Small molecule sensitizers for near-infrared absorption in polymer bulk heterojunction solar cells

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A low band gap small molecule chromophore has been incorporated into a polymer/fullerene bulk heterojunction (BHJ) solar cell yielding increased carrier generation in the near infrared and increased overall short circuit current. The use of a small concentration of a soluble oligothiophene with a diketopyrrolopyrrole core can extend the absorption and photocurrent of poly(3-hexyl thiophene):[6,6]-phenyl C_{71} butyric acid methyl ester solar cells to 800 nm. Photocurrent from the dye embedded within the polymer BHJ is demonstrated, and the use of soluble small molecule sensitizers as a path toward high efficiency solar cells is discussed. © *2008 American Institute of Physics.* [DOI: 10.1063/1.3001802]

Solution processed bulk heterojunction (BHJ) solar cells are emerging as a versatile and low cost alternative to traditional photovoltaic technologies.[1,2] Despite significant recent progress in the synthesis and processing of low band gap polymers, which are capable of absorbing a broad range of solar photons, only a few polymer systems have achieved power conversion efficiencies (PCEs) comparable with devices fabricated from poly(3-hexyl thiophene) (P3HT).[3,4] While P3HT is a nonideal donor polymer in that it has a 2 eV band gap, it was proven highly efficient as well as uniquely robust in terms of accessible processing methods and device lifetimes.[5–7] A possible route to bypass the low performance often observed with low band gap polymers might be to incorporate within a P3HT/fullerene solar cell a low band gap small molecule donor (SMD) with energy levels intermediate to those of polymer and the fullerene.[8,9]

There are several families of solution processable small molecules that have been used as donor materials in BHJ solar cells.[10–12] SMDs often have high mobility, are easily purified, and are more prone to long range order than low band gap polymers.[12] Small molecules in solution, however, may lack the viscosity necessary for film casting via most solution processing techniques and are often prone to unfavorable phase separation in a BHJ structure due to their tendency to crystallize.[3,13]

The SMD material used for these experiments is illustrated in Fig. 1 and will be referred to as SMD1. The details of the material synthesis and characterization will be described elsewhere.[14] When selecting which dye to use, it is crucial that the energy levels of the low band gap chromophore lie between those of the polymer and the fullerene in order to avoid charge trapping on the dye. For the purpose of this investigation, we used significantly less dye than polymer and thus aimed for an interpenetrating network of polymer and fullerene with dye present only as a near-infrared absorbing material which donates holes to the P3HT and electrons to the fullerene. The structures of the three solar cell components as well as their energy levels are shown in Fig. 1.[15,16] The energy levels for the SMD1 were

determined by a combination of ultraviolet photoelectron spectroscopy and optical absorption spectroscopy and will be described elsewhere.[14]

The optical absorption spectra of thin films of P3HT, C_{71}-PCBM ([6,6]-phenyl C_{71} butyric acid methyl ester), and SMD1 can be seen in Fig. 2. P3HT was purchased from EMD Chemicals and C_{71}-PCBM was purchased from Nano-C and used as received. Films of P3HT, SMD1, and C_{71}-PCBM were spun cast onto quartz substrates from chlorobenzene at 10 mg/mL, chloroform at 20 mg/mL, and carbon disulfide at 20 mg/mL, respectively. These can be compared with the absorption of blend films spun cast from chlorobenzene onto quartz substrates also shown in Fig. 2. All the BHJ solutions contained 10 mg/mL of P3HT and 10 mg/mL of C_{71}-PCBM, while some contained an additional amount of SMD1 in solution. The dashed and dotted curves in Fig. 2 are the absorption spectra of annealed P3HT:PCBM films containing 2 and 6 mg/mL of SMD1, respectively. Increasing the SMD1 content in P3HT:PCBM films increases the absorption in the region of 650–800 nm. The blend films were annealed for 30 s at 130 °C then rapidly quenched to room temperature; annealing films containing SMD1 for additional time degrades device performance. The thickness of
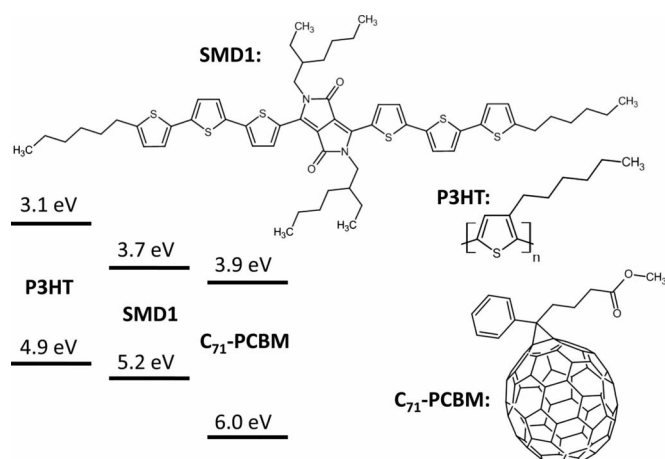

FIG. 1. (Color online) Structures of the three solar cell components are shown along with approximate energy levels.

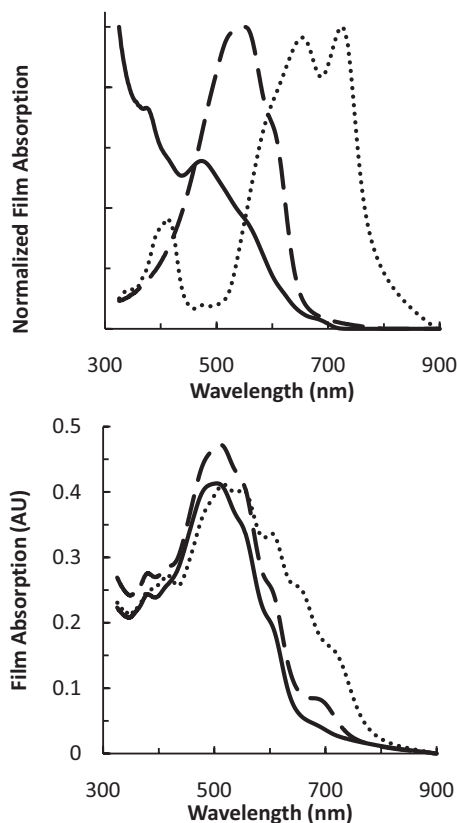[a]Author to whom correspondence should be addressed. Electronic mail: quyen@chem.ucsb.edu.

FIG. 2. Top: normalized optical absorption spectra for thin films of C_{71}-PCBM (solid), P3HT (dashed), and SMD1 (dotted). Bottom: optical absorption spectra of BHJ blend films comprising P3HT:C_{71}-PCBM (10:10) (solid), P3HT:C_{71}-PCBM:SMD1 (10:10:2) (dashed), and P3HT:C_{71}-PCBM:SMD1 (10:10:6) (dotted) after annealing.
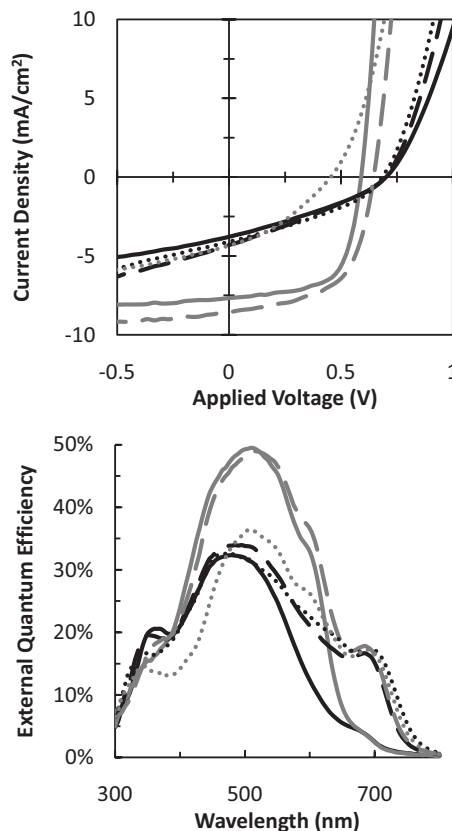

FIG. 3. Device characteristics of BHJ P3HT:C_{71}-PCBM (10:10) (solid), P3HT:C_{71}-PCBM:SMD1 (10:10:2) (dashed), and P3HT:C_{71}-PCBM:SMD1 (10:10:6) (dotted). Top: current density-voltage characteristics of BHJ solar cells before (black) and after (gray) thermal annealing. Bottom: EQE of BHJ devices before (black) and after (gray) thermal annealing.

the films increased with the amount of SMD1 present from 115 nm with no SMD1 to 125 nm with 2 mg/mL of SMD1 and 160 nm with 6 mg/mL of SMD1 in solution as measured using an Ambios XP-100 profilometer.

Photovoltaic cells were fabricated by spin casting the active BHJ layer at 800 rpm onto a 40 nm layer of poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) 4083, PEDOT:PSS, (H.C. Stark) on indium tin oxide-coated glass substrates. A 17 mm^2 aluminum cathode was thermally evaporated. All device fabrication and characterization was conducted in a nitrogen atmosphere. Solar cells were characterized under simulated 100 mW/cm^2 AM1.5G irradiation from a Xe arc lamp with an AM1.5 global filter. Simulator irradiance was characterized using a calibrated spectrometer, and illumination intensity was set using an NREL certified silicon diode with an integrated KG1 optical filter; spectral mismatch factors were calculated for each device in this report to be less than 5%. Quantum efficiencies were measured with a Xe lamp, monochromator, optical chopper, and lock-in amplifier; photon flux was determined by a calibrated silicon photodiode.

The highest efficiency solar cells are those cast from the solutions containing 2 mg/mL of SMD1 along with the P3HT/C_{71}-PCBM blend and annealed for 30 s at 130 °C. The current/voltage characteristics of the solar cells are shown in Fig. 3. The 2 mg/mL SMD1 solution yields devices with both increased short circuit current (I_{sc}) from 7.7 to 8.6 mA/cm^2 and increased open circuit voltage (V_{oc}) from 0.60 to 0.63 V relative to control devices. The increase in the

V_{oc} might be explained by decreased order within the P3HT domains; it has been suggested that crystalline P3HT results in a decreased V_{oc} due to the rise in the highest occupied molecular orbital (HOMO) level that occurs as a result of increased interchain orbital delocalization.[17] The increase in the I_{sc} with SMD1 inclusion is a result of increased absorption breadth leading to a rise in the number of photogenerated carriers. From the external quantum efficiency (EQE) spectra also shown in Fig. 3, it is clear that the dye absorption near 700 nm significantly contributes to the device photocurrent for both samples containing SMD1. The devices cast from solution containing 6 mg/mL of SMD1 have a peak EQE of only 36% compared with 50% for the devices cast from solution containing 2 mg/mL of SMD1 and the control devices. The PCE of the 6 mg/mL devices also reduces from 0.99% to 0.68% after annealing, where the control devices increase from 0.85% to 2.93% and the 2 mg/mL devices increase from 0.90% to 3.21%. The 17% EQE of the 2 mg/mL devices at 700 nm is significant considering that the transmission of the film at that wavelength is about 82%. Although high, this EQE value is not the result of near-unity internal quantum efficiency because, in a device geometry, the absorption may increase due to reflection from the back electrode. The EQE at 700 nm indicates that the SMD1 being dispersed in a matrix consisting of both an electron acceptor and a hole acceptor leads to efficient exciton dissociation and free carrier generation.

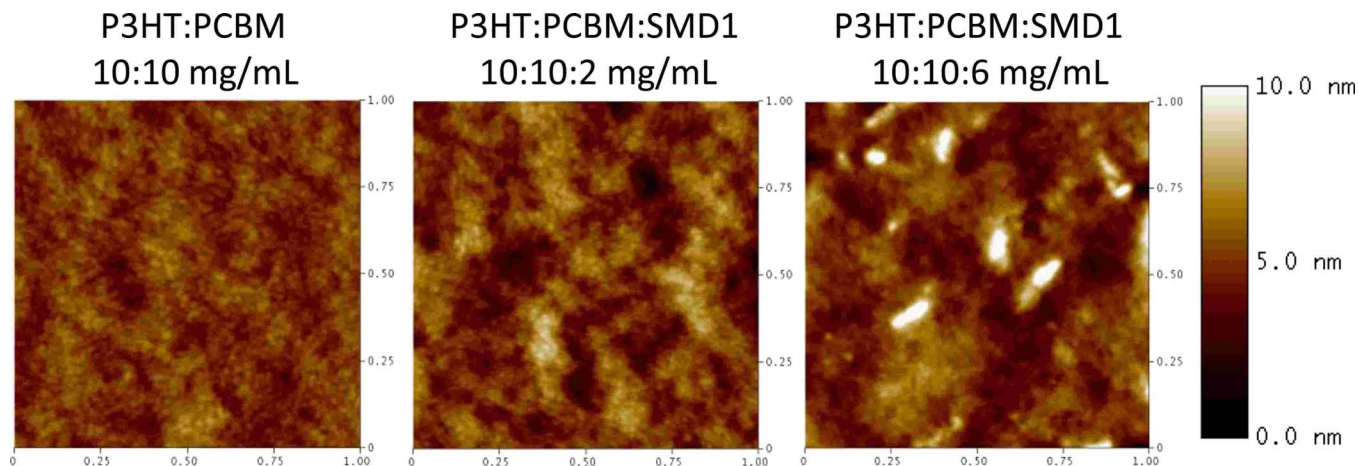In order to probe the nature of the device performance decrease in the 6 mg/mL devices, we imaged the surface

P3HT:PCBM 10:10 mg/mL P3HT:PCBM:SMD1 10:10:2 mg/mL P3HT:PCBM:SMD1 10:10:6 mg/mL

FIG. 4. (Color online) Topography of various blends after thermal annealing at 130 °C for 30 s: P3HT:C_{71}-PCBM (10:10) (left), P3HT:C_{71}-PCBM:SMD1 (10:10:2) (middle), and P3HT:C_{71}-PCBM:SMD1 (10:10:6) (right). Images are 1×1 μm^2 in size.

topography of the P3HT:C_{71}-PCBM/SMD1 films by atomic force microscopy (AFM). The AFM images of the as-cast films with various SMD1 content are similar; the surface roughness values are approximately 0.3 nm. The topography images of the annealed films are shown in Fig. 4. After annealing, the rms roughness are approximately 1.4, 1.2, and 0.7 nm for the 6 mg/mL, the 2 mg/mL, and the control films, respectively.

While the PCEs observed with this system are not unprecedented due to nonoptimal materials and processing, the concept of a small molecule chromophore being used to extend the effective absorption breadth of a polymer BHJ solar cell has been demonstrated. Given additional tailoring of the solid state miscibility between the dye molecule and the polymer, the phase separation could be controlled and the device morphology optimized. Additionally, by carefully controlling the energy levels of the dye, a significantly broader optical absorption could be achieved than that demonstrated here. If the high quantum efficiency of P3HT could be combined with the optical absorption of a low band gap dye molecule, unprecedented levels of device performance could be achieved.

[1] B. C. Thompson and J. M. J. Frechet, Angew. Chem., Int. Ed. **47**, 58 (2008).
[2] C. J. Brabec and J. R. Durrant, MRS Bull. **33**, 670 (2008).
[3] J. Peet, J. Y. Kim, N. E. Coates, W. L. Ma, D. Moses, A. J. Heeger, and G. C. Bazan, Nature Mater. **6**, 497 (2007).
[4] M. M. Wienk, M. Turbiez, J. Gilot, and R. A. Janssen, Adv. Mater. (Weinheim, Ger.) **20**, 2556 (2008).
[5] J. A. Hauch, P. Schilinsky, S. A. Choulis, R. Childers, M. Biele, and C. J. Brabec, Sol. Energy Mater. Sol. Cells **92**, 727 (2008).
[6] C. N. Hoth, P. Schilinsky, S. A. Choulis, and C. J. Brabec, Nano Lett. **8**, 2806 (2008).
[7] F. Padinger, C. J. Brabec, T. Fromherz, J. C. Hummelen, and N. S. Sariciftci, Opto-Electron. Rev. **8**, 280 (2000).
[8] W. J. Belcher, K. I. Wagner, and P. C. Dastoor, Sol. Energy Mater. Sol. Cells **91**, 447 (2007).
[9] A. Ltaief, R. B. Chaabane, A. Bouazizi, and J. Davenas, Mater. Sci. Eng., C **26**, 344 (2006).
[10] A. B. Tamayo, B. Walker, and T.-Q. Nguyen, J. Phys. Chem. C **112**, 11545 (2008).
[11] M. T. Lloyd, A. C. Mayer, S. Subramanian, D. A. Mourney, D. J. Herman, A. Bapat, J. E. Anthony, and G. G. Malliaras, J. Am. Chem. Soc. **129**, 9144 (2007).
[12] S. Roquet, A. Cravino, P. Leriche, O. Aleveque, P. Frere, and J. Roncali, J. Am. Chem. Soc. **128**, 3459 (2006).
[13] L. Valentini, D. Bagnis, A. Marrocchi, M. Seri, A. Taticche, and J. M. Kenny, Chem. Mater. **20**, 32 (2008).
[14] A. B. Tamayo, X.-D. Dang, B. Walker, J. H. Seo, and T.-Q. Nguyen (unpublished).
[15] A. J. Cascio, J. E. Lyon, M. M. Beerbon, R. Schlaf, Y. Zhu, and S. A. Jenekhe, Appl. Phys. Lett. **88**, 062104 (2006).
[16] K. Akaike, K. Kanai, H. Yoshida, J. Tsutsumi, T. Nishi, N. Sato, Y. Ouchi, and K. Seki, J. Appl. Phys. **104**, 023710 (2008).
[17] K. Vandewal, A. Gadisa, W. D. Oosterbaan, S. Bertho, F. Banishoeib, I. V. Severen, L. Lutsen, T. J. Cleij, D. Vanderzande, and J. V. Manca, Adv. Funct. Mater. **18**, 2064 (2008).