sub>BM) on [a] PCE, [b] FF, and [c] space-charge-limited current (SCLC) hole mobility of the devices fabricated from molecules 1, 2, 3 and 4b. As donor content increases, the FF and PCE are enhanced only in molecules with C2-pyrene end-groups.

As shown in Table 1 and Figure 2, the high device PCE of C2-pyrene-based molecules can be mainly attributed to their high fill factors (FFs). FF is known to depend largely on carrier mobility, charge recombination, current leakage, and balanced transport of holes and electrons through the device active layer.<sup>[1,14a,15]</sup> Molecules 4a and 4b exhibit device FFs of 0.55 and 0.58, whereas molecules 1, 2 and 3 exhibit FFs of 0.29, 0.30 and 0.31, respectively. The high FFs are unique to 4a–4c, even at

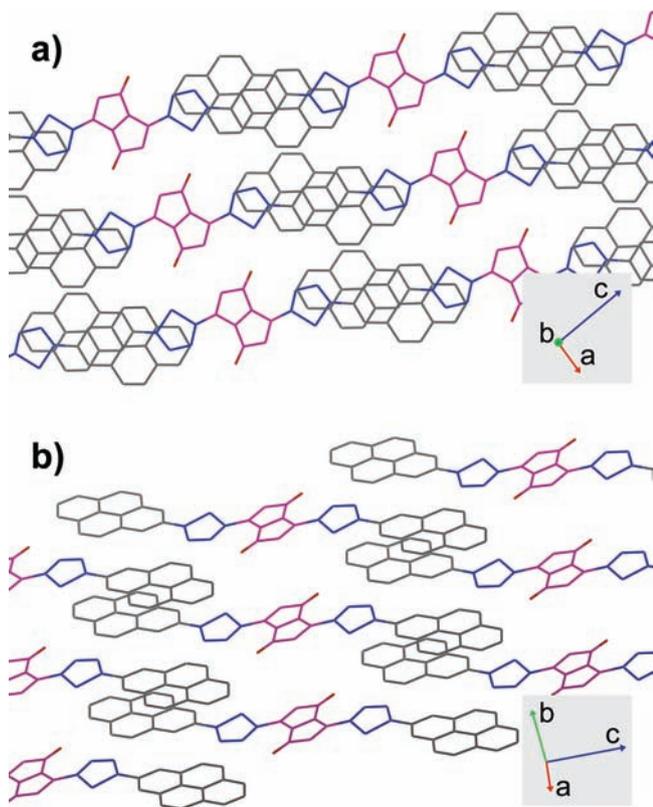


**Figure 4.** 2-D GIXS patterns of thin films of 1, 2, 3 and 4b blended with PC<sub>71</sub>BM, prepared under the same conditions as for optimized device fabrication.

different donor:PC<sub>71</sub>BM ratios (Figure 3b). Devices fabricated with 1, 2 and 3 were optimized at a 1:4 donor:PC<sub>71</sub>BM ratio; further increasing the donor content reduced device FF and PCE even though the hole mobility of these devices increased (Figure 3). In contrast, for molecules containing C2-pyrene end-groups (4a–4c), increasing the donor content enhanced both FF and hole mobility, contributing to the high device efficiency at the optimized ratio of 2:1 donor:PC<sub>71</sub>BM ratio. These results suggest that, relative to the other end-groups studied, the C2-pyrene end-group affects intermolecular interactions which may promote molecular packing and active layer morphology favorable for high device PCE.

To understand how the C2-pyrene end-group can promote molecular assembly, the nanoscale film morphology and solid-state packing of DPP-C2-pyrene were investigated by atomic force microscopy (AFM) and X-ray diffraction. By AFM characterization, the active layers of the thin-film devices fabricated from 1 and 3 appear smooth and relatively amorphous, while the device active layer of 2 exhibits domains approaching the 1- $\mu\text{m}$  length scale. In contrast, the device active layers of 4a and 4b display a network of highly-crystalline features sized  $\sim 10$ –30 nm (S1). Grazing-incidence X-ray scattering (GIXS) pattern of a thin-film BHJ of 4b and PC<sub>71</sub>BM shows sharply defined rings and peaks, suggesting that the packing of 4b is both more crystalline and more aligned than that of 1, 2, and 3, whose scattering patterns indicate relatively amorphous films (Figure 4). Single crystal X-ray analysis of 4a shows a closely-packed, interdigitated crystal structure with extensive overlap of C2-pyrene moieties (Figure 5). The interplanar distance between two pyrene units is 3.50  $\text{\AA}$ , confirming strong face-to-face  $\pi$ – $\pi$  interaction between molecules. With this packing configuration, charges can move both parallel ( $c$  direction) and perpendicular ( $b$  direction) to the long-axis of the molecule, which accounts for the high hole mobilities measured for 4b.

In summary, we demonstrate that efficient OPV materials can be constructed by the attachment of completely planar, symmetric end-groups to electroactive small molecules. Appending C2-pyrene as the small molecule end-group results in materials with tight, aligned crystal packing and favorable



**Figure 5.** (a) View down the *b*-axis and (b) an angle view of the single crystal structure of **4a**, as determined by X-ray crystallography. Alkyl side chains are omitted for clarity. The pyrene-pyrene interplanar distance is  $\sim 3.50$  Å, confirming close  $\pi$ - $\pi$  stacking between pyrene moieties.

morphology dictated by  $\pi$ - $\pi$  interactions. The intermolecular connectivity promoted by C2-pyrene allows devices containing blends of **4b** and PC<sub>71</sub>BM to reach a maximum PCE above 4% with a FF approaching 0.6. This device FF is one of the highest values reported to date in high-performing small molecule BHJ OPVs. The use of end-groups to direct molecular self-assembly represents an effective strategy for designing high-performance small molecule OPV devices.

## Supporting Information

Supporting Information includes details of small molecule synthesis, device preparation, and characterization and is available from the Wiley Online Library or from the author.

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