A Planar Copolymer for High Efficiency Polymer Solar Cells

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Recently, a power conversion efficiency (PCE) of 6.1% was demonstrated,[1] which is very encouraging and promising for commercializing polymer photovoltaics. Both polymer design and device processing play critical roles in achieving high efficiency polymer solar cells.[2] It is striking that the optical and electrical properties of polymers could be tuned to meet the requirements of devices. Material design can tailor absorption; HOMO, LUMO positions; and transport properties of polymers, all of which are essential for harvesting photons from solar radiation, generating free charge carriers, and collecting them at corresponding electrodes. Regioregular poly(3-hexylthiophene) (P3HT) has been proven to be one of the most successful electron donors in polymer bulk heterojunction solar cells.[3] The regularity of P3HT plays an important role in the performance of solar cells.[4] Low regularity P3HT gives very low PCE.[4c] To better match the solar spectrum, many low-band gap polymers have been synthesized and utilized in polymer solar cells;[5] however only a few of them give a PCE higher than 5%.[6] The low efficiency is probably due to the nonplanar structure of the polymer, which is detrimental for the close packing of polymer chains in the solid state.

Here, we demonstrate a strategy for designing planar polymers with better chain packing in film to facilitate charge carrier transport for photovoltaic application. A copolymer, poly(2-(5-(5,6-bis(oc-tyloxy)-4-(thiophen-2-yl)benzo[c][1,2,5]thiadiazol-7-yl)thiophen-2-yl)-9-octyl-9H-carbazole) (**HXS-1**) was designed, synthesized, and used in solar cells. The average of five solar cells based on its blend with PC$_{71}$BM illustrated a short-circuit current (J_{sc}) of 9.6 mA/cm^2, an open-circuit voltage (V_{oc}) of 0.81 V, a fill factor (FF) of 0.69, and a PCE of 5.4% under AM1.5 (100 mW/cm^2). An FF of 0.69 at J_{sc} = 9.6 mA/cm^2 indicates that **HXS-1**:PC$_{71}$BM has a balanced charge transport, which makes **HXS-1** a very promising polymer for solar cell application.

High carrier mobility requires conjugated polymer chains close packed in film. It is very crucial to design and synthesize polymers that can close pack in the solid state and also have good processability. Processable conjugated polymers normally carry flexible lateral chains; however, in many cases the side chains can prevent the polymer backbones from close packing. To achieve planar polymer conformation, **HXS-1** is designed with two octyloxy chains on the benzothiazole ring and an octyl chain on the carbazole ring. The flexible alkyl chains make the polymer soluble in organic solvent at elevated temperature, and meanwhile the polymer chain could have a planar conformation. The synthesis of **HXS-1** is shown in Scheme 1. Starting from 4,7-dibromo-5,6-bis(octyloxy)benzo-2,1,3-thiadiazole (**1**),[7] its coupling with 4,4,5,5-tetramethyl-2-

(thiophen-2-yl)-1,3,2-dioxaborolane with Pd(PPh$_3$)$_4$ as the catalyst precursor and aqueous NaHCO$_3$ and THF as the media afforded compound **2** in a yield of 41%. Bromination of **2** with N-bromosuccinimide furnished **3** in a yield of 88%. Suzuki−Miyaura−Schlüter polycondensation of **3** and 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9-octyl-9H-carbazole (**4**)[8] was carried out with Pd(PPh$_3$)$_4$ as the catalyst precursor in a biphasic mixture of THF−toluene (5:1)/aqueous NaHCO$_3$ to afford polymer **HXS-1** as a black solid in a yield of 69%.

Scheme 1. Synthesis of **HXS-1**
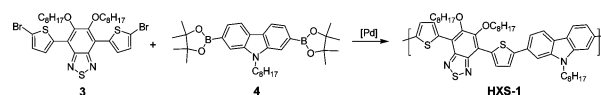
HXS-1 displayed good solubility at elevated temperature in chloroform, 1,2-dichlorobenzene (DCB), THF, 1,2,3-trichloroben-zene, etc. A number average molecular weight of 16.6 kg/mol, a weight average molecular weight of 51.4 kg/mol, and a PDI of 3.1 were determined by gel permeation chromatography (GPC) at 150 °C with 1,2,4-trichlorobenzene as an eluent vs polystyrene standards. Thermogravimetric analysis (TGA) indicated that the polymer was stable up to ∼300 °C. As shown in Figure S1, the X-ray diffraction (XRD) pattern of the powdery sample of **HXS-1** exhibits two peaks; the first peak at 5.2° reveals that the distance between polymer main chains separated by alkyl side chains is ∼17 Å; the second peak at 22.3° reveals a short π−π distance of ∼4.0 Å between polymer main chains,[9a] indicating the polymer chain is of planar conformation in the solid state. The LUMO and HOMO energy levels were determined by a cyclic voltammogram to be −3.35 and −5.21 eV, respectively. The band gap (E_g) was determined from the onset of the absorption to be 1.95 eV. Field effect transistor (FET) mobility measurements on the material combination used in optimized solar cells confirm a quite balanced mobility of ∼1 × 10^{-4} cm^2/(V s) for holes and 3 × 10^{-4} cm^2/(V s) for electrons under high vacuum.

The absorption and photoluminescence (PL) spectra of **HXS-1** film are shown in Figure S2. **HXS-1** shows two broad absorption bands peaked at 404 and 579 nm. **HXS-1** film emits red light with a peak at 674 nm. The absorption and PL spectra of **HXS-1**/PC$_{71}$BM film cast from DCB without and with additive 1,8-diiodooctane (DIO) are also shown in Figure S2.[10] The presence of vibronic features in the absorption spectrum of polymer/PC$_{71}$BM/DIO films further corroborates ordering of the polymer. Using PC$_{71}$BM as an acceptor could significantly improve light absorption in the visible region.[1,11] The PL of **HXS-1** is almost completely quenched in the blend film of **HXS-1** and PC$_{71}$BM, indicating efficient exciton dissociation.

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Photovoltaic properties of **HXS-1** were investigated in devices with the structure of ITO/PEDOT:PSS/**HXS-1**:PC$_{71}$BM/LiF/Al. Solar cells were fabricated from DCB solutions with varied stoichiometries, concentrations of DIO, and spin-coating speeds. The characterization shows that the optimized stoichiometry of **HXS-1** to PC$_{71}$BM is 1:2.5 (w/w), polymer concentration is 5.0 g/L, DIO concentration in DCB is 2.5%, and spin-coating speed is 600 rpm.

The photocurrent of solar cells at optimized conditions under monochromatic illumination was recorded, and a mismatch factor was calculated for calibrating the light intensity of AM1.5. The external quantum efficiency (EQE) of the solar cell is shown in Figure 1a, which covers all of the visible range of the solar spectrum. It is obvious that the photocurrent is generated from the photoexcitation states in both **HXS-1** and PC$_{71}$BM. The complementary absorbance of **HXS-1** and PC$_{71}$BM makes the EQE over 60% from 400 to 580 nm with an onset at 720 nm. The broad coverage of the solar spectrum of the solar cell guarantees a desirable J_{sc} under illumination with white light.
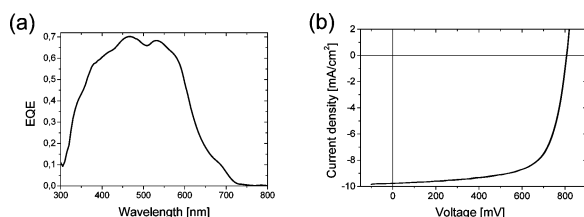

Figure 1. (a) EQE of the solar cell prepared from DCB:DIO with polymer concentration of 5.0 g/L. (b) Current−voltage characteristics of the device under AM 1.5 G illumination.

$I-V$ characteristics of solar cells were recorded under AM 1.5, and PCEs were calculated for different preparation conditions. The statistical graphs of solar cell parameters of three group cells fabricated on the same day under the same conditions are shown in Figure S3, where groups I and II were spin-coated from DCB: DIO solutions with polymer concentrations of 10.0 g/L and 5.0 g/L and group III was included control cells from pure DCB solution with a polymer concentration of 5.0 g/L. Figure S3 presents the clear impact of concentration and DIO on the performance of devices. Comparing groups I and II, we observed J_{sc} increased but V_{oc} and FF decreased with increasing concentration from 5.0 to 10.0 g/L, resulting in smaller PCEs in cells from a high concentration solution. In comparison with group III, using DCB:DIO as solvent, the overall performances were improved in group II. $I-V$ characteristics of a solar cell of group II with an optimized thickness in the range of 100 ± 10 nm is shown in Figures 1b and S4, which gives $J_{sc} = 9.8$ mA/cm^2, $V_{oc} = 0.81$ V, FF = 0.69, and PCE = 5.4%. It is believed that the morphology and molecular packing of the blend layer determine FF.[4d] An FF of 69% at $J_{sc} = 9.6$ mA/cm^2 is a very high value, indicating that a balanced charge transport was achieved in the solar cells prepared from DCB:DIO. To the best of our knowledge, a fill factor of 0.69 is hitherto among the highest in polymer solar cells with a PCE above 5%. The devices were measured directly after evaporation. Long-term stability tests with encapsulated devices outside the glovebox will soon be started.

In conclusion, a planar alternating copolymer, **HXS-1**, was designed and synthesized for photovoltaic application. The closing packing of polymer chains in the solid state was confirmed by XRD results and features in the absorption spectrum of polymer/PC$_{71}$BM/DIO films. **HXS-1** exhibits good solubility in chloroform and DCB at elevated temperature and has a broad absorption in the visible region. With **HXS-1** and PC$_{71}$BM as the active layer in bulk heterojunction solar cells, the optimized device demonstrates a J_{sc} of 9.6 mA/cm^2, a V_{oc} of 0.81 V, an FF of 0.69, and a PCE of 5.4% under AM 1.5 (100 mW/cm^2), indicating that **HXS-1** is a promising material for solar cell application. It was demonstrated that the PCE of solar cells based on poly(N-9''-hepta-decanyl-2,7-carbazole-alt-5,5-(4′,7′-di-2-thienyl-2′,1′,3′-benzothiazole) (PCDTBT) was increased from 3.6%[9b] to 6.1% by replacing PC$_{61}$BM with PC$_{71}$BM together with titanium oxide as the optical spacer and hole blocking layer.[1a] Further investigation of **HXS-1** is still ongoing, and a PCE higher than 6% is anticipated.

Supporting Information Available: Detailed experimental procedures, characterization of all compounds, absorption and PL spectra, DSC and XRD of the polymer, AFM images of the active layer, the statistical graphs of the performance of three group solar cells, $I-V$ characteristics of five optimized solar cells, and device fabrication and measurements. This material is available free of charge via Internet at http://pubs.acs.org.

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