

Tuning the Properties of Polymer Bulk Heterojunction Solar Cells by Adjusting Fullerene Size to Control Intercalation

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ABSTRACT

We demonstrate that intercalation of fullerene derivatives between the side chains of conjugated polymers can be controlled by adjusting the fullerene size and compare the properties of intercalated and nonintercalated poly(2,5-bis(3-hexadecylthiophen-2-yl)thieno[3,2-b]thiophene (pBTTT):fullerene blends. The intercalated blends, which exhibit optimal solar-cell performance at 1:4 polymer:fullerene by weight, have better photoluminescence quenching and lower absorption than the nonintercalated blends, which optimize at 1:1. Understanding how intercalation affects performance will enable more effective design of polymer:fullerene solar cells.

Polymer:fullerene bulk heterojunction (BHJ) organic solar cells have achieved power conversion efficiencies up to 6.8% and are attracting a great deal of attention as a potential low-cost alternative to traditional inorganic photovoltaics.^{1–5} Mayer et al. recently demonstrated that fullerene derivatives intercalate between the polymer side chains in some polymer:fullerene blends (Figure 1) and showed that intercalation plays a key role in determining the optimal polymer:fullerene ratio since fullerenes must fill all available space between the polymer side chains prior to the formation of a pure electron-transporting fullerene phase in blends with intercalation.⁶ Intercalation also likely affects important device characteristics such as light absorption, photoluminescence, and recombination due to the molecular mixing of the donor and acceptor in the intercalated phase and the different polymer:fullerene ratios for optimized blends with and without intercalation. It is important to understand how intercalation affects device performance so that new devices can be designed with intercalation in mind. In this letter, we demonstrate the ability to control intercalation by adjusting the size of the fullerene derivatives. We compare intercalated and nonintercalated blends that use the same polymer, poly(2,5-bis(3-hexadecylthiophen-2-yl)thieno[3,2-b]thiophene (pBTTT)⁷ with C16 side chains, and similar fullerene derivatives, phenyl-c71-butyric acid methyl ester

(PC₇₁BM) (NanoC) and its bisadduct bisPC₇₁BM (Solenne),⁸ so that differences due to factors other than intercalation are minimized (Figure 1).

Because intercalation causes an increase in the lamellar spacing of the polymer as shown in Figure 1, X-ray diffraction can be used to determine if intercalation occurs in crystalline and semicrystalline polymer:fullerene blends.⁶ Specular X-ray diffraction (Figure 2) was performed on pure pBTTT, pBTTT:PC₇₁BM and pBTTT:bisPC₇₁BM films at beamline 2-1 at the Stanford Synchrotron Radiation Light-source (SSRL). All films were spin-cast from ortho-dichlorobenzene (ODCB) onto octadecyltrichlorosilane (OTS)-coated silicon substrates, slow dried in a covered Petri dish and annealed at 180 °C for 10 min. Coating the substrates with OTS and annealing at 180 °C increase the crystalline order but do not significantly affect the peak positions as shown in the Supporting Information. Pure pBTTT has a lamellar spacing of 23.5 Å. Blending PC₇₁BM with pBTTT increases this spacing to 30.6 Å, indicating that intercalation occurs in pBTTT:PC₇₁BM blends. On the other hand, blending bisPC₇₁BM with pBTTT does not increase the lamellar spacing, showing that this fullerene derivative does not intercalate, most likely because the extra side group, which can be attached to the fullerene at a number of different locations, makes bisPC₇₁BM too large to fit between the polymer side chains (Figure 1c).⁸

Solar cells were prepared on poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS)-covered indium tin oxide (ITO)-coated glass substrates (Thin Film Devices)

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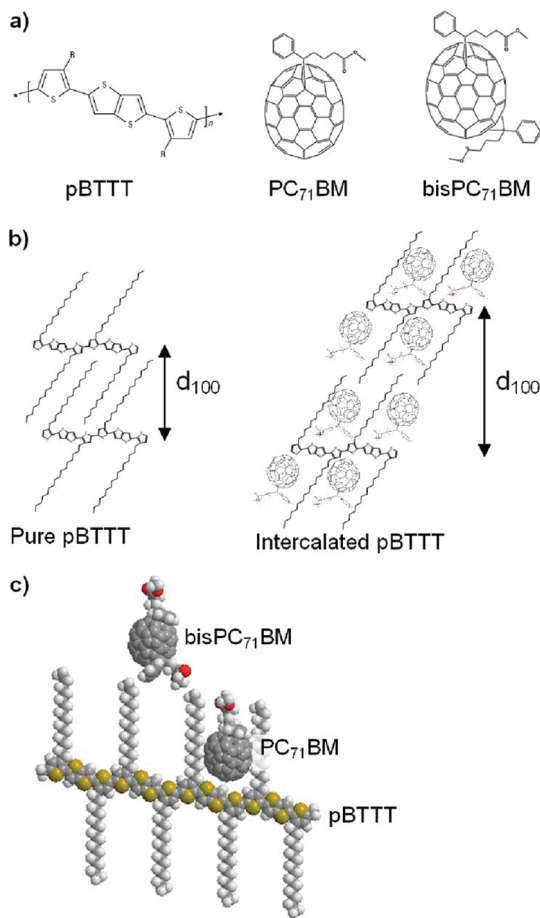


Figure 1. Molecular structures of pBTTT, PC₇₁BM, and bisPC₇₁BM (a), schematics showing possible structures for pure and intercalated pBTTT (b), and a space-filling ChemDraw model of pBTTT, PC₇₁BM, and bisPC₇₁BM to show their relative sizes (c). The second side group on bisPC₇₁BM can attach to the fullerene at a number of different locations.

as described in ref 9. The pBTTT:PC₇₁BM and pBTTT:bisPC₇₁BM active layers were spin-cast from solutions at 60 °C with total concentrations of 24 mg/mL in ODCB and slow dried in a covered Petri dish. The 1:4 pBTTT:PC₇₁BM and 1:1 pBTTT:bisPC₇₁BM active layers were 100 and 135 nm thick, respectively. The pBTTT:bisPC₇₁BM films were annealed at 110 °C for 10 min by placing the samples directly on a hot plate, but the pBTTT:PC₇₁BM films were not annealed since annealing decreased the performance of these blends. Seven nanometers of Ca and 100 nm of Al were evaporated onto the samples to form top electrodes with areas of approximately 0.075 cm². The blend ratios, annealing temperatures and times, drying conditions, and other processing parameters that were varied to optimize the efficiencies of these pBTTT blend solar cells are summarized in the Supporting Information.

Figure 3 shows current–voltage measurements for pBTTT:PC₇₁BM and pBTTT:bisPC₇₁BM solar cells with 1:1 and 1:4 polymer:fullerene weight ratios carried out under simulated AM1.5 conditions. The 1:1 pBTTT:PC₇₁BM cells have very low efficiencies near 0.25%, owing mostly to a low short-circuit current of 1.39 mA/cm². The low current and the resulting low efficiency can be attributed to the inability of

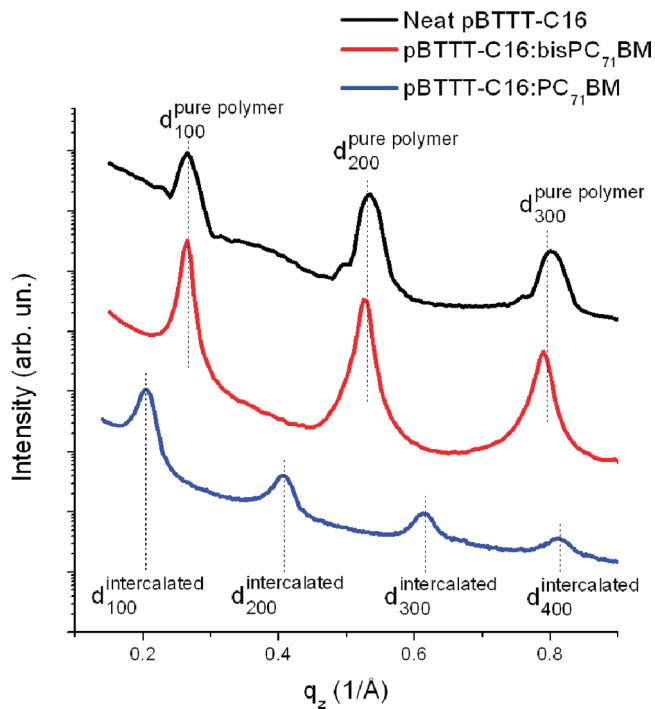


Figure 2. Specular X-ray diffraction patterns for pure pBTTT (black), pBTTT:bisPC₇₁BM (red), and pBTTT:PC₇₁BM (blue). The small peaks in the pure pBTTT pattern are finite thickness fringes.

electrons to be extracted from the device due to the absence of an electron-conducting phase (pure fullerene). Mayer et al. have shown that the electron field-effect transistor mobility is too low to be measured in pBTTT:PC₇₁BM blends with less than 50 wt % PC₇₁BM.⁶ The 1:4 pBTTT:PC₇₁BM blends, which exhibit efficiencies up to 2.51%, have significantly higher efficiencies than the 1:1 blends, primarily because of a considerable increase in the short-circuit current due to the presence of both an electron-conducting phase (pure fullerene) and a hole-conducting phase (intercalated polymer) that enables the extraction of both electrons and holes from the device. The observation of optimal performance at a 1:4 ratio is consistent with Mayer's conclusion that blends with intercalation, including phenyl-c61-butyric acid methyl ester (PC₆₁BM) blends with pBTTT and poly(2-methoxy-5-(3',7'-dimethyloctyloxy)-p-phenylene vinylene) (MDMO-PPV), optimize near a 1:4 ratio so that there are approximately equal volumes of the intercalated phase, which has about one fullerene per monomer, and the pure fullerene phase.^{4,6,9,10}

On the other hand, in the pBTTT:bisPC₇₁BM system, the 1:1 blends outperform the 1:4 blends (Figure 3b). Because intercalation does not occur in these blends, an electron-conducting phase (pure fullerene) forms even at low concentrations of bisPC₇₁BM. A continuous, interpenetrating network of the hole-conducting phase (pure polymer) and electron-conducting phase (pure fullerene), which is required to extract charges from the device, therefore forms near a 1:1 ratio. The addition of extra fullerene, such as in the case of the 1:4 pBTTT:bisPC₇₁BM blend, serves only to dilute the hole-conducting material. The 1:4 pBTTT:bisPC₇₁BM

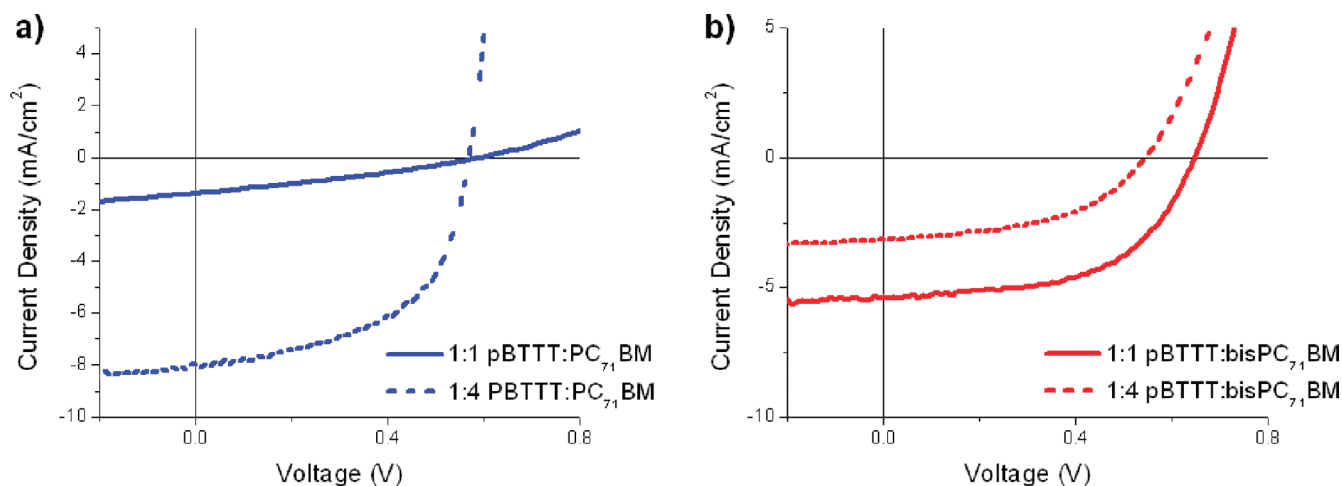


Figure 3. Current–voltage measurements for 1:1 (solid lines) and 1:4 (dashed lines) blends of pBTTT:bisPC₇₁BM (a) and pBTTT:PC₇₁BM (b). The best 1:1 pBTTT:bisPC₇₁BM blends had $J_{SC} = 5.35$ mA/cm², $V_{OC} = 0.645$ V, FF = 0.56, and $\eta = 1.94\%$, and the best 1:4 pBTTT:PC₇₁BM blends had $J_{SC} = 7.99$ mA/cm², $V_{OC} = 0.565$ V, FF = 0.55, and $\eta = 2.51\%$.

blends still show modest performance (0.85% power conversion efficiency) since both electron- and hole-conducting phases exist, albeit in nonoptimal ratios.

To determine the effects of intercalation on pBTTT: fullerene blend device performance, we now compare the best intercalated blend (1:4 pBTTT:PC₇₁BM) with the best nonintercalated blend (1:1 pBTTT:bisPC₇₁BM). The best cells with intercalation are 2.51% efficient, while the best cells without intercalation are 1.94% efficient. The better performance of the intercalated devices is mainly due to a higher short-circuit current of 7.99 versus 5.35 mA/cm² for the nonintercalated devices. The open-circuit voltage of the nonintercalated devices is approximately 80 mV higher than that of the intercalated devices. This difference is most likely due to a higher LUMO of bisPC₇₁BM relative to that of PC₇₁BM, since the open-circuit voltage scales with the difference between the LUMO of the acceptor and the HOMO of the donor. Although the LUMO level of bisPC₇₁BM has not been measured, we expect the difference between the LUMO levels of PC₇₁BM and bisPC₇₁BM to be similar to the difference between the LUMO levels of PC₆₁BM (3.8 eV) and bisPC₆₁BM (3.7 eV).⁸

The absorption spectra of the blends, shown in Figure 4a, demonstrate that the amount of light absorbed by the polymer (absorption centered around 530 nm) and by the fullerene (absorption below about 350 nm) scales roughly with the polymer:fullerene ratio. Since the polymer absorbs the majority of the light, the nonintercalated 1:1 pBTTT:bisPC₇₁BM blend absorbs more light than the intercalated 1:4 pBTTT:PC₇₁BM blend due to the higher polymer concentration at a 1:1 ratio. When there is intercalation, the blends optimize at a higher fullerene ratio, so the light-absorbing polymer is diluted, resulting in decreased absorption. This observation cannot explain the higher current in the intercalated blends versus the nonintercalated blends, since the nonintercalated blends absorb more light but have lower currents.

Photoluminescence (PL) is often used as an indicator of how well excitons can diffuse to a donor–acceptor interface, where they can be split into free charges, since PL occurs when the excitons recombine emissively prior to splitting.^{11,12} Figure 4b shows the PL of pure pBTTT and the pBTTT: fullerene blends when excited with an argon laser at a wavelength of 488 nm. The PL of pure pBTTT is virtually 100% quenched in the intercalated 1:4 pBTTT:PC₇₁BM blends. This almost complete PL quenching is most likely due to the intimate mixing of the polymer and fullerene in the intercalated phase, so that excitons originating on a polymer chain are generated within angstroms of a donor–acceptor interface. The close proximity of the polymer and fullerene in the intercalated phase effectively causes a significant increase in the donor–acceptor interfacial area. As a result, almost all of the excitons in the intercalated phase split, reducing emissive recombination. It remains unclear if electrons originating on intercalated fullerenes can be extracted from the device and contribute to the photocurrent. Nearly complete PL quenching has also been observed in fullerene blends with poly(3,3′′-dialkylquaterthiophene) (PQT), which exhibits intercalation, and MDMO-PPV, which is suspected to exhibit intercalation.^{6,13}

In the nonintercalated 1:1 pBTTT:bisPC₇₁BM blends, 92.5% of the pBTTT PL is quenched, which suggests that the majority of the excitons are split in these blends. The slightly lower quenching (compared to pBTTT:PC₇₁BM blends) is probably because most excitons must now diffuse several nanometers through pure polymer domains to reach a polymer:fullerene interface. More excitons therefore recombine emissively prior to reaching an interface. Furthermore, pBTTT is known to form large crystals, so the crystal size may be too large to allow all of the excitons to diffuse to a donor–acceptor interface during their lifetimes.⁷ The lower short-circuit current and external quantum efficiency (EQE) (Figure 4c) of nonintercalated blends relative to those of the intercalated blends can therefore be partially attributed to incomplete exciton harvesting. Nevertheless, the difference in exciton harvesting cannot completely account for the lower

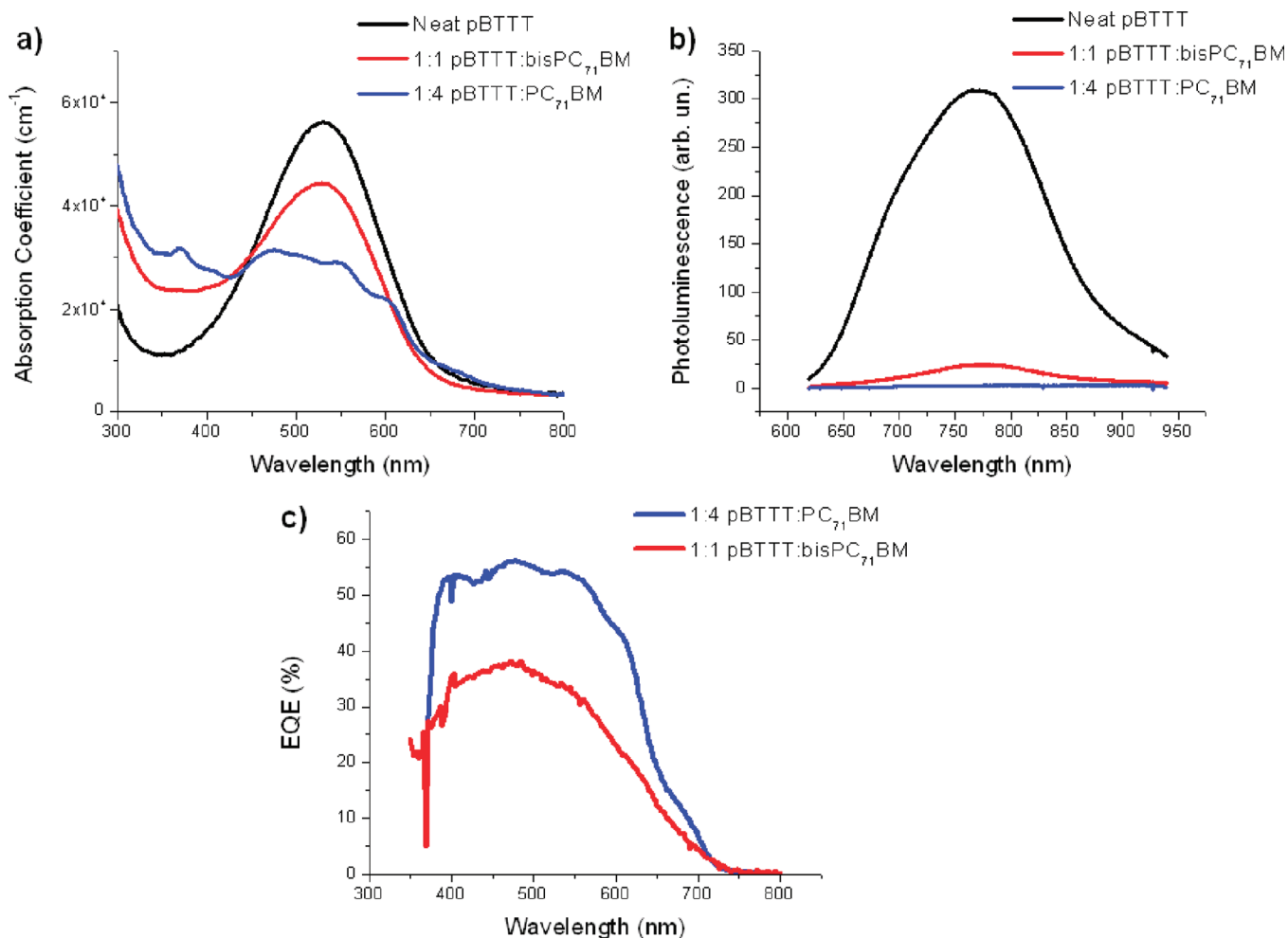


Figure 4. The absorption spectra (a), photoluminescence spectra, which are normalized by the film thicknesses (b), and EQE curves (c) for pure pBTTT (black), 1:1 pBTTT:bisPC₇₁BM (red), and 1:4 pBTTT:PC₇₁BM (blue). The integral of the EQE curves multiplied by the AM 1.5G spectrum gives short-circuit currents of 8.27 and 5.23 mA/cm² for 1:4 pBTTT:PC₇₁BM and 1:1 pBTTT:bisPC₇₁BM, respectively. These currents are within 5% of the observed short-circuit currents.

current in the nonintercalated blends. The additional difference may be explained by a difference in the recombination processes in blends with and without intercalation, since the close proximity of the polymer and fullerene in the intercalated phase is likely to affect recombination.^{14–17} A study to gain a detailed understanding of recombination in the two systems is underway.

In summary, we have compared the properties of pBTTT:fullerene blends with and without intercalation using X-ray diffraction, current–voltage measurements, absorption, and photoluminescence. Although the efficiencies of the intercalated 1:4 pBTTT:PC₇₁BM blends are higher than those of the nonintercalated 1:1 pBTTT:bisPC₇₁BM blends, intercalation may not generally benefit solar-cell performance since intercalation may affect various polymer:fullerene blends differently. However, blends with intercalation will generally have better photoluminescence quenching and lower absorption than nonintercalated blends due to the intimate mixing of the polymer and fullerene on a molecular scale in the intercalated phase and the higher polymer content in the optimized nonintercalated blends. Further knowledge of

intercalation from recombination studies and molecular modeling should lead to a better understanding of the effect of intercalation on solar-cell performance and enable us to determine if intercalation is generally beneficial. This knowledge will allow the design of new polymer:fullerene systems using intercalation as a design parameter, since intercalation can be promoted or inhibited by varying properties such as the side-chain spacing, side-chain branching and fullerene size.

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Supporting Information Available: A summary of the solar-cell optimization parameters and the specular X-ray diffraction patterns of blends annealed at different temperatures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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