Well-defined donor-acceptor rod-coil diblock copolymers based on P3HT containing C_{60} : the morphology and role as a surfactant in bulk-heterojunction solar cells[†][‡]

Changduk Yang,^{ac} Jae Kwan Lee,^b Alan J. Heeger^b and Fred Wudl^{*ab}

Received 27th January 2009, Accepted 20th April 2009 First published as an Advance Article on the web 9th June 2009 DOI: 10.1039/b901732a

The synthesis of well-defined rod–coil block copolymers consisting of P3HT donor and C_{60} acceptor chromophores (**P3HT-***b***-P(S_xA_y)-C₆₀**) in a molecular architecture is reported for use in bulkheterojunction (BHJ) solar cells. In thin films of the resulting block copolymer, reproducible selfassembly into well-defined "nanofibrils" is observed. This is the first example of a block copolymer containing a C_{60} derivative that shows exclusively a nanofibrilar structure. We have investigated the potential utility of the block copolymer as a "surfactant" for controlling the interface morphology of the P3HT:PCBM donor–acceptor phase domains within the composite. We find a substantial improvement in device performance when 5% of block copolymer are introduced to the P3HT:PCBM blend system, resulting in *ca*. 35% improved efficiency relative to the P3HT:PCBM solar cell fabricated without the "surfactant".

Introduction

Organic photovoltaic (OPV) devices based on π -conjugated polymer and fullerene composites, so-called "bulk heterojunction (BHJ)", offer an intrinsically low-cost, scalable approach to photovoltaic technology.^{1,2} Important examples of materials used for fabricating BHJ solar cells include blends of thiophene-based polymers as electron donors (D) and fullerene derivatives as electron acceptors (A).^{3–10} Synthetic effort has focused on improving the power conversion efficiencies (PCEs) by means of development of low band-gap polymers^{8,9} and fullerene derivatives.^{7,10} With the goal of obtaining improved performance, control of the morphology within the BHJ material has utilized processing additives,^{11,12} different solvents (and mixed solvents),¹³ and thermal annealing.^{14–17} These different methods attempt to facilitate the phase separation on length scales of a few nanometers in the devices.^{4,16}

Rod-coil di-(AB-type) copolymers constitute a class of macromolecules that can be uniquely fashioned into self-assembled nanostructures in which the rod blocks align along their long axes into nanoscaled domains, often creating liquid crystalline mesophases.¹⁸⁻²³ Therefore, in the case of the rod-coil block copolymers containing a rigid conjugated polymer segment as a rod block, their ability to self-organize can be used to optimize the morphology in OPV devices.

Reports on rod–coil block copolymers based on P3HT rods and polyolefin coils by using *living* radical polymerization techniques have established the existence of nanofibrilar structures in the solid state.^{24–28} Although there are reports of synthesis directed toward soluble donor–acceptor rod–coil diblock copolymers containing C₆₀ for use as the active layer in solar cells,^{29–32} the difficulty in removing unreacted C₆₀ has limited the success of this approach.

Recently, Fréchet *et al.* have demonstrated the synthesis of a well-defined donor–acceptor amphiphilic diblock copolymer by using ring-opening metathesis polymerization (ROMP). They showed that the diblock copolymer can play a critical role in tuning the device morphology when employed as an additive, leading to stabilization of the device structure against destructive thermal phase segregation.²⁶ Thus, the synthesis and characterization of well-defined "donor–acceptor rod–coil" diblock copolymers promise to be of use in obtaining selfassembled nanostructures in materials for OPV. Very recently, Jo *et al.* also reported a similar work to ours about a block copolymer based on P3HT containing C₆₀ via ATRP and followed by linking a fullerene derivative (PCBA) to the second block. However, the photovoltaic performance was not presented.³³

Herein, we describe the synthesis of a well-defined donoracceptor rod-coil diblock copolymer based on P3HT containing C_{60} (P3HT-*b*-P(S_xA_y)-C₆₀) through a combination of *living* polymerization strategy and subsequent polymer-analogous cycloaddition reaction. Despite the bulky nature of the rigid C₆₀ units in the coil blocks, the observation of a nanofibrilar morphology with corresponding enhancement in performance of BHJ material is demonstrated.

Results and discussion

Among various living polymerization methods, reversible addition fragmentation chain transfer (RAFT) was found to be the

^aMitsubishi Chemical Center for Advanced Materials and Department of Chemistry and Biochemistry, University of California Santa Barbara, Santa Barbara, California, 93106, USA. E-mail: wudl@chem.ucsb.edu; Fax: +1 805 893 4120; Tel: +1 805 893 5817

^bCenter for Polymers and Organic Solids, University of California Santa Barbara, Santa Barbara, California, 93106, USA

^cSchool of Energy Engineering, Ulsan National Institute of Science and Technology, Ulsan, 689-805, South Korea

[†] This paper is part of a *Journal of Materials Chemistry* theme issue on solar cells. Guest editors: Michael Grätzel and René Janssen.

[‡] Electronic Supplementary Information (ESI) available: ¹H and ¹³C NMR spectra for all new compounds. See DOI: 10.1039/b901732a

most convenient for the synthesis of the rod-coil block copolymer containing polyolefin since it does not involve the use of a transition metal catalyst.^{34,35} This protocol is applicable to a whole range of monomers.³⁶ The synthetic method is outlined in Scheme 1. The polymerization of 2,5-dibromo-3-hexylthiophene was performed by (GRIM) reaction with i-PrMgCl·LiCl-nickel catalyst,37 followed by the treatment of a second Grignard reagent (allyl magnesium bromide), resulting in the mono-end-capped P3HT ($M_n = 8.3 \text{ kg mol}^{-1}$, PDI = 1.11, against PS standard). This is a slight synthetic modification of McCullough's method.²⁵ The allyl-mono-capped P3HT typically contained two populations, one major and one minor, which correspond to allyl/Br and allyl/H, respectively.38 To completely rule out the halogen defect on electronic applications, the allyl/Br fractions in the polymer were debrominated by a Grignard reaction and quenched with water to give well-defined monocapped P3HT (allyl/H). The allyl end group was easily converted to hydroxypropyl mono-terminated P3HT and then treated with 3-benzylsulfanylthiocarbonylsulfanylpropionic acid chloride,³⁹ vielding a trithiocarbonate macro-RAFT agent based on P3HT.25

The fullerene-containing block must retain a large degree of freedom for the fullerenes to be able to interact with each other with minimum inhibition. This requires a long, flexible tether to ameliorate the rigidity imposed by the backbone. Therefore, an acrylate monomer **2** with a very flexible tether was designed for the route to functionalization through the addition of diazo compounds to buckminsterfullerene (Scheme 1). The ketone compound **1** was prepared by esterification of 4-benzoylbutyric acid with 1,8-dibromooctane in the presence of potassium carbonate and subsequently coupled with acrylic acid *via* a second esterification to generate the desirable acrylate monomer **2** in 60% overall yield (two steps). To avoid the radical incorporation of C₆₀,⁴⁰ the synthetic approach generated the target block copolymer *via* initial polymerization and subsequent polymer-analogous reaction with C₆₀.

To prepare a soluble methanofullerene–polyolefin linkage with a "charm bracelet" type pendent fullerene structure, various polyketones with long flexible chains were synthesized in our initial synthetic attempts. These resulting polymers were converted to the corresponding polytosylhydrazones, and these were allowed to react with C_{60} . Unfortunately, however, soluble



Scheme 1 Synthetic approach toward the donor-acceptor rod-coil diblock copolymer (P3HT-b-P(S_xA_v)-C₆₀).

View Article Online

polymers could not be isolated. A likely rationale for this result is the occurrence of crosslinking *via* the multifunctionality of C_{60} . Therefore, we settled on styrene units as an unreactive group that can suppress the crosslinking and act as a flexible and inert spacer between the balls, presumably resulting in soluble polymers with C_{60} .

With this in mind, statistical copolymers with different feed ratios of styrene to **2** were prepared and subsequently tested for functionalization with C_{60} . Depending on the degree of the styrene feed, this did, indeed, create a solution-processable "charm bracelet" polymer containing C_{60} .

Rod-coil diblock copolymers based on P3HT (**P3HT**-*b*-**P**(**S**_{*x*}**A**_{*y*}) (P3HT = poly(3-hexylthiophene), S = styrene, A = acrylate) with feed ratios of styrene to acrylate monomer **2** (x : y, 6 : 4 and 8 : 2 mol%, respectively) were synthesized *via* RAFT polymerization (Scheme 1). Table 1 summarizes the physical properties and composition as determined by ¹H NMR and GPC.^{24,25}

Condensation of the polyketones with *p*-tosylhydrazide in THF generated the corresponding precursor polytosylhydrazones, which after sequential treatment with sodium methoxide in pyridine and C_{60} in refluxing *o*-dichlorobenzene (o-DCB) gave the donor-acceptor rod-coil diblock copolymers (P3HT-b-P(S₆A₄)-C₆₀ and P3HT-b-P(S₈A₂)-C₆₀). According to the reported purification to remove unreacted C_{60} ,⁴¹ the crude polymer was subjected to Soxhlet extraction with hexane for 7 d. However, thin layer chromatography (TLC) showed the presence of a sizable amount of unreacted C₆₀. It was also reported that the solubility of C₆₀ in THF is negligible.^{42,43} Thus, as an alternative purification, the crude compound was redissolved in a large amount of THF and filtered to remove any unreacted C_{60} . The procedure was repeated five times, and the polymer was filtered through a micron filter (0.45 µm) twice. Despite several filtrations, a trace amount of C₆₀ was still observed by TLC, an observation at odds with the report by Hadziioannou et al.^{29,30} For further purification, the crude product was repeatedly dissolved (about five times) in o-dichlorobenzene (o-DCB) and precipitated into hot hexane, until any trace (via TLC) of the unreacted C_{60} was removed. The P3HT-b-P(S₈A₂)-C₆₀ is readily soluble in organic solvents (THF, toluene, chlorobenzene, o-DCB, etc.) whereas P3HT-b-P(S₆A₄)-C₆₀, after complete drying, exhibited only limited solubility. This has also been observed by other groups^{29,44} and currently lacks a logical explanation. However, it most likely arises from strong interdigitation between the polymer backbone and C₆₀ in the solid state due to the high content of C_{60} . The low solubility of P3HT-b-P(S₆A₄)-C₆₀ limited the NMR characterization. Inspection of the ¹H NMR spectrum of P3HT-b-P(S₈A₂)-C₆₀

showed that the signal from hydrogen (N=CCH₂-) adjacent to the tosylhydrazone unit in the precursor polymer at $\delta = 2.64$ ppm completely vanished, and a new peak (*ca.* $\delta = 3.07$ ppm) associated with the hydrogen (PhCCH₂-) on neighboring C₆₀ appeared. Also, in the ¹³C NMR spectrum a broad set of resonances were observed between 137 and 148 ppm, with the characteristic sharp peak at 143 ppm that arises from unreacted C₆₀ being absent (see ESI[‡]).

Fig. 1 depicts the UV-Vis absorption spectra of P3HT*b*-P(S_xA_y), a mixture of P3HT-*b*-P(S_xA_y) and C₆₀, and the donor-acceptor diblock copolymers (P3HT-*b*-P(S_6A_4)-C₆₀ and P3HT-*b*-P(S_8A_2)-C₆₀) in solution in chloroform. To precisely clarify the effect of buckminsterfullerene functionalization on the absorption features, P3HT-*b*-P(S_xA_y) and the mixed P3HT*b*-P(S_xA_y) and C₆₀ solutions were also investigated. While P3HT-*b*-P(S_6A_4)-C₆₀ and P3HT-*b*-P(S_8A_2)-C₆₀ exhibited a shoulder at around 330 nm, arising from absorbed C₆₀. Hadziioannou *et al.* claimed that fullerene polymers exhibit a distinguishable sharp band at 330 nm.³⁰ However, such an optical feature is only observed in the case of the polymer containing unreacted C₆₀ (see a mixture of P3HT-*b*-P(S_xA_y) and C₆₀ in Fig. 1).

In the case of P3HT-*b*-P(S_6A_4)-C₆₀, only a long tailing band into the visible part of the spectrum was observed, presumably originating from the scattering of the particles in the solution due to limited solubility. The absorption bands centered at 453 nm that originate from the P3HT segment in P3HT-*b*-P(S_6A_4)-C₆₀ and P3HT-*b*-P(S_8A_2)-C₆₀ are dramatically reduced, compared to P3HT-*b*-P(S_xA_y).



Fig. 1 UV-Vis absorption spectra of the copolymers in CHCl₃ ($-\Diamond -$, P3HT-*b*-P(S_xA_y); $-\Rightarrow -$, a mixture of P3HT-*b*-P(S_xA_y) and C₆₀; $-\bigtriangleup -$, P3HT-*b*-P(S₆A₄)-C₆₀; $-\bigcirc -$, P3HT-*b*-P(S₈A₂)-C₆₀).

Table 1 Characteristics of P3HT-*b*-P($S_x A_y$)-C₆₀^{*a*}

Compound	P3HT ^b /mol%	PS ^b /mol%	PA ^b /mol%	$M_{ m n}{}^c$	PDI ^c
РЗНТ	100	0	0	8300	1.11
P3HT-b-P(S ₆ A ₄)-C ₆₀	17	51	32	23 100	1.59
P3HT-b-P(S ₈ A ₂)-C ₆₀	12	71	17	18 500	1.61

^{*a*} **P3HT-b-P**($S_x A_y$); P3HT = poly(3-hexylthiophene, S = styrene, A = acrylate, x : y = feed ratio of styrene to acrylate. ^{*b*} Determined by ¹H NMR peak integrals. ^{*c*} Estimated from GPC (eluent = THF, polystyrene standard).



Fig. 2 TGA of $-\diamond -$, P3HT-*b*-P(S_xA_y); $-\triangle -$, P3HT-*b*-P(S₆A₄)-C₆₀; $-\bigcirc -$, P3HT-*b*-P(S₈A₂)-C₆₀ under N₂. Heating rate 10 °C min⁻¹.

The C₆₀ content obtained from the TGA usually shows a somewhat higher value since crosslinking of polymers can occur upon heating, resulting in a larger residue.³⁰ However, TGA is still a reliable technique to verify the amount of C₆₀ in the polymers. **P3HT-b-P(S_xA_y**) completely decomposed when heated up to 550 °C, leaving residues at this temperature in the order of 47 and 35 wt% for **P3HT-b-P(S₆A₄)-C₆₀** and **P3HT-b-P(S₈A₂)-C₆₀**, respectively (Fig. 2). These results confirm that the donor–acceptor diblock copolymers contain substantial amounts of C₆₀. Broadly, the values can also be considered as the corresponding C₆₀ content since the pure C₆₀ is stable up to 550 °C.

Only **P3HT-***b***-P**(**S**₈**A**₂)-**C**₆₀ was investigated in detail for device fabrication since the poor solubility of **P3HT-***b***-P**(**S**₆**A**₄)-**C**₆₀ prevented deposition of thin films. The UV-Vis spectrum of the block copolymer (**P3HT-***b***-P**(**S**₈**A**₂)-**C**₆₀) was recorded from thin films obtained by spin-casting from chlorobenzene solution (5 wt%). A pronounced bathochromic shift (~50 nm) is not only observed but the intensity of the π - π * transition band also increased relative to that in solution, indicating the presence of P3HT chain ordering within the rod building block in the solid state (Fig. 3a).

Tapping mode atomic force microscopy (AFM) was employed to investigate the surface topography. Fig. 3b and c show the height and corresponding phase images for **P3HT-***b***-P(S₈A₂)-C₆₀** pristine film cast from chlorobenzene. Surprisingly, despite having a bulky, rigid C₆₀ in the coil block, typical features are clearly visualized by AFM as very well-defined micron-sized "nanofibrils". This is the first time that a rod-coil block copolymer with C_{60} units has been observed to exhibit long nanofibrilar structures. We are currently endeavoring to further clarify the nanofibrilar structure *via* various tools such as WAXS, SAXS, and TEM in our cooperative group in detail and will be published in due course.⁴⁵

Such supramolecular organization is in good agreement with our concept that P3HT-b-P(S_8A_2)-C₆₀ can allow controlled assembly into unique morphologies. Therefore, it is possible to replace the traditional BHJ system (P3HT:PCBM) by P3HT-b-P(S_8A_2)-C₆₀ containing ordered donor- and acceptor-type moieties in a single framework, a novel architecture for OPV devices. Applications of P3HT-b-P(S_8A_2)-C₆₀ in solar cells and field-effect transistors (FETs) were explored in preliminary studies, but showed disappointing device performance. This is most likely a result of large amounts of insulating moieties such as styrene units and long flexible chains in the coil segments that were required for solubility.

Exciton dissociation in the BHJ solar cells occurs at the interface between the two immiscible components (P3HT and PCBM). Thus, the strategy toward improving miscibility between the P3HT and PCBM domains implies phase separation with a large interfacial area, resulting in higher performance of BHJ devices.^{26,46} These ideas prompted us to utilize P3HT-*b*-P(S₈A₂)-C₆₀ as a "surfactant" for improved self-organization of the two ingredients (*e.g.* P3HT and PCBM). While the results presented here were being collected a similar approach using conjugated block copolymer surfactants for BHJ devices was reported; however, their characteristics in solar cells were not described in detail.^{47,48} Traditionally, diblock copolymers can play a critical role in compatibilizing immiscible pairs in the condensed phases.^{26,49}

The effectiveness of the diblock copolymer surfactants is sensitive to their concentration in the immiscible systems.^{49,50} Thus, BHJ films (P3HT:PCBM, at weight ratio 1: 0.7 w/w) with the addition of various P3HT-*b*-P(S₈A₂)-C₆₀ concentrations (0, 5, 10, and 20 wt%) were prepared by casting from chlorobenzene at 300 rpm, followed by slow evaporation at room temperature for 10 min. Note that the slow drying process was necessary to allow the P3HT-*b*-P(S₈A₂)-C₆₀ to behave as a morphology modifier in the blend film. The as-cast film of P3HT:PCBM shows a smooth surface. Upon adding 5 wt% P3HT-*b*-P(S₈A₂)-C₆₀ to the blend mixture, the film constituents



Fig. 3 UV-Vis absorption spectrum (a) and tapping mode AFM images (height (b), phase (c)) of the P3HT-b-P(S₈A₂)-C₆₀ pristine film.



Fig. 4 Tapping mode AFM images of P3HT:PCBM (1 : 0.7 w/w) BHJ films processed with P3HT-*b*-P(S_8A_2)-C₆₀; none (a), 5 wt% (b), 10 wt% (c), and 20 wt% (d).

diffuse and the phase domains increased in size (Fig. 4b). A rationale for this feature is migration of the block copolymer as a surfactant into the interface between P3HT and PCBM, resulting in the improved miscibility of the P3HT and PCBM. As the amount of **P3HT-b-P(S_8A_2)-C_{60}** increased in the blend, up to 20 wt%, detectable phase segregation, most likely attributed to the further enhancement of compatibility between P3HT and PCBM components, was observed.

We have shown, therefore, that the surfactant-like property of **P3HT-***b***-P**(**S**₈**A**₂)-**C**₆₀ can affect the phase segregation within a P3HT:PCBM blend. To determine the effect of the surfactant on the performance of P3HT:PCBM solar cells, devices with **P3HT-***b*-**P**(**S**₈**A**₂)-**C**₆₀ as an additive (0, 5, 10, and 20 wt%) were fabricated (Fig. 5), as described in detail in the Experimental



Fig. 5 Current (*J*)-voltage (*V*) characteristics of P3HT:PCBM composite films with P3HT-*b*-P(S₈A₂)-C₆₀ additives: (a) none ($-\Rightarrow$ -), (b) 5 wt% ($-\bullet$ -), (c) 10 wt% ($-\bullet$ -), (d) 20 wt% ($-\bullet$ -).

section. Post-production annealing at high temperature (~150 °C) was performed since it has been shown to be an efficient method for improving the electrical characteristics of P3HT:PCBM-based solar cells. Performance optimization involved over 500 devices made from over 100 independently prepared P3HT:PCBM blends. The data points from the optimized devices in Fig. 5 are representative; variations were within $\pm 15\%$, an error range that resulted from the poor uniformity of the BHJ film formed during the slow drying process. The optimum thickness of the BHJ films obtained under these conditions was approximately 300 nm. All data were obtained under white light AM1.5G illumination from a calibrated solar simulator with irradiation intensity of 100 mW cm⁻².

For comparison of the efficiencies upon addition of P3HT-b-P(S₈A₂)-C₆₀, a device fabricated with only P3HT:PCBM in the active layer was used as a standard reference. The P3HT:PCBM device had a short circuit current density (J_{sc}) of 8.79 mA cm⁻², an open circuit voltage (V_{oc}) of 0.62 V, and a fill factor (FF) of 48%, yielding a PCE (η_e) of 2.6%. Solar cells made with P3HT:PCBM processed with 5 wt% P3HT-b-P(S₈A₂)-C₆₀ showed a considerably improved $J_{sc} = 11.6 \text{ mA cm}^{-2}$, while the V_{oc} (0.63 V) and FF (48%) remained similar to those of the devices without P3HT-b- $P(S_8A_2)-C_{60}$. The corresponding PCE (η_e) was 3.5%, approximately 35% higher than that obtained from a pristine P3HT:PCBM device. This positive effect in photocurrent can be ascribed to improvement in the bicontinuous interpenetrating networks of the BHJ composite due to the surfactant effect from the diblock copolymer. This conclusion is supported by features observed in the AFM. Increasing the amount of P3HT-b- $P(S_8A_2)-C_{60}$ in the blend film to 10 wt% lowers the J_{sc} value and leads to an overall decrease in PCE (η_e) to 3.1%. The performance of the BHJ solar cells processed with 20 wt% P3HT-b-P(S₈A₂)- C_{60} was markedly lower. Such deterioration in the photocurrent is likely the origin of the aggressive phase segregation observed in the film morphology. Additionally, we cannot rule out that in the presence of large amounts of P3HT-b-P(S₈A₂)-C₆₀, it is possible to suppress the charge carrier transport in the BHJ device due to the non-conjugated styrene units and long flexible chains in the coil blocks. We are currently studying the surfactant effect of the block copolymer on device efficiency of BHJ solar cells with different component materials as a route toward a logical design to improve the device performance.

Conclusion

In summary, well-defined "donor-acceptor rod-coil" diblock copolymers comprising P3HT as donor and C_{60} as acceptor blocks (P3HT-b-P(S_xA_y)- C_{60}) have been synthesized by a straightforward synthetic strategy of *living* polymerization and subsequent cycloaddition. In spite of the bulky, rigid C_{60} units in the coil segments, the resulting copolymer exhibits a long-range nanofibrilar structure, similar to those of typical rod-coil block copolymers. This is the first time that the formation of nanofibrils has been demonstrated in a block copolymer bearing C_{60} . By adding small amounts of the diblock copolymer to P3HT:PCBM, the interfacial morphology between the two immiscible components can be altered, resulting in a noticeable difference in phase segregation of the BHJ films. The characteristics of the solar cells were evaluated by the addition of various amounts of the diblock copolymer (0, 5, 10, and 20 wt%) as a processing surfactant in the BHJ system (P3HT:PCBM, 1 : 0.7 w/w). The BHJ device obtained by adding 5% diblock copolymer afforded a significant enhancement of J_{sc} by creating suitable phase domains, leading to about 35% increase in PCE (η_e) to 3.5%, when compared to the reference cell without the surfactant. Studies are underway to further optimize and clarify the surfactant effect of the diblock copolymer in a variety of BHJ configurations that may lead to improved PCE (η_e). The use of new block copolymers as additives provides an important opportunity for control of the BHJ morphology.

Experimental section

General

All solvents were purified and freshly distilled prior to use, following literature procedures. The synthesis of 3-benzylsulfanylthiocarbonylsulfanylpropionic acid chloride³⁹ and trithiocarbonate terminated poly(3-hexylthiophene) (macro-RAFT agent)²⁵ was also adapted from the literature procedures. Commercially available materials were used as received unless otherwise noted. ¹H and ¹³C NMR spectra were recorded on a Varian Mercury Vx 200 MHz or Varian Unity Inova 500 MHz spectrometer and referenced to the solvent peak. Mass spectrometry and elemental analysis were performed by the UC Santa Barbara Mass Spectrometry Lab and elemental analysis center.

Device fabrication

The BHJ films were prepared under optimized conditions according to the following procedure reported previously:¹² the indium tin oxide (ITO)-coated glass substrate was first cleaned with detergent, ultrasonicated in acetone and isopropyl alcohol, and subsequently dried overnight in an oven. Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS, Baytron PH) in aqueous solution was spin-cast to form a film with thickness of approximately 40 nm. The substrate was dried for 10 min at 140 °C in air and then transferred into a glove box to spin-cast the photoactive layer. A solution containing a mixture of 1 wt% P3HT:PCBM (1 : 0.7 w/w) in chlorobenzene with varying additive weight concentration from 0 to 20 wt% additives was then spin-cast on top of the PEDOT layer. Then, the device was pumped down to lower than 10^{-7} torr and a ~100 nm thick Al electrode was deposited on top.

For calibration of the solar simulator, we first carefully minimized the mismatch of the spectrum (the simulating spectrum) obtained from the Xenon lamp (300 W Oriel) and the solar spectrum using an AM1.5G filter. We then calibrated the light intensity using calibrated standard silicon solar cells with a proactive window made from KG5 filter glass traced to the National Renewable Energy Laboratory (NREL). Measurements were done with the solar cells before encapsulation inside the glove box using an optical fiber to guide the light from the solar simulator outside the glove box, and also were done with the solar cell after encapsulation outside the glove box from the solar simulator. Current density–voltage curves were measured with a Keithley 236 source measurement unit. The tapping mode AFM images were obtained with a Dimension 3100 atomic force microscope.

8-Bromooctyl benzoylbutyrate (1). A mixture of benzoylbutyric acid (9.0 g, 46.8 mmol), 1,8-dibromooctane (31.5 g, 117.0 mmol), potassium carbonate (16.4 g, 117.0 mmol), dry DMF (70 mL), and a catalytic amount of tetra-n-butylammonium iodide (1.0 mol%) was stirred and heated at 50 °C overnight. The solvent was evaporated. The residue was washed with dilute HCl and then extracted into diethyl ether, washed with brine, and dried over MgSO₄. The solvent and excess 1.8-dibromooctane were removed under reduced pressure. The crude product was chromatographed on silica using 0-20% ethyl acetate in hexane. Isolated yield = 13.5 g (75%) as a colorless liquid. ¹H NMR $(CDCl_3, 200 \text{ MHz})$: δ ppm 7.95 (dd, J = 8.24, 1.49 Hz, 2H), 7.47 (m, 3H), 4.05 (t, J = 6.64 Hz, 2H), 3.37 (t, J = 6.81, 2H), 3.04 (t, J = 7.13 Hz, 2H), 2.42 (t, J = 7.20 Hz, 2H), 2.01 (m, 2H), 1.82–1.73 (m, 2H), 1.69–1.51 (m, 2H), 1.47–1.21 (m, 8H). ¹³C NMR (CDCl₃, 50.28 MHz): & 199.29, 173.25, 136.75, 133.00, 128.52, 127.94, 64.41, 37.40, 33.90, 33.34, 32.67, 28.96, 28.50, 27.97, 25.76, 19.34. HRMS (EI) m/z: 405 ((M + Na)⁺⁺). Elemental analysis: calculated for C₁₉H₂₇BrO₃: C, 59.53; H, 7.10; Br, 20.85; O, 12.52. Found: C, 59.77; H, 7.52%.

8-Acryloyloxyoctyl benzoylbutyrate (2). A mixture of compound 1 (8.0 g, 20.0 mmol), potassium carbonate (2.25 g, 30.0 mmol), dry DMF (35 mL), and a catalytic amount of tetra*n*-butylammonium iodide (1.0 mol%) was stirred and heated at 50 °C overnight. The solvent was evaporated. The residue was washed with dilute HCl and then extracted into diethyl ether, washed with brine, and dried over MgSO₄. The crude product was chromatographed on silica using 0-20% ethyl acetate in hexane. Isolated yield = 6.0 g (80%) as a colorless oil. ¹H NMR (CDCl₃, 200 MHz): δ ppm 7.95 (d, J = 6.11 Hz, 2H), 7.67–7.17 (m, 3H), 6.39 (d, J = 16.11 Hz, 1H), 6.26-5.99 (m, 1H), 5.86 (dd, J = 23.61, 10.04 Hz, 1H), 4.36–3.86 (m, 4H), 3.01 (m, 2H), 2.43 (m, 2H), 2.02 (m, 2H), 1.72–1.51 (m, 4H), 1.37–1.21 (s, 8H). ¹³C NMR (CDCl₃, 50.28 MHz): δ 199.32, 173.28, 166.24, 136.76, 133.00, 130.39, 128.53, 127.96, 64.41, 37.41, 33.34, 29.03, 28.50, 25.78, 19.36. HRMS (EI) m/z: 397 ((M + Na)⁺⁺). Elemental analysis: calculated for C₂₂H₃₀O₅: C, 70.56; H, 8.07; O, 21.36. Found: C, 71.00; H, 7.95%.

Allyl terminated P3HT. A dry Schlenk flask was flame-dried under vacuum and was charged with 2,5-dibromo-3-hexylthiophene (5 g, 15.32 mmol), Ni(dppp)Cl₂ (0.248 g, 510 mmol) and anhydrous THF (100 mL). The flask was evacuated and purged with argon three times. The reaction was placed in an ice-water bath and then a 1 M solution of *i*-PrMgCl·LiCl (15.5 mL, 15.5 mmol) was added dropwise manually via syringe over 20 min. The polymerization was allowed to proceed for 1 h at 0 °C followed by the addition of a 1 M solution of allyl magnesium bromide (10 mL, 10 mmol). The reaction mixture was stirred for an additional 30 min followed by quenching with MeOH (200 mL). The resulting solid was filtered off and subjected to sequential Soxhlet extraction with methanol (1 d), acetone (1 d), and hexane (1 d) to remove the low molecular weight fractions. The residue was extracted with THF to give a dark reddish product after precipitating again from methanol and drying in *vacuo*. GPC analysis $M_{\rm p} = 8300 \text{ g mol}^{-1}$, $M_{\rm w} = 9200 \text{ g mol}^{-1}$, and PDI = 1.1 (against PS standard). The NMR spectrum is identical to that of the literature described previously.^{25,38}

Procedure for RAFT polymerization. Trithiocarbonate terminated P3HT as a macro-RAFT agent (0.10 g, ~12 µmol estimated by GPC result), AIBN (0.75 mg, 4.5 µmol) as an initiator, and anhydrous toluene (2.5 mL) were mixed in a Schlenk flask which was then purged with argon for 15 min. To this solution, an appropriate feed ratio of styrene to acrylate monomer 2 and anhydrous toluene (3 mL) were added and the mixture was degassed by freeze-pump-thaw cycles $(3\times)$, and then back-filled with dry argon. The mixture was immersed in an oil bath at 75 °C for 24 h. The polymer solution was transferred to a centrifuge tube, precipitated with MeOH (200 mL), centrifuged, and decanted. The crude product was treated with MeOH twice in the same manner and subjected to Soxhlet extraction with hexane (1 d). Then, the residue was redissolved in hot ethyl acetate and filtered to remove the trace amounts of unreacted P3HT since the P3HT was not completely soluble in ethyl acetate, and then the filtrate was evaporated. After being redissolved in THF, the polymer was again precipitated into hexane, centrifuged, decanted, washed with MeOH, and dried in vacuo to give a viscous reddish polymer. Representative ¹H NMR (CDCl₃, 200 MHz): δ ppm 7.97 (br d), 7.66–7.33 (br m), 7.18–6.90 (br m), 6.82–6.40 (br s), 4.07 (br m), 3.79–3.34 (br s), 3.06 (br m), 2.81 (br s), 2.44 (br m), 2.09 (br m), 1.83–1.17 (br m), 0.93 (br m).

P3HT-b-P(S_6A_4). Styrene (0.7 g, 6.73 mmol) and acrylate monomer **2** (1.68 g, 4.48 mmol) were used, following the procedure as well as purification described above.

GPC analysis $M_n = 23 \ 110 \ \text{g mol}^{-1}$, $M_w = 36 \ 720 \ \text{kg mol}^{-1}$, and PDI = 1.59 (against PS standard).

P3HT-*b***-P**(S_8A_2). Styrene (1.5 g, 14.42 mmol) and acrylate monomer 2 (1.35 g, 3.60 mmol) were used, following the procedure as well as purification described above.

GPC analysis $M_n = 18530$ g mol⁻¹, $M_w = 29750$ kg mol⁻¹, and PDI = 1.61 (against PS standard).

Polytosylhydrazones. The block copolymers (P3HT-*b*-P(S_xA_y)), *p*-toluene-sulfonyl hydrazide (5.0 equiv. relative to the built-in amount of coil blocks), and THF (50 mL) were stirred and refluxed overnight. The polymer solution was transferred into a centrifuge tube, precipitated with MeOH (200 mL), centrifuged, and decanted. The crude product was treated with MeOH twice in the same manner, washed with MeOH, collected by filtration, and dried *in vacuo* to give a reddish solid polymer. Representative ¹H NMR (CDCl₃, 200 MHz): δ ppm 9.35 (br s), 7.93 (br d), 7.65 (br m), 7.40–7.25 (br m), 7.19–6.91 (br m), 6.85–6.43 (br s), 4.17 (br m), 3.81–3.29 (br s), 2.81 (br s), 2.64 (br m), 2.41–2.21 (br m), 1.79–1.12 (br m), 0.89 (br m).

Donor–acceptor rod–coil diblock copolymers (P3HT-*b***-** $P(S_xA_y)$ **-** C_{60} **).** A similar procedure for the synthesis of the PCBM derivatives as reported in our group⁷ was used. A mixture of polytosylhydrazone (360 mg), sodium methoxide (36 mg, 0.66 mmol), and dry pyridine (20 mL) was placed under argon and stirred at rt for 30 min. To the mixture, a solution of C_{60} (0.28 g, 0.39 mmol) in *o*-DCB (100 mL) was added, and the homogeneous reaction mixture was stirred at 70 °C under argon for 2 d. The solution was heated to reflux and the reaction allowed to continue overnight again. The resulting mixture was

concentrated *in vacuo* and precipitated into MeOH (200 mL). The crude product was subjected to Soxhlet extraction with MeOH for 1 d and hexane for 7 d. The residue was redissolved in THF (500 mL) and filtered (five times). The filtrate was evaporated and washed with hexane (twice). The crude product was redissolved in THF (500 mL) and filtered by using a micron filter (0.45 μ m) twice, and then evaporated. The obtained residue was redissolved in *o*-DCB and precipitated into hot hexane (200 mL), which was repeated until the disappearance (TLC) of the unreacted C₆₀ (about five times). The product was collected and dried to give a reddish brown polymer.

P3HT-b-*P*(*S*₈*A*₂)-*C*₆₀. ¹H NMR (CDCl₃, 500 MHz): δ ppm 7.97 (br d), 7.55–7.33 (br m), 7.17–6.91 (br m), 6.81–6.32 (br s), 4.07 (br m), 3.81–3.25 (br s), 3.07 (br s), 2.81 (br s), 2.54–2.30 (br m), 2.19–2.02 (br m), 1.93–1.11 (br m), 0.93 (br m). ¹³C NMR (CDCl₃, 125.70 MHz): see ESI‡ for the spectrum.

Acknowledgements

We thank the Mitsubishi Center for Advanced Materials (MC-CAM) for support.

References

- 1 S. E. Shaheen, D. S. Ginley and G. E. Jabbour, *MRS Bull.*, 2005, **30**, 10.
- 2 S. Günes, H. Neugebauer and N. S. Sariciftci, *Chem. Rev.*, 2007, **107**, 1324.
- 3 J. Y. Kim, S. H. Kim, H.-H. Lee, K. Lee, W. Ma, X. Gong and A. J. Heeger, *Adv. Mater.*, 2006, **18**, 572.
- 4 G. Li, V. Shrotriya, J. Huang, Y. Yao, T. Moriarty, K. Emery and Y. Yang, *Nat. Mater.*, 2005, **4**, 864.
- 5 W. Ma, C. Yang, X. Gong, K. Lee and A. J. Heeger, Adv. Funct. Mater., 2005, 15, 1617.
- 6 M. Reyes-Reyes, K. Kim and D. L. Carroll, *Appl. Phys. Lett.*, 2005, **87**, 083506.
- 7 C. Yang, J. Y. Kim, S. Cho, J. K. Lee, A. J. Heeger and F. Wudl, J. Am. Chem. Soc., 2008, 130, 6444.
- 8 F. L. Zhang, E. Perzon, X. J. Wang, W. Mammo, M. R. Andersson and O. Inganäs, *Adv. Funct. Mater.*, 2005, **15**, 745.
- 9 D. Muhlbacher, M. Scharber, M. Morana, Z. G. Zhu, D. Waller, R. Gaudiana and C. Brabec, *Adv. Mater.*, 2006, 18, 2931.
- 10 S. A. Backer, K. Sivula, D. F. Kavulak and J. M. J. Frechet, *Chem. Mater.*, 2007, **19**, 2927.
- 11 J. Peet, J. Y. Kim, N. E. Coates, W. L. Ma, D. Moses, A. J. Heeger and G. C. Bazan, *Nat. Mater.*, 2007, 6, 497.
- 12 J. K. Lee, W. L. Ma, C. J. Brabec, J. Yuen, J. S. Moon, J. Y. Kim, K. Lee, G. C. Bazan and A. J. Heeger, *J. Am. Chem. Soc.*, 2008, 130, 3619.
- 13 M. Al-Ibrahim, O. Ambacher, S. Sensfuss and G. Gobsch, *Appl. Phys. Lett.*, 2005, 86, 201120.
- 14 F. Padinger, R. S. Rittberger and N. S. Sariciftci, Adv. Funct. Mater., 2003, 13, 85.
- 15 D. Chirvase, J. Parisi, J. C. Hummelen and V. Dyakonov, *Nanotechnology*, 2004, 15, 1317.
- 16 X. N. Yang, J. Loos, S. C. Veenstra, W. J. H. Verhees, M. M. Wienk, J. M. Kroon, M. A. J. Michels and R. A. J. Janssen, *Nano Lett.*, 2005, 5, 579.
- 17 T. Erb, U. Zhokhavets, G. Gobsch, S. Raleva, B. Stühn, P. Schilinsky, C. Waldauf and C. J. Brabec, *Adv. Funct. Mater.*, 2005, **15**, 1193.
- 18 H. A. Klok and S. Lecommandoux, Adv. Mater., 2001, 13, 1217.
- 19 S. A. Jenekhe and X. L. Chen, Science, 1998, 279, 1903.
- 20 B. D. Olsen and R. A. Segalman, Macromolecules, 2007, 40, 6922.
- 21 M. Lee, B. K. Cho and W. C. Zin, Chem. Rev., 2001, 101, 3869.
- 22 S. I. Stupp, Curr. Opin. Colloid Interface Sci., 1998, 3, 20.
- 23 B. Gallot, Prog. Polym. Sci., 1996, 21, 1035.

- 24 J. S. Liu, E. Sheina, T. Kowalewski and R. D. McCullough, Angew. Chem., Int. Ed., 2002, 41, 329.
- 25 M. C. Iovu, C. R. Craley, M. Jeffries-El, A. B. Krankowski, R. Zhang, T. Kowalewski and R. D. McCullough, *Macromolecules*, 2007, **40**, 4733.
- 26 K. Sivula, Z. T. Ball, N. Watanabe and J. M. J. Fréchet, *Adv. Mater.*, 2006, **18**, 206.
- 27 A. de Cuendias, M. Le Hellaye, B. Lecommandoux, E. Cloutet and H. Cramail, J. Mater. Chem., 2005, 15, 3264.
- 28 C. P. Radano, O. A. Scherman, N. Stingelin-Stutzmann, C. Müller, D. W. Breiby, P. Smith, R. A. J. Janssen and E. W. Meijer, J. Am. Chem. Soc., 2005, 127, 12502.
- 29 M. H. van der Veen, B. de Boer, U. Stalmach, K. I. van de wetering and G. Hadziioannou, *Macromolecules*, 2004, 37, 3673.
- 30 U. Stalmach, B. de Boer, C. Videlot, P. F. van Hutten and G. Hadziioannou, J. Am. Chem. Soc., 2000, **122**, 5464.
- 31 S. Barrau, T. Heiser, F. Richard, C. Brochon, C. Ngov, K. van de Wetering, G. Hadziioannou, D. V. Anokhin and D. A. Ivanov, *Macromolecules*, 2008, **41**, 2701.
- 32 B. de Boer, U. Stalmach, P. F. van Hutten, C. Melzer, V. V. Krasnikov and G. Hadziioannou, *Polymer*, 2001, 42, 9097.
- 33 J. U. Lee, A. Cirpan, T. Emrick, T. P. Russell and W. H. Jo, J. Mater. Chem., 2009, 19, 1483.
- 34 J. Chiefari, Y. K. Chong, F. Ercole, J. Krstina, J. Jeffery, T. P. T. Le, R. T. A. Mayadunne, G. F. Meijs, C. L. Moad, G. Moad, E. Rizzardo and S. H. Thang, *Macromolecules*, 1998, **31**, 5559.
- 35 K. Matyjaszewski and T. P. Davis, *Handbook of Radical Polymerization*, Wiley-Interscience, Hoboken, NJ, 2002.

- 36 T. P. Le, G. Moad, E. Rizzardo and S. H. Thang, *International Patent* WO 9801478, 1998.
- 37 A. Krasovskiy and P. Knochel, Angew. Chem., Int. Ed., 2004, 43, 3333.
- 38 M. Jeffries-El, G. Sauvé and R. D. McCullough, *Macromolecules*, 2005, **38**, 10346.
- 39 M. H. Stenzel, T. P. Davis and A. G. Fane, *J. Mater. Chem.*, 2003, **13**, 2090.
- 40 A. G. Camp, A. Lary and W. T. Ford, *Macromolecules*, 1995, **28**, 7959.
- 41 Z. Tan, J. H. Hou, Y. J. He, E. J. Zhou, C. H. Yang and Y. F. Li, *Macromolecules*, 2007, 40, 1868.
- 42 R. S. Ruoff, D. S. Tse, R. Malhotra and D. C. Lorents, J. Phys. Chem., 1993, 97, 3379.
- 43 M. T. Beck and G. Mándi, Fullerene Sci. Technol., 1997, 5, 291.
- 44 B. Liu, C. E. Bunker and Y. P. Sun, Chem. Commun., 1996, 1241.
- 45 T. Chatterjee, C. Yang, E. J. Kramer and F. Wudl, unpublished results.
- 46 H. Spanggaard and F. C. Krebs, Sol. Energy Mater. Sol. Cells, 2004, 83, 125.
- 47 F. Richard, C. Brochon, N. Leclerc, D. Eckhardt, T. Heiser and G. Hadziioannou, *Macromol. Rapid Commun.*, 2008, 29, 885.
- 48 C. Brochon, F. Richard, N. Leclerc, R. Bechara, P. Lévêque, T. Heiser and G. Hadziioannou, presented at the Europolymer Conference (EUPOC 2008), Gargnano, Italy, 2008.
- 49 P. Bahadur, Curr. Sci., 2001, 80, 1002.
- 50 P. H. Ni, M. Z. Zhang, L. J. Zhuge and S. K. Fu, J. Polym. Sci., Part A: Polym. Chem., 2002, 40, 3734.