

Orthogonal Solubility in Fully Conjugated Donor-Acceptor Block Copolymers: Compatibilizers for Polymer/Fullerene Bulk-Heterojunction Solar Cells*

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Abstract Donor-acceptor (D-A) type fully conjugated block copolymer systems have been rarely reported due to the challenges in synthetic approaches to prepare well-defined low-polydispersity products. In this work, fully conjugated block copolymers are synthesized in a one-pot reaction through Stille coupling polycondensation, by utilizing the end-functional polymer copolymerization method. End-functional P3HT are copolymerized with AA (2,7-dibromo-9-(heptadecan-9-yl)-9H-carbazole) and BB (4,7-bis(5-(trimethylstannyl)thiophen-2-yl)benzo[c][1,2,5]thiadiazole, TBT) type monomers, respectively. The orthogonal solubility between the very soluble P3HT donor and the insoluble PCDTBT acceptor block improves the purity of block copolymers as well as distinct nano-scale phase-separation compared with other reports on miscibility of donor and acceptor polymer block. Further purification *via* preparative GPC is carried out to remove the excess of unreacted P3HT and free PCDTBT as well as to achieve low polydispersity of block copolymers. The chemical structure of the P3HT-*b*-PCDTBT block copolymers are verified *via* ¹H-NMR, and further confirmed by FTIR spectra. The block copolymer shows broad absorption and moderate optical band gap of 1.8 eV. Furthermore, the fully conjugated block copolymer films exhibit significant fine structures, much smoother film morphology compared to P3HT/PCDTBT polymer blends. By adding a small amount of block copolymer P3HT-*b*-PCDTBT as a compatibilizer into the bulk-heterojunction of P3HT:PC₆₁BM blends, polymer solar cells with an 8% increase of short circuit current (*J*_{sc}) and 10% increase of power conversion efficiency (PCE) are achieved owing to the improvement of the active-layer film morphology. To the best of our knowledge, this is the first report on donor-acceptor type fully conjugated block copolymer as an effective ternary additive in polymer: fullerene bulk heterojunction solar cells.

Keywords Block copolymers; Donor; Acceptor; Bulk heterojunction solar cells; Compatibilizer

Electronic Supplementary Material Supplementary material is available in the online version of this article at <http://dx.doi.org/10.1007/s10118-017-1889-6>.

* This work was financially supported by the National Natural Science Foundation of China (No. 21304047), Natural Science Foundation of Jiangsu Province (No. 13KJB430017), Research Fund for the Doctoral Program of Higher Education (No. 20133221120015) and Synergetic Innovation Center for Organic Electronics and Information Displays.

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Invited paper for special issue of “Opto-electronic Functional Polymer”

Received July 18, 2016; Revised August 14, 2016; Accepted August 15, 2016

doi: 10.1007/s10118-017-1889-6

INTRODUCTION

Polymer bulk-heterojunction (BHJ) solar cells, involving a blend of donor and acceptor materials in the bulk active layer of the devices, have attracted intense investigation due to their predominant features such as low cost, flexibility, light weight and large area mass production^[1–7]. One of the key factors to enhance device performance is the well-defined morphology with nano-scale phase-separated interpenetrating networks between the blended donor and acceptor materials, which provides suitable interfaces for efficient exciton dissociation and simultaneously affords favorable route for charge carriers to transport to the corresponding electrodes^[8–10]. However, the polymer/fullerene blended system is not easy to achieve the aforementioned well-defined film morphology, because of uncontrolled donor/acceptor (D/A) domain size distribution and inherent morphological instability^[11]. The morphology usually shows significant structural disorder with many domains that are too large, too small, or discontinuous, resulting in exciton loss, geminate charge recombination, and poor charge mobility, respectively^[12]. Thus the control of the well-defined interface in state-of-the-art organic photovoltaics is not easy. Several techniques such as solvent, additives, and processing condition have been optimized to realize effective morphology of the blend films^[12–16]. However, this may be a tedious procedure and suppressed the rapid development of organic photovoltaic cells (OPVs)^[17].

The use of block copolymers (BCPs) in the active layer is a new approach to efficiently control the well-defined nano-scaled morphology, because block copolymers consisting of covalently linked different blocks constitutionally have the ability to self-assemble into phase separation nanostructure^[18–22]. For example, our group previously reported the all-conjugated block copolymers P3HT-*b*-PNDT films showing significant fine structures and much smoother film morphologies than P3HT/PNDIT homopolymer blends^[23]. Ku *et al.* also proposed a strategy for the synthesis of fully conjugated donor-acceptor block copolymers P3HT-*b*-DPP, which provided a rich self-assembly behavior with two separate crystalline domains^[24]. Power conversion efficiency of up to 3% was realized by using P3HT-*b*-PFTBT block copolymer as the active layer, demonstrating efficient photo conversion well beyond devices composed of P3HT/PFTBT homopolymer blends^[25]. Block copolymers were also added to blends as compatibilizers to tune domain morphology at the donor/acceptor interface^[26, 27]. For example, non-fully conjugated block copolymers, which comprised regioregular P3HT donor blocks and non-conjugated acceptor blocks with pyrene bismide (PBI) as side chains, promoted in controlling the large-scale phase separation of P3HT and PBI blends, thus enhancing the PCE of device performance from 0.37% to 0.55% in the presence of the compatibilizer^[28]. By adding the fully conjugated block copolymer P3HT-*b*-PFTBT to the homopolymer blends of P3HT/PFTBT as a compatibilizer, the blend film exhibited phase separation of the blocks and self-assembly behavior^[12]. Up to date, fully conjugated donor-acceptor block copolymers used in photovoltaic cells have still been less investigated due to the distinct synthetic challenges, regardless of their potential application for high-performance photovoltaic cells^[29–39].

Herein, we present the design, synthesis, purification and characterization of all-conjugated block copolymers P3HT-*b*-PCDTBT, comprising P3HT donor block and PCDTBT acceptor block. P3HT is the most widely used donor materials either in donor-acceptor block copolymers and BHJ polymer solar cells, due to its desirable optoelectronic properties and convenient massive synthetic method^[40–42]. On the other hand, poly(2,7-carbazolealt-4,7-dithienyl-2,1,3-benzothiadiazole) (PCDTBT) which contains the strong electron-accepting benzothiadiazole unit has shown considerable PCEs approaching 7% in PCDTBT:fullerene BHJ solar cells by judicious device optimization^[43–45]. Besides, in P3HT/PCDTBT polymer donor/polymer acceptor blends, the HOMO-HOMO and LUMO-LUMO energy levels offsets for P3HT and PCDTBT was detected to be 0.30 and 0.43 eV, respectively, which provides satisfactory driving force for charge separation at donor/acceptor interface. After careful purification of P3HT-*b*-PCDTBT through preparative GPC to obtain narrow polydisperse block copolymers, the structure, optical and electrochemical properties, as well as the film morphologies of the newly purified fully conjugated block copolymers were investigated in detail. The fully conjugated copolymer films exhibited self-assembly behavior and phase separation of the donor/acceptor blocks. Such all-conjugated block copolymers were also used as compatibilizers to improve the short-current and power conversion efficiency of the well-known P3HT/PCBM blended photovoltaic cells.

EXPERIMENTAL

Materials

All reagents were purchased from Energy Chemical, Suna Tech Inc, Stream, Sigma Aldrich and used without further purification. Reagent grade solvents used in this study were freshly dried using standard distillation methods, except *N,N*-dimethylformamide (DMF) was purchased from Sigma-Aldrich.

Characterization

¹H-NMR spectra were recorded on a Bruker DRX-400 spectrometer. Number-average (M_n) and weight-average (M_w) molecular weight of all polymers were determined by Agilent Technologies 1200 series GPC running in chlorobenzene at 80 °C, using two PL mixed B columns in series, and calibrated against narrow polydispersity polystyrene standards. Preparative GPC utilized a Shimadzu recycling GPC system running in chlorobenzene at 80 °C, using Agilent PL gel MIXED-D column, DGU-20A3 Degasser, LC-20A Pump, CTO-20A Column Oven and SPD-20A UV Detector. The ultraviolet-visible (UV-Vis) absorption spectra were recorded on a Shimadzu UV-2500 recording spectrophotometer. Fourier transform infrared spectroscopy (FTIR) measurements were performed on a Nicolet 6700 spectrometer equipped with a MCT detector. Cyclic voltammetry (CV) was carried on a CHI660D electrochemical workstation with a solution of 0.1 mol/L tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) in acetonitrile, and the polymer film on a Pt plate as the working electrode, a platinum wire as auxiliary electrode, and an Ag wire as pseudo-reference electrode with ferrocenium-ferrocene (Fc⁺/Fc) as the internal standard. The scan rate was 100 mV/s. Atomic force microscopy (AFM) was conducted on SPA300HV in tapping mode using an SPI3800 controller, Seiko Instruments Industry, Co., Ltd.

Device Fabrication and Measurements

The polymer solar cells comprised the structure of indium tin oxide (ITO)-coated glass substrate /PEDOT:PSS/active layer/Ca/Al. Poly(ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) (Baytron P4083) was initially spin-coated on the pre-cleaned ITO substrate to produce a 35 nm thick anode buffer layer. The ~85 nm thick active layer with a concentration of 10 mg/mL in chloroform solution was spin-coated onto the PEDOT:PSS layer. The samples were then transferred into a vacuum evaporator and a cathode including 5 nm of Ca and 100 nm of Al was thermally deposited on top of the active layer to produce an active area of 0.12 cm² for each device. Devices with thermal annealing were carried out in a glove box at 150 °C for 15 min. The illuminated current density-voltage (*J-V*) characteristics of the devices were measured using a computer-controlled Keithley 236 source meter under 100 mW/cm² AM1.5G simulated solar light illumination. The light intensity was determined by a calibrated silicon diode with KG-5 visible color filter. The external quantum efficiency (EQE) of the devices was measured under short-circuit condition with a lock-in amplifier (SR830, Stanford Research System) at a chopping frequency of 280 Hz during illumination with the monochromatic light from a Xenon lamp.

Synthesis

PCDTBT synthesis

A mixture of 2,7-dibromo-9-(heptadecan-9-yl)-9*H*-carbazole (109.7 mg, 0.2 mmol), 4,7-bis(5-(trimethylstannyl)thiophen-2-yl)benzo[c][1,2,5]thiadiazole (125.2 mg, 0.2 mmol), Pd(PPh₃)₄ (10.0 mg, 0.0080 mmol) was placed in a 20 mL Schlenk tube and flushed with nitrogen. Dry toluene (6 mL) and DMF (0.6 mL) were injected into the Schlenk tube. The mixture was heated at 120 °C for 12 h. After cooling to room temperature, the mixture was poured into methanol, and the resulting precipitate was filtered. The raw polymer was purified by subsequent Soxhlet extraction with methanol, acetone, dichloromethane, chloroform, and chlorobenzene as final solvent. The chlorobenzene fraction was concentrated and precipitated into cold methanol again. After drying, a dark solid was collected (60%). GPC, M_n = 9000 g/mol, M_w = 1.59×10^4 g/mol, PDI = 1.77.

Block copolymer P3HT-*b*-PCDTBT (BCP) synthesis

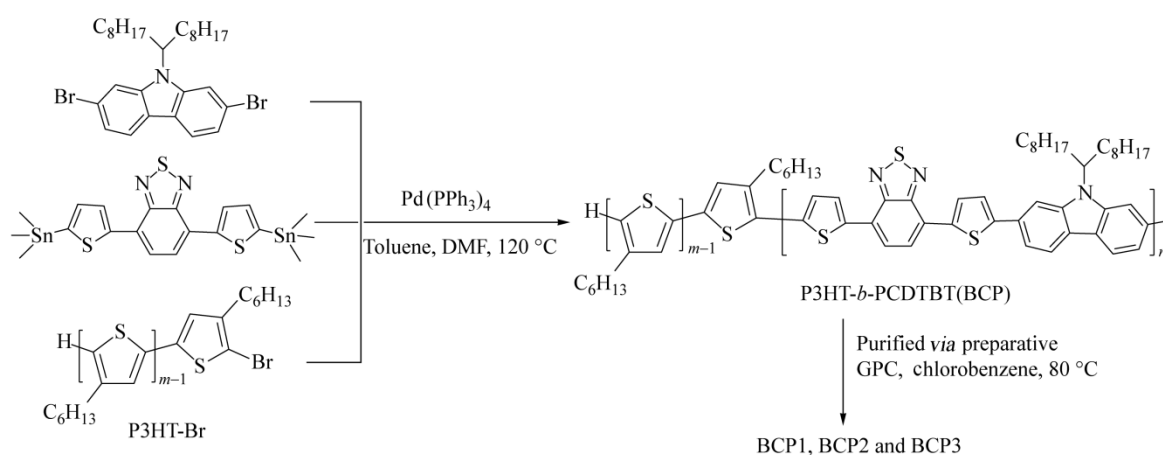
A mixture of P3HT-1 (M_n = 17 kg/mol) (165.0 mg, 0.011 mmol), 2,7-dibromo-9-(heptadecan-9-yl)-9*H*-carbazole (164.5 mg, 0.3 mmol), 4,7-bis(5-(trimethylstannyl) thiophen-2yl)benzo[c][1,2,5]thiadiazole (187.8 mg,

0.3 mmol), $\text{Pd}(\text{PPh}_3)_4$ (15.0 mg, 0.012 mmol) was placed in a 50 mL Schlenk tube and the atmosphere was replaced with nitrogen. Dry toluene (9 mL) and DMF (1 mL) were injected into the Schlenk tube, and then heated at 120 °C for 12 h. After cooling to room temperature, the mixture was poured into methanol, and the resulting precipitate was filtered off and purified by subsequent Soxhlet extraction with methanol, acetone, ethyl acetate, dichloromethane and chloroform as final solvent. The chloroform fraction was concentrated and then precipitated into cold methanol again. After drying, a dark solid with a yield of 225 mg was collected. GPC, $M_n = 1.88 \times 10^4$ g/mol, $M_w = 3.07 \times 10^4$ g/mol, PDI = 1.63.

RESULTS AND DISCUSSION

Synthesis and Characterization

As outlined in Scheme 1, P3HT-Br was synthesized and purified following our previous report^[23]. The block copolymers BCP were synthesized by Stille coupling polymerization of 2,7-dibromo-9-(heptadecan-9-yl)-9H-carbazole, 4,7-bis(5-(trimethylstannyl)thiophen-2-yl)benzo[c][1,2,5]thiadiazole, and P3HT-Br, in a one-pot reaction with good yield. After the reaction, the resulting products were purified *via* Soxhlet extraction with methanol, acetone, ethyl acetate, dichloromethane and chloroform in succession. The chloroform section was collected for the final crude product. However, as previously reported^[24], this synthetic method is not flawless, contamination with unreacted P3HT and free acceptor homopolymer is feasible. In comparison, PCDTBT homopolymer was also synthesized under the same polymerization conditions, and chlorobenzene section was collected instead of chloroform due to the poor solubility of PCDTBT homopolymer. This poor solubility resulted in the low molecular weight of PCDTBT, with M_n of only 9.0 kg/mol. It is noted that by introducing the well soluble P3HT into the conjugated backbone of insoluble PCDTBT, the solubility of block copolymer can be significantly improved to easily dissolve it in chloroform. In addition, most of the unreacted free P3HT as well as the rather low molecular weight PCDTBT homopolymer or oligomers could be removed by Soxhlet extraction during dichloromethane section, while other high molecular weight PCDTBT homopolymer remained in the thimble when Soxlet extracted with chloroform to collect the block copolymers. Thus the final crude product mainly contained the P3HT-*b*-PCDTBT block copolymers (BCP). Compared to other block copolymers with similar donor and accept polymer solubility, the orthogonal solubility between the donor P3HT and acceptor PCDTBT block in this work is beneficial to reduce the possibility of multi-components especially the free acceptor polymer and unreacted P3HT due to the distinct synthetic challenges of block copolymers. On the other side, this orthogonality system may promote the self-assembly and phase-separation between the donor and acceptor block in block copolymers.



Scheme 1 Synthesis of block copolymer P3HT-*b*-PCDTBT (BCP)

BCP was further purified and separated *via* preparative GPC to obtain low polydisperse D-A block copolymers fragments with gradual decrease of molecular weight from BCP1, BCP2 to BCP3.

The number average molecular weights (M_n) of the crude BCP was 18.8 kg/mol, with polydispersity (PDIs) of 1.65. The as-synthesized block polymers were further purified *via* high-temperature preparative GPC by using chlorobenzene as an eluent at 80 °C. Besides, this separation procedure simultaneously decreases the PDI of block copolymers^[29]. The crude block copolymers were separated into six to seven fractions according to different molecular weight of polymers. During fractionation, the solutions eluting from the preparative GPC with descending molecular weight was collected in vials every 60–90 s, thus to acquire low PDI. And the concentrations of the polymers was simultaneously monitored by UV-Vis absorption intensity through two different wavelength channel of 500 and 600 nm, the former mainly indicating the existence of P3HT and the later for PCDTBT. Solutions with corresponding signals only at 500 or 600 nm was disposed, therefore, unreacted P3HT or free PCDTBT homopolymers was further removed after Soxhlet extraction with dichloromethane. Fractions with both highest absorption intensity at 500 and 600 nm were collected to measure the molecular weight. Finally, only three effective fractions (BCP1, BCP2 and BCP3) exhibiting monomodal GPC curves and high molecular weight were selected for further investigation. Molecular weight and polydispersity for all polymers are summarized in Table 1. The M_n of BCP1, BCP2 and BCP3 was 49.9, 33.4 and 24.8 kg/mol respectively, and PDI was as low as 1.25–1.30, significantly lower than 1.65 of the crude BCP. Since the PCDTBT homopolymer with M_n of 9.0 kg/mol was insoluble in hot chloroform but dissolved only in hot chlorobenzene, it is deduced that the residual rather low molecular weight PCDTBT homopolymer which might be Soxhlet extracted in chloroform section together with the crude block copolymer was successively separated out through preparative GPC. Since current synthetic chemistry has not reached the level of simultaneously controlled chain growth polymerization for both fully-conjugated effective *p*-type and *n*-type polymers suitable for photovoltaic investigation in a one pot catalyzed polymerization, so far, the synthetic strategy reported for fully-conjugated D-A block copolymers involves a combination of Kumada catalyst transfer polymerization (KTCP) and other step growth polycondensation methods, such as Suzuki-Miyaura, Stille and Yamamoto coupling reactions^[18]. However, this synthetic method unavoidably comprises of free donor and acceptor polymers in the final block copolymer product. It is worth noting that block copolymers selecting orthogonal solubility between donor and acceptor block as well as further separation through preparative GPC in this work can resolve the problem of the distinct difficulties on current synthetic technology especially the removal of acceptor homopolymer^[12, 24, 25].

Table 1 Molecular weights and polydispersity values determined from GPC of various polymeric materials investigated in this work, and weight ratio of P3HT in block copolymers

Polymer	M_n (kg/mol)	M_w (kg/mol)	PDI	Weight ratio of P3HT ^a (wt%)
PCDTBT	9.0	15.9	1.77	0
P3HT	17.0	20.2	1.19	100
BCP	18.9	30.7	1.63	–
BCP1	49.9	65.0	1.30	78
BCP2	33.4	42.9	1.28	73
BCP3	24.8	30.9	1.25	78

^a Determined from the ¹H-NMR

Figure 1 shows the GPC curves of BCP1, BCP2 and BCP3 as well as P3HT which was initially used for one-pot polymerization. As the molecular weight of P3HT was only 16.9 kg/mol, it could be mostly or completely extracted by dichloromethane upon Soxhlet extraction for BCP crude polymer. Furthermore, the relevant free P3HT could also be separated by preparative GPC. It is obvious that GPC curves of all fractions of BCP1, BCP2 and BCP3 were different from P3HT. Three BCP1-3 segments exhibited sharp and monomodal profiles, which were clearly shifted to shorter elution times compared to P3HT. No shoulder peaks were observed within the overlapping range between BCP1-3 and P3HT curves, indicating that block copolymers were purified effectively *via* preparative GPC.

According to the ¹H-NMR spectra of P3HT-Br and BCP1 (Fig. S1), distinct resonances for both the P3HT

and PCDTBT units, and the disappearance of peaks at about $\delta = 2.50$ resulting from the linkage between the bromo-chain end of the P3HT block and PCDTBT segment can be visualized^[18, 31]. P3HT weight ratio was determined by comparing the integral area of the branched chain peak ($\delta = 5.14$) from the PCDTBT and the branched chain peak ($\delta = 2.80$) of P3HT. Thus various block copolymers with different P3HT weight rates were investigated and summarized in Table 1, and further confirmed by FTIR spectra. It is unexpected that the weight ratio of P3HT for BCP1, BCP2 and BCP3 was similar with 78 wt%, 73 wt% and 78 wt%, respectively, nearly independent of the molecular weight of the block copolymers. This result was greatly different from previous reports on block copolymer with miscibility between donor and acceptor block, in which the weight ratio of P3HT was gradually increased by decreasing block copolymer molecular weight through separation by preparative GPC^[23, 29]. Since P3HT was synthesized by controlled polymerization with PDI as low as 1.19, the abnormal P3HT weight ratio trends in this work might be attributed from orthogonal solubility for donor/acceptor block.

To access the structural and molecular characteristic of the block copolymers, and further to verify the weight ratio of P3HT in block copolymers calculated from ¹H-NMR spectra, FTIR was then carried out. As shown in Fig. 2, the spectra of block copolymers P3HT-*b*-PCDTBT and P3HT/PCDTBT polymer blends are almost identical, with exactly similar absorption peak and intensities because of the same chemical component. From the fingerprint region for all the two groups of block copolymer and polymer blends, it is found that both spectra overlap very well, indicating the weight ratio of P3HT in block copolymers are similar with that in P3HT/PCDTBT polymer blends, respectively. The 1290–1415 cm⁻¹ bands are typically characteristic for vibrations of (CH₂) and (CH₃) groups^[46], and the about 1510 cm⁻¹ band corresponding to the C=C stretching band of the aromatic ring of polythiophene^[47].

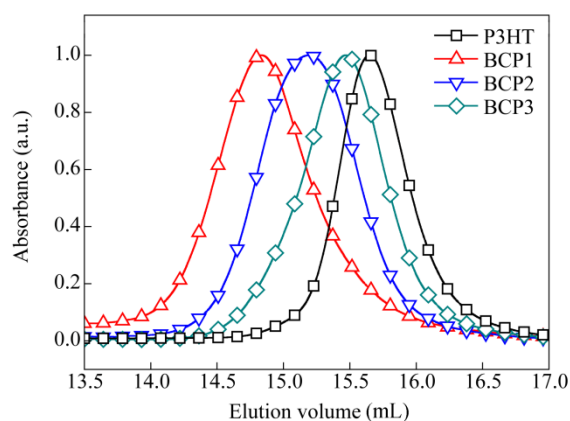


Fig. 1 GPC analysis of various block copolymer fractions purified by preparative GPC, with P3HT chain length of 17.0 kg/mol (M_n)

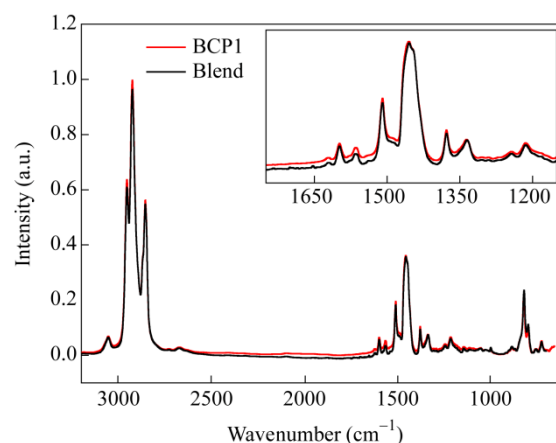


Fig. 2 Room temperature FTIR spectra of selected block copolymer fraction BCP1 (red line), P3HT and PCDTBT homopolymer blends with the same P3HT weight ratio calculated from the ¹H-NMR (black line) (Inset: the enlarged spectra with wave number ranging from 1750–1150 cm⁻¹.) (The online version is colorful.)

Optical and Electrochemical Properties

UV-Vis absorption spectra of the purified block copolymers, P3HT and PCDTBT homopolymers in chloroform solutions and thin films are shown in Fig. 3 and the related data are summarized in Table 2. In dilute solutions, all block copolymers exhibit similar absorption behavior with a broad absorption in the visible regions. The absorption spectra of block copolymers demonstrate both of the P3HT and PCDTBT absorption features and are almost the overlap of the two components, indicating the deficit of ground state electronic interactions as expected^[38]. In the film state, all block copolymers exhibit similar absorption profiles with a broad absorption

peak from 300 nm to 700 nm, as well as significant red-shift for the longer wavelength absorption as compared to that in solution, suggesting there might be certain molecular self-organization and highly ordered structures in the film which could facilitate charge transfer for photovoltaic application^[48]. The optical band gaps of each block copolymer calculated from the onset of the film absorption spectra are about 1.8 eV, which is almost identical to that of the regioregular P3HT.

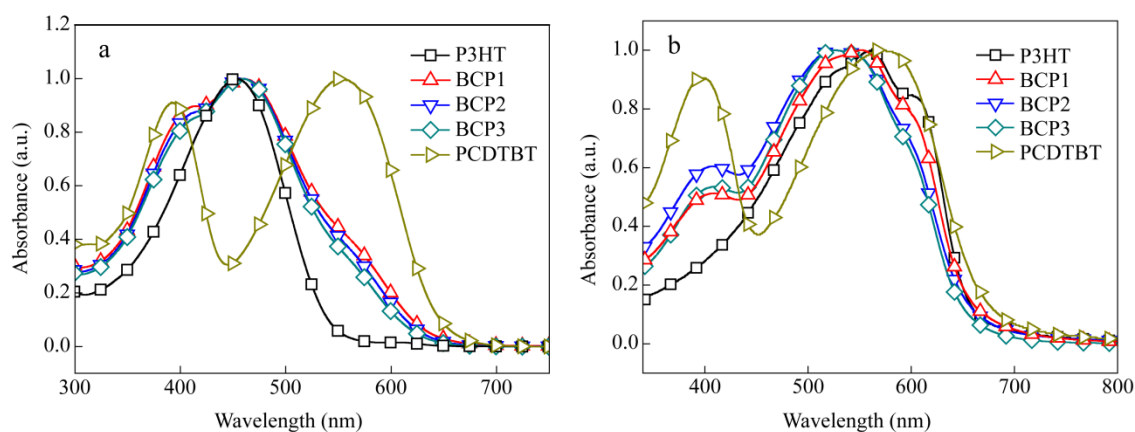


Fig. 3 UV-Vis absorption spectra of selected effective block polymer fractions, P3HT and PCDTBT homopolymers in (a) CHCl_3 solution and (b) film state

Table 2 Electrochemical and optical properties of polymers

Polymer	$\lambda_{\text{max}}^{\text{a}}$ (nm)	$\lambda_{\text{max}}^{\text{b}}$ (nm)	E_{g}^{c} (eV)	$E_{\text{HOMO}}^{\text{d}}$ (eV)	$E_{\text{LUMO}}^{\text{e}}$ (eV)
P3HT	453	555	1.85	5.07	3.22
BCP1	461	553	1.78	5.18	3.40
BCP2	459	525	1.80	5.21	3.41
BCP3	459	525	1.86	5.17	3.31
PCDTBT	392, 553	398, 570	1.72	5.37	3.65

^a Maximum absorption peak, measured in dilute chloroform solution; ^b As-cast film from chloroform solution onto a glass substrate; ^c Determined by UV-Vis absorption edge measurements of film; ^d HOMO measured by CV; ^e LUMO calculated from the difference of HOMO and bandgap

Electrochemical properties of different block copolymers, donor and acceptor polymers were studied by cyclic voltammetry (CV). For this measurement, the polymer films were prepared by dispensing polymer chloroform solutions onto the working electrode at room temperature under a nitrogen atmosphere, and ferrocene was used as the internal reference. Relevant cyclic voltammograms of polymers are shown in Fig. 4 and the corresponding data are summarized in Table 2. The covalently linked block copolymers exhibited one oxidation

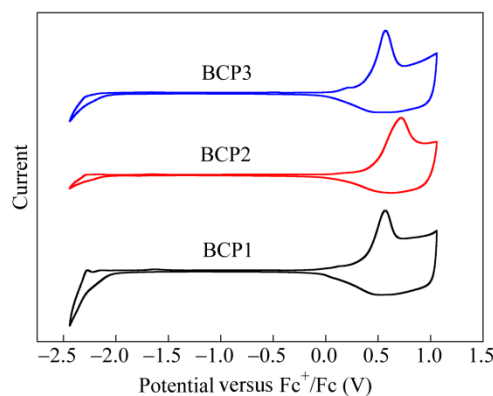


Fig. 4 Cyclic voltammograms of the block copolymers

peak, due to the P3HT segments. The highest occupied molecular orbitals (HOMO) level, calculated from the onset of oxidation curve, was 5.18, 5.21, and 5.17 eV for BCP1, BCP2 and BCP3, respectively. It is interesting to note that the HOMO levels of block copolymers were located in between the donor P3HT (5.07 eV) and acceptor PCDTBT (5.37 eV) homopolymer. And the lowest unoccupied molecular orbitals (LUMO) levels were calculated from the difference of HOMO and optical bandgap.

Film Morphology

To illustrate the advantages of all-conjugated block copolymers against homopolymer blends, atomic force microscopy (AFM) images of the corresponding spin-coated films of D-A block copolymer and D/A blends on top of silicon wafer were recorded under the same conditions. BCP1 (P3HT: 78 wt%) exhibiting the most monomodal and least overlapping GPC curves with P3HT was selected as the representative. As shown in Fig. 5, the surface topography (a–b) of block copolymers and homopolymer blends showed essentially flat and almost featureless surface at room temperature. However, the root mean square roughness (RMS) of the homopolymer blended film was 7.39 nm, significantly higher than that of 1.53 nm for chemically bonded D-A block copolymers. The smooth surface of film ensures a better contact with the electrode, which might be conducive to increase the charge collection efficiency. From the phase images, (Figs. 5c and 5d), it is noted that even without thermal annealing, both as-cast films exhibited clear nano-scale phase-separation between the donor P3HT and acceptor PCDTBT, which could be contributed by their orthogonal solubility inducing two distinct phases. However, significant traps and collapse could be observed in D/A homopolymer blends, while the block copolymer BCP1 with the covalent connectivity between the two D-A blocks showed the well-defined structures and significantly enhanced domain ordering, indicating that block copolymers with orthogonal solubility between the D and A block have potential applications in the direction of nano-structured interpenetrating networks for active layers in bulk-heterojunction polymer solar cells.

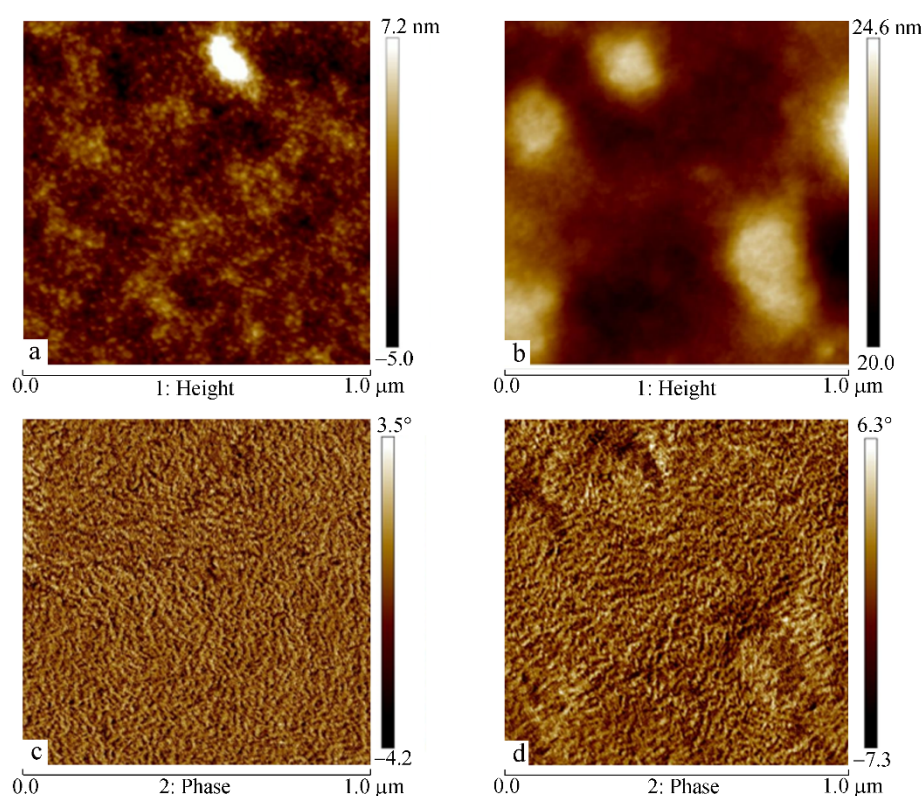


Fig. 5 AFM topography (top) and phase (bottom) images (1 μm × 1 μm) of film spin-coated on silicon wafer from chlorobenzene solutions, (a, c) BCP1 as-spun, (b, d) P3HT/PCDTBT blends with 78 wt% of P3HT as-spun

Polymer Solar Cells

Due to the synthetic challenges on effective BCP material systems for high performance organic photovoltaics, fully conjugated donor-acceptor block copolymers have less been studied in the application of PSC^[29–39]. For example, BCP as single-component active layer for polymer solar cells with PCE up to 3%^[25], or as ternary additives to improve the photovoltaic performance in polymer/polymer blended solar cells^[12]. In this work, for the first time, the potential application of D-A fully-conjugated block copolymer as a compatibilizer in active layer of polymer/fullerene BHJ polymer solar cells was investigated. Similarly, BCP1 with the best purity was selected for the experiments. The device architecture is as follows: ITO/PEDOT: PSS/Polymer:PC₆₁BM/Ca/Al. Detailed fabrication and characterization of devices could be found in the experimental section. The current density voltage (J - V) curves of the fabricated polymer solar cells under 100 mW/cm² AM1.5G solar illuminations are shown in Fig. 6. The open-circuit voltage (V_{oc}), short current (J_{sc}), fill factor (FF), and PCEs are summarized in Table 3.

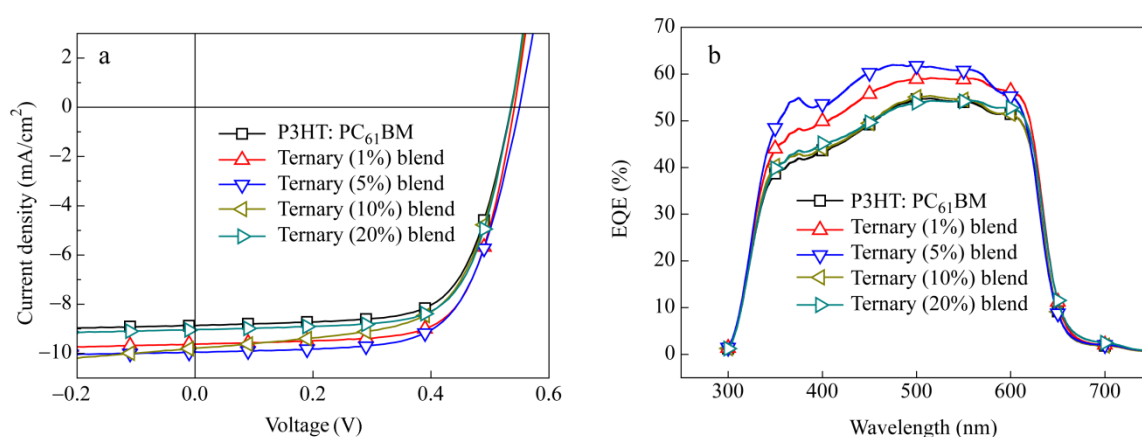


Fig. 6 (a) J - V characteristics and (b) EQE curves of the solar cells based on P3HT/PC₆₁BM blended with different composition of BCP1

Table 3 Device statistics for P3HT/PC₆₁BM blend films with different ratios of BCP1 compatibilizers

Ratio of BCP1 (wt%)	V_{oc} (V)	J_{sc} (mA/cm ²)	FF (%)	PCE (%)
0	0.54 ($\pm$ 0.00)	9.0 ($\pm$ 0.4)	69 ($\pm$ 1)	3.31 ($\pm$ 0.12)
1	0.54 ($\pm$ 0.00)	9.5 ($\pm$ 0.2)	69 ($\pm$ 1)	3.57 ($\pm$ 0.05)
5	0.55 ($\pm$ 0.01)	9.7 ($\pm$ 0.2)	68 ($\pm$ 2)	3.64 ($\pm$ 0.15)
10	0.53 ($\pm$ 0.01)	9.4 ($\pm$ 0.4)	67 ($\pm$ 1)	3.35 ($\pm$ 0.09)
20	0.53 ($\pm$ 0.01)	9.0 ($\pm$ 0.2)	68 ($\pm$ 1)	3.27 ($\pm$ 0.09)

Data have been averaged for 12 devices

The weight ratio of P3HT:PC₆₁BM blended was optimized at 1:1. And the active layer film was then thermally annealed at 150 °C. When chloroform was used as the solvent, PCE of 3.31% was obtained without any additives, with a J_{sc} of 9.0 mA/cm², V_{oc} of 0.54 V, and FF of 69%. Further optimization involved using a small amount of block copolymer BCP1 to manipulate the morphology. BCP1 was added as a compatibilizer into P3HT:PC₆₁BM blends with concentration from 1 wt%, 5 wt%, 10 wt% and 20 wt%. As shown in Table 3, polymer solar cell devices fabricated with different BCP1 contents exhibited a relatively stable V_{oc} (0.53–0.55 V), which was insensitive to BCP1 weight ratio and no obvious relationship could be observed (Fig. 7). However, the J_{sc} and PCE of the devices was considerably influenced by the block copolymer content. After adding 1 wt% BCP1, J_{sc} increased from 9.0 mA/cm² to 9.5 mA/cm², and the PCE increased from 3.31% to 3.57%. Further increasing the BCP1 to 5 wt%, J_{sc} of the corresponding device was increased to 9.7 mA/cm², with PCE simultaneously ascended to 3.64%. This increase in J_{sc} is a direct indication of the formation of a better interpenetrating morphology with obvious and larger interfacial area, as shown in AFM images of Figs. 8(f)–8(h). The root-mean square roughness of the films was 6.99, 2.49, 4.34, 3.10 and 2.24 nm for bare

P3HT:PC₆₁BM, blended films with 1%, 5%, 10% and 20% of BCP1 compatibilizers respectively. For P3HT:PC₆₁BM blends without any compatibilizers, the aggregation of PC₆₁BM phase with large domains or islands could be obviously observed. However, by adding only 1 wt% of BCP1 into P3HT:PC₆₁BM blends to enhance the miscibility of P3HT and PC₆₁BM, significantly inhibited PC₆₁BM aggregation and improved film morphology with phase-separated bicontinuously interpenetrating networks was achieved. The disappearance of PC₆₁BM large domains and improvement of film morphology could also be observed when with 5 wt% and 10 wt% of BCP1 additives. However, when the BCP1 concentration was further increased to 10 wt% and 20 wt%, the J_{sc} and PCE gradually reduced, especially at 20 wt%, the PCE of 3.27% was even lower than that of the control P3HT:PC₆₁BM device without any additives. The decrease in device performance at higher block copolymer contents of 20% was probably due to the excess of BCP1 compatibilizers to increased improvement of the miscibility between P3HT and PC₆₁BM, which formed a weakened phase-separation with smooth morphology in the thin film (Fig. 8j).

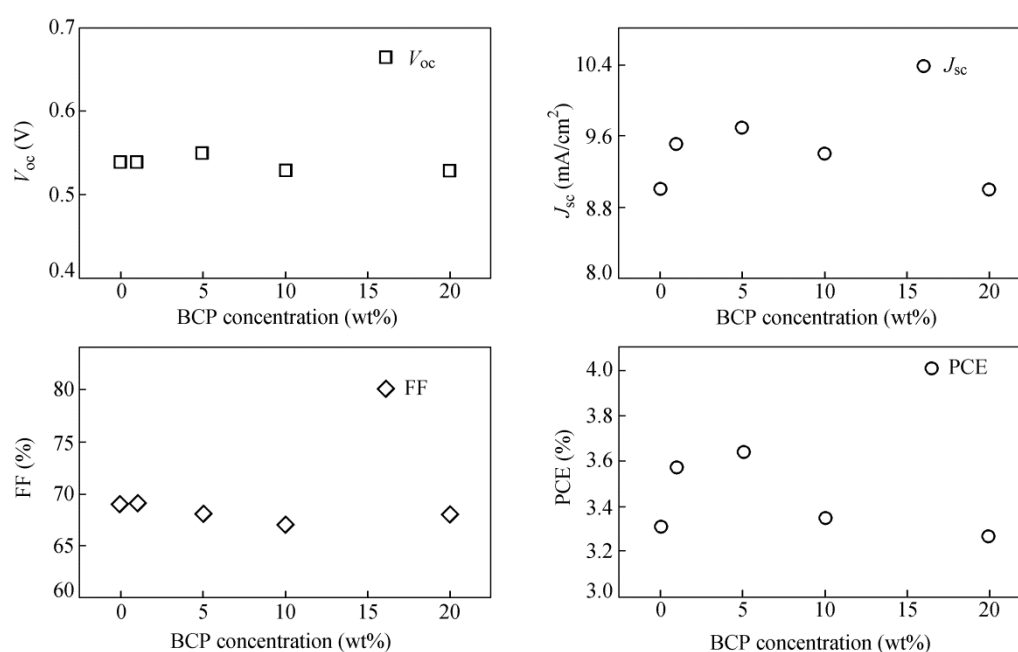


Fig. 7 V_{oc} , J_{sc} , FF and PCE change with different amounts of BCP1

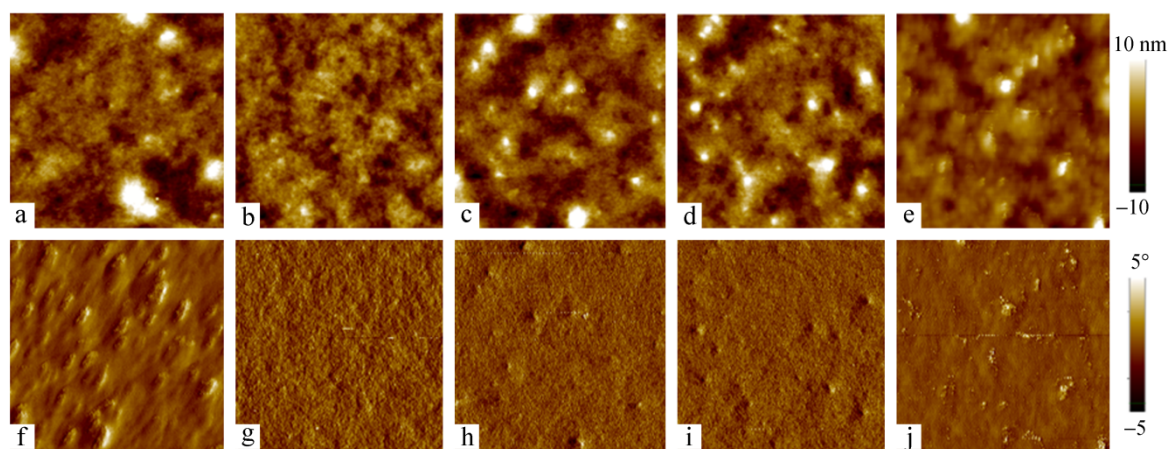


Fig. 8 AFM topography (top) and phase (bottom) images ($5\ \mu\text{m} \times 5\ \mu\text{m}$) of P3HT/PC₆₁BM blend with (a, f) 0%, (b, g) 1%, (c, h) 5%, (d, i) 10% and (e, j) 20% of BCP1

CONCLUSIONS

In conclusion, fully conjugated D-A block copolymers of P3HT-*b*-PCDTBT have been synthesized through an end-functional polymer copolymerization method. The immiscibility of the P3HT donor and PCDTBT acceptor block has been demonstrated to improve the phase-separation and promote the purification of block copolymers. Various block copolymers with low PDI and different molecular weight as well as unexpected similar P3HT weight content of ~75% has been obtained *via* careful purification through preparative GPC. The advantages of block copolymers P3HT-*b*-PCDTBT against P3HT/PCDTBT homopolymer blends on finely-ordered nano-structured film morphology has been judged by AFM images. Compared to bare P3HT:PC61BM devices, adding 5 wt% block copolymer as a compatibilizer resulted in a 8% and 10% increase in J_{sc} and PCE, respectively. Our work provides new avenues for the application of fully conjugated donor-acceptor block copolymers in polymer/fullerene bulk heterojunction polymer solar cells. Combined with other examples of fully conjugated D-A block copolymers, it is concluded that the nano-scale phase separation can be altered by tuning the relative solubility between the donor and acceptor blocks, the orthogonality and miscibility between the donor and acceptor block polymer induces the distinct phase separation and featureless film morphology, respectively.

REFERENCES

- 1 Yu, G., Gao J., Hummelen, J.C., Wudl, F. and Heeger, A.J., *Science*, 1995, 270: 1789
- 2 M. Halls, J.J., Walsh, C.A., Greenham, N.C., Marseglia, E.A., Friend, R.H., Moratti, S.C. and Holmes, A.B., *Nature*, 1995, 376: 498
- 3 You, J., Dou, L., Yoshimura, K., Kato, T., Ohya, K., Moriarty, T., Emery, K., Chen, C.C., Gao, J., Li, G. and Yang, Y., *Nat. Commun.*, 2013, 4: 1446
- 4 He, Z., Zhong, C., Su, S., Xu, M., Wu, H. and Cao, Y., *Nat. Photon.*, 2012, 6: 593
- 5 Keshtov, M.L., Marochkin, D.V., Fu, Y., Xie, Z., Geng, Y., Kochurov, V.S. and Khokhlov, A.R. *Chinese J. Polym. Sci.*, 2014, 32: 844
- 6 Qian, M., Zhang, R., Hao, J., Zhang, W., Zhang, Q., Wang, J., Tao, Y., Chen, S., Fang, J. and Huang, W., *Adv. Mater.*, 2015, 27: 3546
- 7 Wang, S., Yang, J., Zhang, Z., Hu, Y., Cao, X., Li, H., Tao, Y., Li, Y. and Huang, W., *RSC Adv.*, 2015, 5: 68192
- 8 Slota, J.E., He, X. and Huck, W.T.S., *Nano Today*, 2010, 5: 231
- 9 Etxebarria, I., Ajuria, J. and Pacios, R., *Org. Electron.*, 2015, 19: 34
- 10 Chan, S., Lai, C., Chen, H., Ting, C. And Chen, C.P., *Macromolecules*, 2011, 44: 8886
- 11 Riede, M.K., Sylvester-Hvid, K.O., Glatthaar, M., Keegan, N., Ziegler, T., Zimmermann, B., Niggemann, M., Liehr, A.W., Willeke, G. and Gombert, A., *Prog. Photovolt: Res. Appl.*, 2008, 16: 561
- 12 Mulherin, R.C., Jung, S., Huettner, S., Johnson, K., Kohn, P., Sommer, M., Allard, S., Scherf, U. and Greenham, N.C., *Nano Lett.*, 2011, 11: 4846
- 13 Chang, L., Lademann, H.W.A., Bonekamp, J.B., Meerholz, K. and Moulé, A.J., *Adv. Funct. Mater.*, 2011, 21: 1779
- 14 Pavlopoulou, E., Kim, C.S., Lee, S.S., Chen, Z., Facchetti, A., Toney, M.F. and Loo, Y., *Chem. Mater.*, 2014, 26: 5020
- 15 Lou, S.J., Szarko, J.M., Xu, T., Yu, L., Marks, T.J. and Chen, L.X., *J. Am. Chem. Soc.*, 2011, 133: 20661
- 16 Padinger, F., Rittberger, R.S. and Sariciftci, N.S., *Adv. Funct. Mater.*, 2003, 13: 85
- 17 Saeki, A., Yoshikawa, S., Tsuji, M., Koizumi, Y., Ide, M., Vijayakumar, C. and Seki, S., *J. Am. Chem. Soc.*, 2012, 134: 19035
- 18 Robb, M.J., Ku, S. and Hawker, C.J., *Adv. Mater.*, 2013, 25: 5686
- 19 Lai, Y., Ohshimizu, K., Takahashi, A., Hsu, J., Higashihara, T., Ueda, M. And Chen, W., *J. Polym. Sci., Part A: Polym. Chem.*, 2011, 49: 2577
- 20 Wang, J. and Higashihara, T., *Polym. Chem.*, 2013, 4: 5518

- 21 Scherf, U., Gutacker, A. and Koenen, N., *Acc. Chem. Res.*, 2008, 41: 1086
- 22 Lee, Y. and Gomez, E.D., *Macromolecules*, 2015, 48: 7385
- 23 Wang, S., Guo, Y., Yang, J., Tao, Y. and Huang, W., *Chin. J. Chem.*, 2015, 33: 865
- 24 Ku, S.Y., Brady, M.A., Treat, N.D., Cochran, J.E., Robb, M.J., Kramer, E.J., Chabinye, M.L. and Hawker, C.J., *J. Am. Chem. Soc.*, 2012, 134: 16040
- 25 Guo, C., Lin, Y.H., Witman, M.D., Smith, K.A., Wang, C., Hexemer, A., Strzalka, J., Gomez, E.D. and Verduzco, R., *Nano Lett.*, 2013, 13: 2957
- 26 Bolag, A., Hayashi, H., Charbonnaz, P., Sakai N. and Matile, S., *Chemistry Open*, 2013, 2: 55
- 27 Jea Uk, L., Jae Woong, J., Todd, E., Thomas, P.R. and Won Ho, J., *Nanotechnology*, 2010, 21: 105201
- 28 Rajaram, S., Armstrong, P.B., Kim, B.J. and Fréchet, J.M.J., *Chem. Mater.*, 2009, 21: 1775
- 29 Wang, S., Yang, Q., Tao, Y., Guo, Y., Yang, J., Liu, Y., Zhao, L., Xie, Z. and Huang, W., *New J. Chem.*, 2016, 40: 1825
- 30 Mok, W., Lin, Y., Yager, K.G., Mohite, A.D., Nie, W., Darling, S.B., Lee, Y., Gomez, E., Gosztola, D., Schaller, R.D. and Verduzco, R., *Adv. Funct. Mater.*, 2015, 25: 5578
- 31 Nakabayashi, K. and Mori, H., *Macromolecules*, 2012, 45: 9618
- 32 Lin, Y.H., Smith, K.A., Kempf, C.N. and Verduzco, R., *Polym. Chem.*, 2013, 4: 229
- 33 Bu, L.J., Guo, X.Y., Yu, B., Qu, Y., Xie, Z.Y., Yan, D.H., Geng, Y.H. and Wang, F.S., *J. Am. Chem. Soc.*, 2009, 131: 13242
- 34 Gao, D., Hollinger, J. and Seferos, D.S., *ACS Nano*, 2012, 6: 7114
- 35 Kozycz, L.M., Gao, D., Hollinger, J. and Seferos, D.S., *Macromolecules*, 2012, 45: 5823
- 36 Hollinger, J., Sun, J., Gao, D., Karl, D. and Seferos, D.S., *Macromol. Rapid Commun.*, 2013, 34: 437
- 37 Chi, C., Chen, M., Liaw, D., Wu, H., Huang, Y. and Tai, Y., *ACS Appl. Mater. Inter.*, 2014, 6: 12119
- 38 Qu, J.F., Gao, B.R., Tian, H.K., Zhang, X.J., Wang, Y., Xie, Z.Y., Wang, H.Y., Geng, Y.H. and Wang, F.S., *J. Mater. Chem. A*, 2014, 2: 3632
- 39 Lombeck, F., Komber, H., Sepe, A.R., Friend, H. and Sommer, M., *Macromolecules*, 2015, 48: 7851
- 40 Salleo, A., Kline, R.J., DeLongchamp, D.M. and Chabinye, M.L., *Adv. Mater.*, 2010, 22: 3812
- 41 Sirringhaus, H., Tessler, N. and Friend, R.H., *Science*, 1998, 280: 1741.
- 42 Duong, D.T., Phan, H., Hanifi, D., Jo, P.S., Nguyen, T.Q. and Salleo, A., *Adv. Mater.*, 2014, 26: 6069
- 43 Blouin, N., Michaud, A. and Leclerc, M., *Adv. Mater.*, 2007, 19: 2295
- 44 He, Z., Zhong, C., Huang, X., Wong, W.Y., Wu, H., Chen, L., Su, S. and Cao, Y., *Adv. Mater.*, 2011, 23: 4636
- 45 Ashraf, R.S., Schroeder, B.C., Bronstein, H.A., Huang, Z., Thomas, S., Kline, R.J., Brabec, C.J., Rannou, P., Anthopoulos, T.D., Durrant, J.R. and McCulloch, I., *Adv. Mater.*, 2013, 25: 2029
- 46 Verswyvel, M., Steverlynck, J., Hadj Mohamed, S., Trabelsi, M., Champagne, B. and Koeckelberghs, G., *Macromolecules*, 2014, 47: 4668
- 47 Dhibi, O., Ltaief, A. and Bouazizi, A., *Mater. Sci. Semicond. Process.*, 2014, 25: 173
- 48 Guo, Y., Jiang, L., Ma, X., Hu, W. and Su, Z., *Polym. Chem.*, 2013, 4: 4308
- 49 Verduzco, R., Botiz, I., Pickel, D.L., Kilbey, S.M., Hong, K., Dimasi, E. and Darling, S.B., *Macromolecules*, 2011, 44: 530