

Slight Structural Disorder in Bithiophene-based Random Terpolymers with Improved Power Conversion Efficiency for Polymer Solar Cells

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Electronic Supplementary Information

Abstract A series of random terpolymers **P2–P5** were designed and synthesized by randomly embedding 5 mol%, 10 mol%, 15 mol% and 25 mol% feed ratios of low cost 2,2-bithiophene as the third monomer to the famous donor-acceptor (D-A) type copolymer **PTB7-Th (P1)**. All polymers showed similar molecular weight with number-average molecular weight (M_n) and weight-average molecular weight (M_w) in the range of (59–74) and (93–114) $\text{kg}\cdot\text{mol}^{-1}$, respectively, to ensure a fair comparison on the structure-property relationships. Compared with the control copolymer **PTB7-Th**, the random terpolymers exhibited enhanced absorption intensity in a wide range from 400 nm to 650 nm in both solution and film as well as in polymer/PC₇₁BM blends. From grazing incident wide-angle X-ray diffraction (GIWAXS), compared with the regularly alternated copolymer **PTB7-Th**, the random terpolymers demonstrated mild structural disorder with reduced (100) lamellar stacking and slightly weakened (010) π - π stacking for the polymers as well as slightly reduced PC₇₁BM aggregation in polymer/PC₇₁BM blends. However, the measured hole mobility for terpolymers ($(1.20\text{--}3.73) \times 10^{-4} \text{ cm}^2\cdot\text{V}^{-1}\cdot\text{s}^{-1}$) was evaluated to be comparable or even higher than $1.35 \times 10^{-4} \text{ cm}^2\cdot\text{V}^{-1}\cdot\text{s}^{-1}$ of the alternative copolymer. Enhanced average power conversion efficiency (PCE) from 7.35% to 8.11% and 7.79% to 8.37% was observed in both conventional and inverted device architectures from copolymer **P1** to terpolymers **P4**, while further increasing the 2,2-bithiophene feed ratio decreased the PCE.

Keywords Bithiophene-based random terpolymers; Structural disorder; Polymer solar cells; Photovoltaic properties

Citation: Wang, M. H.; Xue, Z. Y.; Wang, Z. W.; Ning, W. H.; Zhong, Y.; Liu, Y. N.; Zhang, C. F.; Huettnner, S.; Tao, Y. T. Slight Structural Disorder in Bithiophene-based Random Terpolymers with Improved Power Conversion Efficiency for Polymer Solar Cells. *Chinese J. Polym. Sci.* 2018, 36(10), 1129–1138.

INTRODUCTION

Bulk-heterojunction (BHJ) polymer solar cells (PSCs) have been intensively investigated as the new potential photovoltaic technology owing to the advantages of low cost, light weight, simple fabrication, flexibility and large area mass production^[1–7]. Traditional molecular design has been mostly focused on the D-A conjugated copolymers which comprise the alternatively linked electron-rich (donor, D) and electron-deficient (acceptor, A) moieties along the polymer backbone^[8, 9]. Through judicious combination of different donor and acceptor units, optoelectronic properties such as the HOMO and LUMO energy levels as well as optical band-gaps can be rationally tuned^[10]. However, the understandings on structure-property relationships for actual charge transport ability and photovoltaic performance are less clear, as the

film morphology plays a critical role^[11, 12]. Unfortunately, achieving the desired film morphology with mesoscale phase separation and domain sizes close to exciton diffusion length in the active layer of BHJ PSCs is not trivial, which depends on several parameters, such as substrates, solvent, additives, annealing conditions as well as the subtle chemical modifications of polymer structures^[13, 14]. Therefore, among huge numbers of D-A alternating copolymers, only limited examples have been successfully developed for high power conversion efficiency photovoltaic devices^[15–18].

Recently, a new molecular design strategy of terpolymer approach has attracted much attention. The involvement of a new appropriate third electron-donating or accepting monomer into the D-A copolymers to form the 2D/1A (two different donor units and one acceptor unit) or 2A/1D (two different acceptor units and one donor unit) type terpolymers, is expected to increase the solubility and miscibility, broaden the absorption spectrum, finely tune the energy level and improve the charge transport behavior for

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Received January 17, 2018; Accepted February 14, 2018; Published online March 29, 2018

conjugated polymer material^[19, 20]. Normally, terpolymers could be divided into two categories. On one hand, the regular terpolymers with three subunits regularly alternating along the polymer backbone could quantify the well-defined architecture and precise chemical compositions, which are favorable to form thin films with ordered π - π stacking structure^[8, 21]. For example, Janssen *et al.* reported a regular terpolymer PDPP3T*alt*TPT by alternating the electron-deficient (A) diketopyrrolopyrrole (DPP) with electron-rich terthiophene ($D_1 = 3T$) and thiophene-phenylene-thiophene ($D_2 = TPT$) segments in a regular sequence. The optimized energy levels and optical band gap located in between the parent copolymers were observed on the terpolymer, thus, an improved power conversion efficiency (PCE) to 8.0% was achieved compared to 7.1% and 7.4% of the D_1 -A and D_2 -A type copolymers of PDPP3T and PDPPTPT, respectively^[8].

On the other hand, random terpolymers with the D_1 -A and D_2 -A (or A_1 -D and A_2 -D) subunits randomly arranged through the conjugated polymer chain allow for the relatively convenient chemical synthesis^[22, 23]. Therefore, internal structural defects with less regularity are thought to exist in random terpolymers, which are unbeneficial for the molecular π - π stacking, and may cause unexpected traps to suppress the charge carrier transport^[24]. However, by utilization of the reduced crystallinity and π - π stacking in terpolymer to improve the solubility and device processability, D- A_1 -D- A_2 random terpolymer using two electron deficient 5,6-difluoro-4,7-dithieno[2,1,3]thiadiazole (DTffBT) and 5,6-difluorobenzo[2,1,3]thiadiazole (ffBT) and one electron rich benzo[1,2-*b*:4,5-*b'*]dithiophene (BDT) as monomers, demonstrated an increased PCE to 8.0% of the terpolymer Th25, significantly higher than 4.9% (Th00) and 6.9% (Th100) of the two alternative copolymers^[25].

In our previous work, by replacing 25 mol% of extremely expensive 3-fluorothieno[3,4-*b*]thiophene-2-carboxylate monomer in the famous PTB7-Th with a 34-times lower-cost 2,2'-bithiophene (T2), we preliminarily found that the new random terpolymer showed comparable PCE with PTB7-Th^[22]. In this work, we further optimized the feed ratios of bithiophene to 5 mol%, 10 mol% and 15 mol% for a series of random terpolymers to conduct an in-depth investigation on the structure-property relationship. We found that the random terpolymers exhibited slight structural disorder, reflected by reduced polymer lamellar and π - π stacking in polymer/PC₇₁BM blends, whereas simultaneously maintained or even enhanced the hole mobility. Besides slightly reduced PC₇₁BM aggregation, a more efficient slow charge separation process was also observed for random terpolymer/PC₇₁BM blends than that for copolymer PTB7-Th. At the comparable molecular weight conditions, enhanced maximum PCE was achieved from 7.48% of the control PTB7-Th copolymer based conventional photovoltaic device to 8.34%, 8.29% and 8.26% of the bithiophene containing terpolymers PTB7-ThT2-5, PTB7-ThT2-10 and PTB7-ThT2-15, respectively. The improvement was also demonstrated in inverted architectures, with average PCE increased from 7.79% of PTB7-Th to 8.05%–8.37% of random terpolymers.

EXPERIMENTAL

General Considerations

¹H-NMR spectra were recorded on a Bruker DMX-500 spectrometer in 1,1,2,2-tetrachloroethane-*d* by using tetramethylsilane as the internal standard. The polymer molecular weight was measured by gel permeation chromatography (GPC) with *o*-dichlorobenzene as the eluent at 120 °C and polystyrenes as the internal reference. UV-Visible absorption spectra were measured on a Shimadzu UV-2500 recording spectrophotometer. Elemental analyses were carried out on a flash EA 1112 elemental analyzer. Thermogravimetric analysis (TGA) was conducted at a NETZSCH STA 449C instrument under N₂ atmosphere with a heating rate of 10 °C·min⁻¹. The cyclic voltammetry was carried out on a CHI voltammetric analyzer, by using 0.1 mol·L⁻¹ of tetrabutylammonium hexafluorophosphate (*n*-Bu₄NPF₆) as electrolyte in acetonitrile solution at a scan rate of 100 mV·s⁻¹. The conventional three-electrode set-up includes a platinum working electrode, platinum auxiliary electrode, and Ag/AgCl reference electrode with ferrocenium-ferrocene (Fc⁺/Fc) as the internal standard (vacuum energy level of -4.8 eV). The polymer films were coated to the Pt working electrode. The highest occupied molecular orbital (HOMO) was calculated from the equation of $E_{\text{HOMO}} = -(E_{\text{onset (ox)}} + 4.8)$ eV through oxidation scan. All the solutions were deaerated by bubbling nitrogen for a few minutes prior to the electrochemical measurements. Atomic force microscopy (AFM) was conducted on SPA300HV in tapping mode using an SPI3800 controller, Seiko Instruments Industry, Co., Ltd.

Materials and Synthesis

The synthesis of the control polymer PTB7-Th could be found in our previous work^[20, 22]. And the synthetic methods for all other terpolymers P2–P5 were similar with that of control PTB7-Th. The total feed ratio for the monomers 5,5'-dibromo-2,2'-bithiophene and 2-ethylhexyl-4,6-dibromo-3-fluorothieno[3,4-*b*]thiophene-2-carboxylate is equal to that of 2,6-bis(trimethyltin)-4,8-bis(5-ethylhexyl-2-thienyl)-benzo[1,2-*b*:4,5-*b'*]dithiophene. All monomers were purchased from Suna Tech Inc.

PTB7-Th (P1)

Yield: 64%. ¹H-NMR (500 MHz, CDCl₂CDCl₂, δ , ppm): 7.71–7.45 (br, 4H), 7.02–6.92 (br, 2H), 4.30–4.20 (br, 2H), 3.03–2.80 (br, 4H), 2.16–0.83 (br, 45H). GPC: $M_n = 62$ kg·mol⁻¹, $M_w = 97$ kg·mol⁻¹, PDI = 1.56. Anal. Calcd. (%): C, 66.17; H, 6.46; Found: C, 66.75; H, 6.40.

PTB7-ThT2-5 (P2)

Yield: 66%. ¹H-NMR (500 MHz, CDCl₂CDCl₂, δ , ppm): 7.76–7.37 (br, 4H), 7.01–6.98 (br, 2H), 4.28–4.14 (br, 2H), 3.01–2.78 (br, 4H), 2.16–0.85 (br, 44H). GPC: $M_n = 74.5$ kg·mol⁻¹, $M_w = 114$ kg·mol⁻¹, PDI = 1.53. Anal. Calcd. (%): C, 66.25; H, 6.44; Found: C, 66.58; H, 6.41.

PTB7-ThT2-10 (P3)

Yield: 64%. ¹H-NMR (500 MHz, CDCl₂CDCl₂, δ , ppm): 7.81–7.35 (br, 4H), 7.08–6.95 (br, 2H), 4.32–4.10 (br, 2H), 3.02–2.82 (br, 4H), 2.01–0.83 (br, 44H). GPC: $M_n = 67.9$ kg·mol⁻¹, $M_w = 93.8$ kg·mol⁻¹, PDI = 1.38. Anal. Calcd.

(%): C, 66.33; H, 6.42. Found (%): C, 66.67; H, 6.46.

PTB7-ThT2-15 (P4)

Yield: 62%. $^1\text{H-NMR}$ (500 MHz, $\text{CDCl}_2\text{CDCl}_2$, δ , ppm): 7.88–7.32 (br, 4H), 7.01–6.97 (br, 2H), 4.28–4.15 (br, 2H) 3.02–2.85 (br, 4H), 2.02–0.83 (br, 43H). GPC: $M_n = 65.1 \text{ kg}\cdot\text{mol}^{-1}$, $M_w = 93.0 \text{ kg}\cdot\text{mol}^{-1}$, PDI = 1.43. Anal. Calcd. (%): C, 66.42; H, 6.40. Found (%): C, 66.84; H, 6.50.

PTB7-ThT2-25 (P5)

Yield: 64%. $^1\text{H-NMR}$ (500 MHz, $\text{CDCl}_2\text{CDCl}_2$, δ , ppm): 7.77–7.24 (br, 4H), 7.01–6.81 (br, 2H), 4.27–4.02 (br, 2H) 3.07–2.88 (br, 4H), 2.01–0.85 (br, 42H). GPC: $M_n = 59.0 \text{ kg}\cdot\text{mol}^{-1}$, $M_w = 93 \text{ kg}\cdot\text{mol}^{-1}$, PDI = 1.56. Anal. Calcd. (%): C, 66.54; H, 6.41; Found. (%): C, 66.35; H, 6.37.

Fabrication and Characterization of PSCs

The polymer photovoltaic devices were fabricated with conventional configuration of ITO/PEDOT:PSS (30 nm)/polymer:PC₇₁BM/Ca or ZrAcac/Al, where ITO is indium tin oxide and PEDOT:PSS is poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate). Ca or zirconium acetyl acetonate (ZrAcac) serves as a cathode interlayer to lower the work function of Al cathode. A thin layer of PEDOT:PSS was firstly spin-coated on pre-cleaned ITO-glass with a PEDOT:PSS aqueous solution (Baytron PVP AI 4083 from H. C. Starck) at 4000 $\text{r}\cdot\text{min}^{-1}$ for about 40 nm and dried subsequently at 150 °C for 15 min in air, and then the device was transferred into a nitrogen glove box, where the active layer of polymer: PC₇₁BM was spin-coated onto the PEDOT:PSS layer at the ratio of 1:1.5 (*W/W*) in *o*-dichlorobenzene (*o*-DCB) with a total concentration of 25 $\text{mg}\cdot\text{mL}^{-1}$. 3% volume ratio of 1,8-diiodooctane (DIO) was added to *o*-DCB solutions and stirred before use. The polymer:PC₇₁BM blends were subsequently spin-coated at speed of 1000 $\text{r}\cdot\text{min}^{-1}$ onto the PEDOT:PSS layer to form a *ca.* 100 nm thick layer. The film thickness was measured by a Proflometer (Ambios Tech. XP-2). The ethanol solution of ZrAcac at a concentration of 1.4 $\text{mg}\cdot\text{mL}^{-1}$ was then spin-coated on the active layer at 3500 $\text{r}\cdot\text{min}^{-1}$ for 30 s, giving a thin layer with thickness of *ca.* 14 nm. An aluminum (*ca.* 100 nm) electrode layer was subsequently evaporated onto the cathode interface layer under vacuum (*ca.* 10^{-5} Pa). The active area of the cell device was 5 mm^2 . The current density-voltage (*J-V*) characteristics were measured on a computer-controlled Keithley 2400 Source-Measure Unit. Oriol Sol3A Class AAA Solar Simulator (model, Newport 94023A) with a 450 W xenon lamp and an air mass (AM) 1.5

filter was used as the light source. The light intensity was calibrated to 100 $\text{mW}\cdot\text{cm}^{-2}$ by a Newport Oriel 91150V reference cell. The IPCE (EQE) was measured by Solar Cell Spectral Response Measurement System QE-R3-011 (Enli Technology Co., Ltd., Taiwan). The light intensity at each wavelength was calibrated with a standard single-crystal Si photovoltaic cell.

GIWAXS Characterization

GIWAXS were carried out at the SAXS/WAXS beamline of the Australian Synchrotron. The silicon wafer substrates were cleaned and the polymer films were spin-coated by the same way as the active layer of the devices. Samples were analyzed with an X-ray energy of 11 keV and in a range of incident angles of $\Omega = 0.02$ –0.35 with 0.005 increments to allow signal optimization near the critical angle of the polymer film but below the critical angle of the substrate. Data from GIWAXS experiments were analyzed using a customized version of NIKA 2D based in IgorPro.

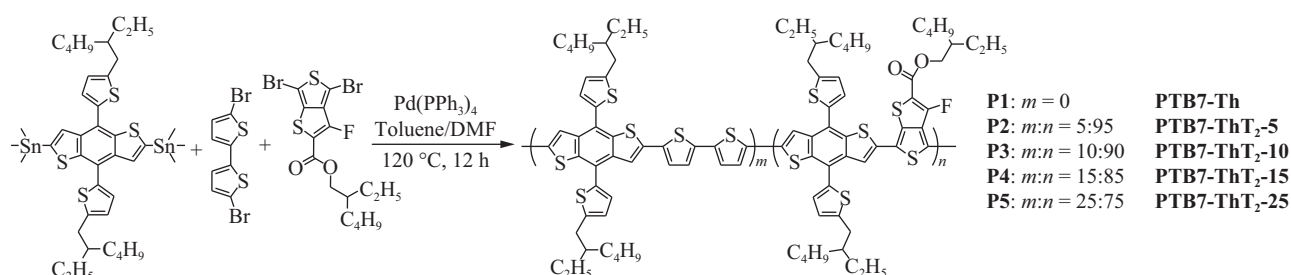
Mobility Measurements

Hole mobility was measured using the space charge limited current (SCLC) method. Device structures are ITO/PEDOT:PSS/polymer:PC₇₁BM/Au for hole-only devices. The SCLC mobilities were calculated through literature methods^[26, 27].

RESULTS AND DISCUSSION

Synthesis and Characterization

As shown in Scheme 1, all random terpolymers **P2–P5** were facially synthesized *via* a one-step Stille coupling polycondensation at 60% yield among the three monomers of 2-ethylhexyl-4,6-dibromo-3-fluorothiopheno[3,4-*b*]thiophene-2-carboxylate, 2,6-bis(trimethyltin)-4,8-bis(5-ethylhexyl-2-thienyl)-benzo[1,2-*b*:4,5-*b'*]dithiophene and 5,5'-dibromo-2,2'-bithiophene. The feed ratio for the third monomer T₂ was gradually increased from 5 mol%, 10 mol%, 15 mol% to 25 mol% for corresponding **P2–P5** which was named as **PTB7-ThT₂-x** ($x = 5, 10, 15$, and 25), and the D-A copolymer **PTB7-Th (P1)** was also prepared for comparison. The polymer structures were characterized by $^1\text{H-NMR}$ spectroscopy and elemental analysis (EA) which were in accordance with the predicted values. The molecular weight including number-average molecular weight (M_n), weight-average molecular weight (M_w) and polydispersity index (PDI) was measured by gel permeation chromatography (GPC) in *o*-dichlorobenzene (*o*-DCB) eluant at 120 °C with polystyrene as standards. As shown in Table 1, at the same



Scheme 1 Synthetic routes for **PTB7-Th** based series polymers

Table 1 Characteristics of PTB7-Th based series polymers **P1–P5**

Polymer	M_n/M_w (kg·mol ⁻¹)	PDI	T_d (°C)	$\lambda_{\max}^{\text{sol}}$ (nm)	$\lambda_{\max}^{\text{film}}$ (nm)	E_g^{opt} (eV)	E_{HOMO}^a (eV)	E_{LUMO}^b (eV)
P1 PTB7-Th	62/97	1.56	370	320,636/693	325,649/708	1.61	-5.40	-3.79
P2 PTB7-ThT ₂ -5	74/114	1.53	372	320,636/693	325,646/704	1.60	-5.42	-3.82
P3 PTB7-ThT ₂ -10	68/94	1.38	376	318,644/687	326,646/701	1.61	-5.44	-3.83
P4 PTB7-ThT ₂ -15	65/93	1.43	382	319,631/679	324,642/693	1.60	-5.44	-3.84
P5 PTB7-ThT ₂ -25	59/93	1.58	388	320,673/668	326,641/688	1.61	-5.22	-3.61

^a E_{HOMO} was measured by cyclic voltammograms; ^b E_{LUMO} was calculated across the formula $E_{\text{LUMO}} = E_g^{\text{opt}} - (-E_{\text{HOMO}})$

polymerization conditions, all random terpolymers exhibited comparable molecular weight with the control copolymer **PTB7-Th**. The M_n and M_w were estimated in the range of (59–74) and (93–114) kg·mol⁻¹, respectively, and PDI was slightly shifted from 1.38 to 1.58. It should be noted that the similar molecular weights for the copolymer **PTB7-Th** and all the terpolymers ensure a reliable comparison in the optoelectronic properties as well as the photovoltaic performance in this work. Thermogravimetric analysis (TGA) measurement was carried out to evaluate the thermal stability of the conjugated polymer materials. From the TGA curves in Fig. S1 (in electronic supplementary information, ESI), the T₂-based terpolymers exhibited favorable thermal stabilities with the decomposition temperature (T_d : 5% weight loss) ranging from 372 °C to 388 °C (Table 1), which was slightly higher than 370 °C of the control copolymer. The T_d increased progressively in a small range by increasing the rigid T₂ third monomer contents.

Optical and Electrochemical Properties

The UV-Vis absorption spectra of polymers **P1–P5** in dilute CHCl₃ solutions and neat films are shown in Fig. 1, and their characteristic absorption peaks are summarized in Table 1. Compared with solutions, all polymers exhibited slightly red-shifted absorption maximum in film state. By gradually increasing the T₂ unit from 0 mol%, 5 mol%, 10 mol%, 15 mol% to 25 mol% for **P1–P5**, the absorption intensity increased progressively in a wide wavelength range from 400 nm to 650 nm for both solution and film, suggesting that the optical absorption could be rationally tuned by the introduction of third monomer T₂ in terpolymers. The short wavelength absorption band (300–400 nm) was ascribed to π - π^* transitions within the aromatic monomers, while the longer wavelength absorption bands (> 500 nm) were attributed to the intramolecular charge-transfer (ICT) transitions from the electron-donating to accepting segments. Almost identical optical bandgaps (E_g^{opt}) of 1.60–1.61 eV for all polymers **P1–P5** were determined from their corresponding thin film absorption edge.

In addition, cyclic voltammetry (CV) measurements were conducted to determine the HOMO (highest occupied molecular orbital) energy levels of the polymers from the onset of oxidation potential by using ferrocene as the internal standards. As shown in Fig. 2, all polymers **P1–P5** displayed quasi-reversible oxidation and non-detectable reduction behavior. At low T₂ content, the terpolymers **P2–P4** exhibited comparable HOMO levels (-5.42 eV to -5.44 eV) with the control copolymer **P1** (-5.40 eV), while at the high feed ratio (25 mol%) of T₂, the HOMO level of **P5** rose to -5.22 eV, because enough electron-donating 2,2'-bithiophene moieties to replace the electron-withdrawing

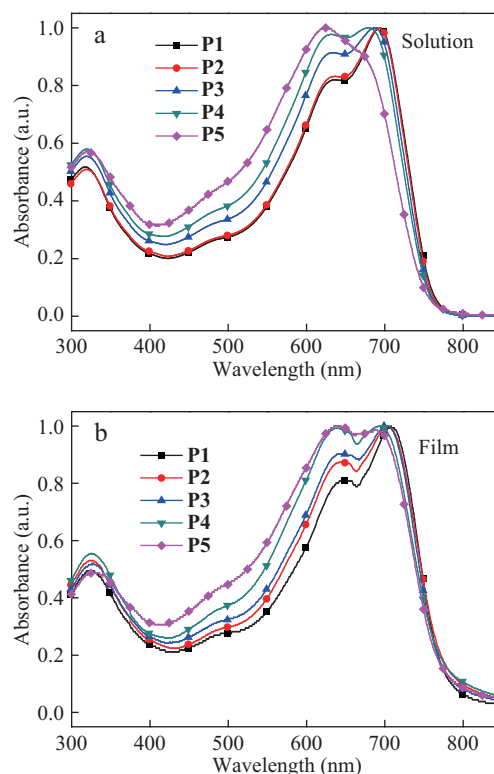


Fig. 1 Normalized UV-Vis absorption spectra of PTB7-Th based **P1–P5** in dilute CHCl₃ solution (a) and neat film (b)

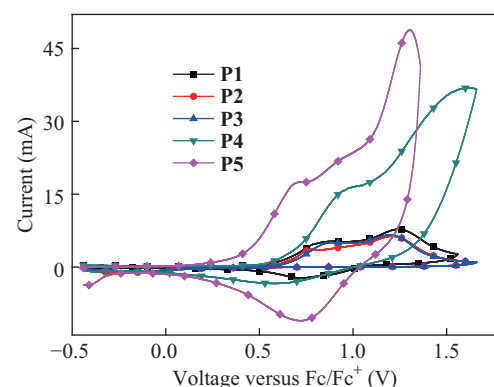


Fig. 2 Cyclic voltammograms of the oxidation curves for **P1–P5**

TTF units in the polymer conjugated backbone are sufficient to influence the energy levels.

Deduced from the HOMO and optical bandgap (E_g^{opt}) [$E_{\text{LUMO}} = E_g^{\text{opt}} - (-E_{\text{HOMO}})$], the lowest unoccupied molecular orbital (LUMO) energy levels for **P1–P4** were determined to be similar as -3.79 eV to -3.84 eV, while for **P5** was -3.61 eV.

Photovoltaic Properties

In order to investigate photovoltaic performance of the terpolymers, BHJ polymer solar cells with the conventional device configuration of ITO/PEDOT:PSS/donor polymer **P1–P5**:PC₇₁BM/ZrAcac/Al were initially fabricated, where poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) and zirconium acetyl acetonate (ZrAcac) were used as the anode and cathode interface materials, respectively^[28]. To achieve a meaningful comparison between the copolymer **P1** and terpolymers **P2–P4**, identical fabrication conditions for all five devices were employed. The active layer with the optimized weight ratio of 1:1.5 for polymer donors:PC₇₁BM acceptor was spin-coated from the 1,2-dichlorobenzene solution with 3 vol% of 1,8-diiodooctane (DIO) as solvent additives. The representative current density-voltage (*J*-*V*) characteristics and external quantum efficiency (EQE) curves are shown in Fig. 3, and the key photovoltaic parameters are summarized in Table 2 with an average of over 18 devices. As shown, device based on the control D-A type copolymer **PTB7-Th (P1)** exhibited a maximum PCE of 7.48%, and the corresponding open-circuit voltage (*V*_{oc}), short current density (*J*_{sc}), and fill factor (FF) of 0.80 V, 14.7 mA·cm⁻², and 63.6%, respectively. By increasing the T₂ third monomer feed ratio from 0 mol% in **P1** to 5 mol%, 10 mol%, 15 mol% in **P2–P4**, the average device PCE increased from 7.35% to 8.11%, 7.90% and 8.11%. However, further increase of T₂ feed ratio to 25 mol% reduced the average PCE value to 7.50% in **P5** containing devices. At the lower third monomer ratio, terpolymers **P2–P4** exhibited comparably enhanced PCE, with maximum values of 8.34%, 8.29% and 8.26%, respectively. It is noted that under the similar polymer molecular weight and device preparation conditions, the terpolymer based devices exhibited higher PCE than the copolymer of **PTB7-Th**, and this improvement was mainly attributed to the increased short current density (*J*_{sc}). As shown in Table 2, the selected representative *J*_{sc} values for terpolymers **P2–P4** based devices were detected over 16.0 mA·cm⁻², obviously higher than that of copolymer **P1**. Besides, from the EQE curves, the terpolymers particularly **P2–P4** containing devices showed significantly stronger absorption in the broad range of 450–700 nm, which further confirmed the improvement of

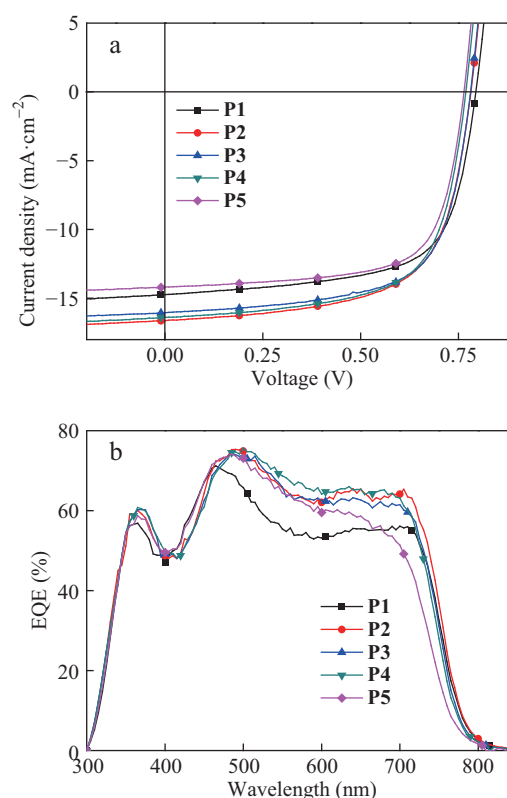


Fig. 3 The representative *J*-*V* curves (a) and EQE spectra (b) of polymer:PC₇₁BM based devices with the structure of ITO/PEDOT:PSS/**P1–P5**:PC₇₁BM/ZrAcac/Al

*J*_{sc} in the devices.

To further verify the improvement of PCE by the random terpolymer approach, inverted device architectures based on representative polymers **P1–P4** with the configuration of ITO/ZnO/**P1–P4**:PC₇₁BM/MoO₃/Ag were also fabricated^[29]. And the representative *J*-*V* characteristics and EQE curves are shown in Fig. 4, with the key photovoltaic device data listed in Table 3. Similarly with the conventional devices, under the same device conditions, an improved PCE and *J*_{sc} were achieved in the terpolymer based devices. The average PCE increased from 7.79% of the copolymer **P1** to 8.37% of the terpolymer **P3**. Differently, the *V*_{oc} remained unchanged for copolymer **P1** and terpolymers **P2** and **P3** with low third

Table 2 Summary of the key device data for the conventional structures of ITO/PEDOT:PSS/**P1–P5**:PC₇₁BM/ZrAcac/Al

	Polymer	<i>M</i> _n / <i>M</i> _w (kg·mol ⁻¹)	<i>V</i> _{oc} (V)	<i>J</i> _{sc} (mA·cm ⁻²)	FF (%)	PCE _{max} (avr ^a) (%)
P1	PTB7-Th	62/97	0.80	14.7	63.6	7.48 (7.35)
P2	PTB7-ThT₂-5	74/114	0.78	16.6	64.2	8.34 (8.11)
P3	PTB7-ThT₂-10	68/94	0.78	16.0	66.2	8.29 (7.90)
P4	PTB7-ThT₂-15	65/93	0.77	16.4	65.6	8.26 (8.11)
P5	PTB7-ThT₂-25	59/93	0.76	15.2	67.4	7.83 (7.50)

^a The maximum PCE and average values obtained from over 18 devices

Table 3 Summary of the key device data for the inverted architectures of ITO/ZnO/**P1–P4**:PC₇₁BM/MoO₃/Ag

	Polymer	<i>V</i> _{oc} (V)	<i>J</i> _{sc} (mA·cm ⁻²)	FF (%)	PCE _{max} (avr ^a) (%)
P1	PTB7-Th	0.80	16.07	64	8.22 (7.79)
P2	PTB7-ThT₂-5	0.80	16.71	64	8.54 (8.11)
P3	PTB7-ThT₂-10	0.80	16.32	66	8.60 (8.37)
P4	PTB7-ThT₂-15	0.80	16.24	66	8.34 (8.05)

^a The maximum PCE and average values obtained from over 18 devices

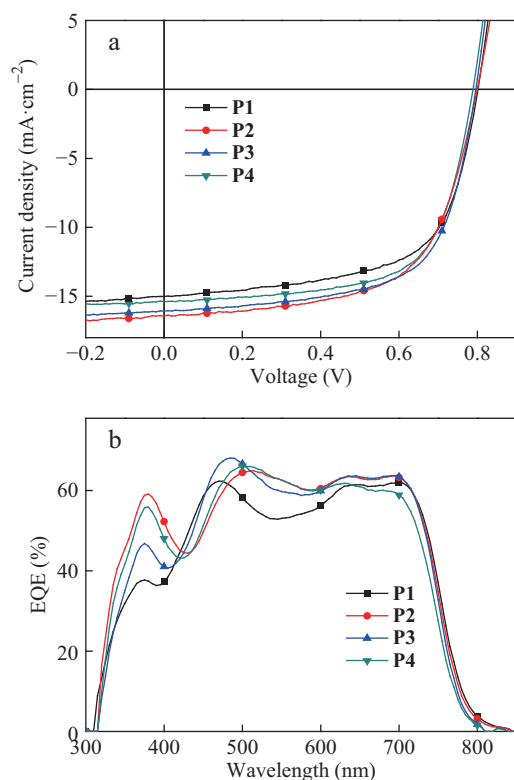


Fig. 4 The representative J - V curves (a) and EQE spectra (b) of polymer:PC₇₁BM based inverted devices with the structure of ITO/ZnO/P1–P4:PC₇₁BM/MoO₃/Ag

monomer contents, and the increased EQE with enhanced light absorption in terpolymers was observed at 350–400 and 500–650 nm in inverted devices. In addition, the enhanced light absorption could be also observed from the UV-Vis absorption for the neat polymers in solutions and films (Fig. 2). The improved PCEs in both conventional and inverted device structures convincingly demonstrate that the random terpolymer approach is a simple and effective molecular design strategy to enhance the PCE based on the current high efficiency conjugated D-A copolymers.

To gain insight into the possible structural changes of the bithiophene based random terpolymers compared with the control D-A copolymer of PTB7-Th, grazing incident wide-angle X-ray scattering (GIWAXS) of the polymer:PC₇₁BM blends was conducted. The two-dimensional GIWAXS patterns and the corresponding scattering profiles at the in-plane and out-of-plane directions for polymer:PC₇₁BM blended films are shown in Fig. 5. Generally, no tremendous differences on the pattern properties could be observed for all samples, due to the low ratio of T₂ monomer in the PTB7-Th polymer backbone for the terpolymers. However, after careful comparison, the pattern intensities of the broad peak arisen at $q \approx 1.38 \text{ \AA}^{-1}$, which is ascribed to the aggregation of PC₇₁BM, were slightly weakened in the terpolymers P2–P5:PC₇₁BM blends than that of the copolymer PTB7-Th blends. P2 and P3 based samples exhibited the lowest intensity, indicating the least aggregation of PC₇₁BM. By varying the third organic T₂

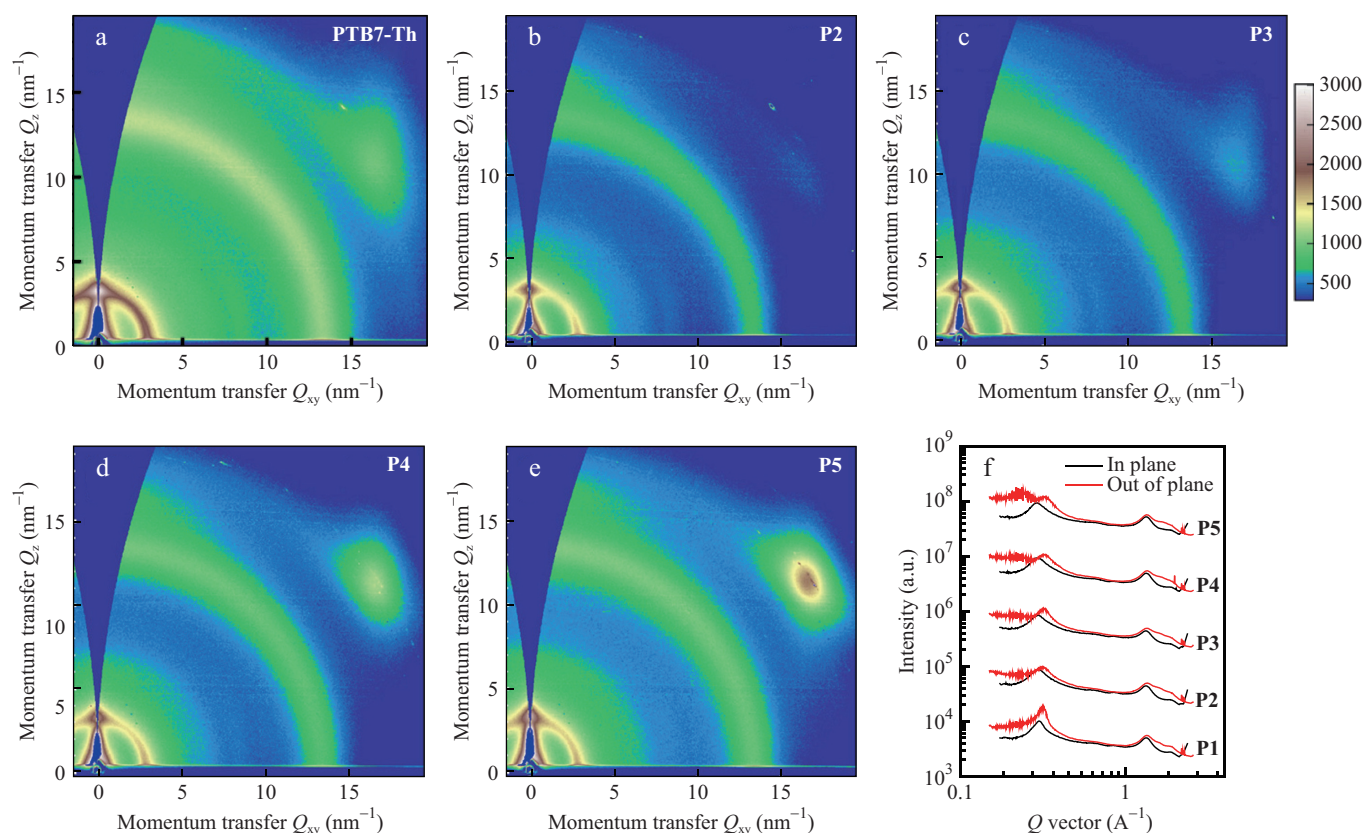


Fig. 5 2D GIWAXS patterns (a–e) and scattering profiles of in-plane and out-of-plane directions (f) for the corresponding polymers P1–P5:PC₇₁BM (1:1.5, W/W , with DIO) blended samples

monomer feed ratio from 5 mol% and 10 mol% to 15 mol% and 25 mol%, the PC₇₁BM aggregation was in turn slightly increased^[20, 25, 30, 31]. Besides, the strong arc-like scattering arising from the Bragg diffraction with $q \approx 0.32 \text{ \AA}^{-1}$ was corresponded to (100) lamellar stacking of the copolymer **PTB7-Th** and terpolymers **P2–P5**. Similarly, the terpolymers **P2–P5**:PC₇₁BM blends displayed lower intensities, while the copolymer **PTB7-Th** demonstrated a much sharper out-of-plane peak (Fig. 5f, **P1**), suggesting that the structure disorder in random terpolymers reduced the degree of lamellar stacking of conjugated polymers compared with the D-A copolymer **PTB7-Th**. In previous reports, the pattern intensity of the face-on (010) π - π stacking peak with $q_z \approx 1.73 \text{ \AA}^{-1}$ for **PTB7-Th**:PC₇₁BM blends was greatly weaker than that for the pure **PTB7-Th** films because PC₇₁BM destroys the crystallinity of donor polymer **PTB7-Th**^[32]. Therefore, in this work, the already very weak broad arc-like scattering intensities from $q = 1.7\text{--}1.9 \text{ \AA}^{-1}$ in the out-of-plane direction for polymer π - π stacking in the random terpolymers **P2–P5** blends were also lower than that of the copolymer **PTB7-Th** blended samples, further indicating a slight structure disorder. Together with our previous work on randomly embedding extremely low ratio of heavy metal Ir and Pt complex to conjugated backbone of **PTB7-Th**, the random terpolymers with structural disorder destroyed the essential structural symmetry and integrality on the polymer backbone, and thus mildly weakened the molecular packing of the donor polymers as well as reduced the PC₇₁BM aggregation^[20, 30].

Besides, from the AFM images (Fig. S2, in ESI) of the active layers of polymer:PC₇₁BM blends with DIO additives, it is observed that the control copolymer **PTB7-Th** blended films showed featureless film morphology with root-mean-square roughness (RMS) of 1.43 nm. And all the random terpolymer blends exhibited slightly smoother films with RMS from 1.04 nm to 1.17 nm. However, a more featured morphology with obviously interpenetrated networks between the donor and acceptors could be achieved in the random terpolymer:PC₇₁BM blends, which might be contributed from the structural changes on the polymers.

Since the random terpolymers exhibited reduced molecular stacking than the control copolymer **PTB7-Th** in polymer:PC₇₁BM blends, to further understand the effect of donor polymer structural difference on PCE and J_{sc} values, the hole transport behavior in the bulk phase of polymer:PC₇₁BM blended films was evaluated through space charge-limited current (SCLC) method^[33, 34]. Hole only devices with the device configuration of ITO/PEDOT:PSS/polymers **P1–P4**:PC₇₁BM/Au were fabricated, and the plots of current-voltage for the hole mobility measurements are shown in Fig. 6. After parallel experiments, the hole mobility (μ_h) of the polymer:PC₇₁BM blends for copolymer **PTB7-Th** was calculated to be $1.35 \times 10^{-4} \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$, and the values for terpolymers **P2–P4** were 3.73×10^{-4} , 1.20×10^{-4} and $2.19 \times 10^{-4} \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$, respectively. It is noted that the hole mobility for random terpolymers **P2–P4** was comparable or even higher than that for the control copolymer **PTB7-Th** in polymer:PC₇₁BM blends. The

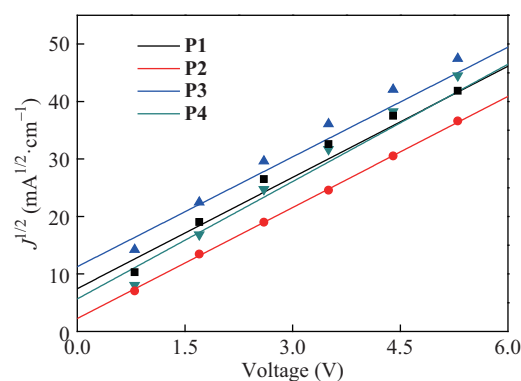


Fig. 6 $J^{1/2} \sim (V_{\text{appl}} - V_{\text{bi}})$ plots of the blended films of donor polymers **P1–P4**:PC₇₁BM blends (solid lines are the fitted data)

results indicated that structural disorder in random terpolymers with slightly weakened polymer stacking may not have a negative impact on the charge carrier mobilities.

To further explain the improvement on photovoltaic device efficiency for random terpolymers, a series of optical measurements on the absorption and photoluminescence (PL) behavior of polymer based films were conducted. The UV-Vis absorption for **P1–P4**:PC₇₁BM blended films was firstly carried out. As shown in Fig. 7(a), in the range of 450–700 nm, the terpolymers **P2–P4** exhibited enhanced optical absorption than the control copolymer **P1**, which is consistent with the trend in the absorption curves of neat polymers as well as the broad and amplified photo-response from EQE curves in photovoltaic devices, indicating more efficient photon harvesting ability of the random terpolymers, due to the involvement of 2D/1A terpolymer structure to enhance the short wavelength absorption^[35]. The terpolymers **P2–P4** exhibited slightly blue-shifted emission peaks (742–750 nm) than 755 nm of **P1** in the neat film state (Fig. 7b). It is demonstrated that the PL of all polymer donors (peak at ~750 nm) was almost completely quenched by PC₇₁BM compared with the PL of their corresponding pure films, suggesting efficient electron-transfer from **PTB7-Th** polymer donor to PC₇₁BM acceptor. From the enlarged part in the inset of Fig. 7(b), the new weak PL signal from ~830 nm to 900 nm could be attributed to the polymer:PC₇₁BM charge transfer (CT) state emission. In polymer:PC₇₁BM blends, from the time-resolved photoluminescence spectra, when the PL decay was taken from 755 nm which was ascribed to the donor polymer emission, the terpolymers **P2–P4** presented a slightly slower decay. When taken at 850 nm for the CT state emission, a biexponential decay behavior was observed, which was attributed to a combination of the fast and slow process of charge separation. The fast decay channel which may result from the dissociation of CT state excitons at the polymer:PC₇₁BM interface is similar for all polymer blends, while the significantly slower decay channel could possibly be attributed to the effective radiative lifetime of PC₇₁BM^[36]. It is found that all the random terpolymer blends exhibited an accelerated PL decay than the control **PTB7-Th**:PC₇₁BM, suggesting a more efficient slow process of charge separation. As described in the GIWAXS experiments, the

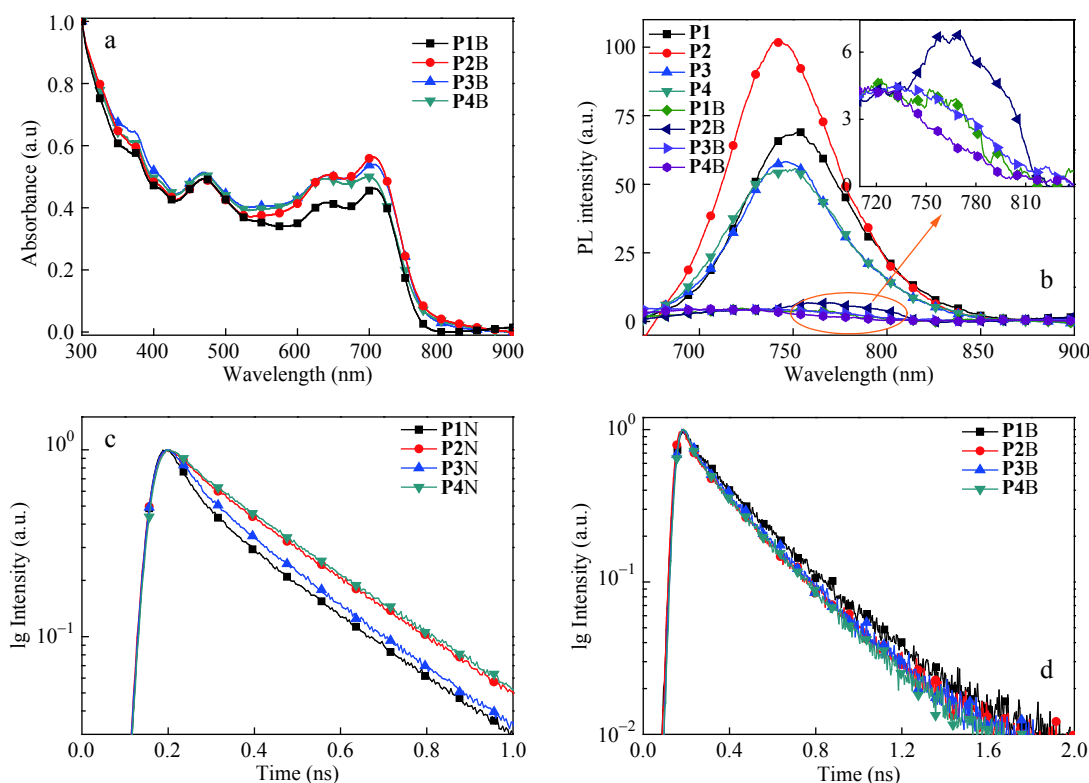


Fig. 7 Normalized UV-Vis absorption for **P1–P4**:PC₇₁BM blended films (a); PL spectra excited at 620 nm of polymer neat (N) film and polymer:PC₇₁BM blended (B) films (b); Time-resolved PL transients excited for polymer:PC₇₁BM blended films taken at 755 nm for donor polymers (c) and 850 nm for charge transfer state of polymer:PC₇₁BM blends (d)

structural disorder in the random terpolymers **P2–P4** could induce a slightly reduced PC₇₁BM aggregation. Thus, the smaller average domain size for PC₇₁BM allowed more singlet excitons to migrate to the hetero-interface than **P1** based blends^[20, 30, 37]. Therefore, the enhanced PCE in the random terpolymers of **P2–P4** could be ascribed to a synergistic impact effect on better light-harvesting ability and more efficient slow process of charge separation.

CONCLUSIONS

In summary, we have presented a simple facial random terpolymer approach to improve the PCE of polymer/fullerene BHJ PSCs. Through incorporating 5 mol%, 10 mol% and 15 mol% feed ratios of lower cost 2,2'-bithiophene monomer to the famous **PTB7-Th** polymer backbone, the two-different donor/one acceptor type terpolymers were constructed. It was found that compared with the regularly alternated copolymer **PTB7-Th**, all the random terpolymers with the structural defects destroyed the essential molecular symmetry and integrality on the polymer backbone, and thus reduced the polymer packing and the PC₇₁BM aggregation in polymer:PC₇₁BM blends. However, the hole transport property was unaffected by the structural disorder in terpolymers. Enhanced power conversion efficiency was observed in both conventional and inverted device architectures owing to the increased short current density, which was originated from enhanced light absorption as well as a more efficient slow charge separation

process. The random terpolymer approach demonstrated in this work can provide a simple lower-cost molecular design strategy to increase the PCE of polymer solar cells based on current high-efficiency conjugated photovoltaic polymers.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://dx.doi.org/10.1007/s10118-018-2128-5>.

ACKNOWLEDGMENTS

This work was financially supported by the the National Natural Science Foundation of China (No. 61761136013) and the Natural Science Foundation of Jiangsu Province (Nos. BK20160042 and BK20160990). S.H. is thankful to DFG (392306670) and Y.Z. is thankful to the CSC for financial support. Parts of this research were undertaken at the SAXS/WAXS beamline of the Australian Synchrotron.

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