Donor–acceptor liquid crystalline conjugated cooligomers for the preparation of films with the ideal morphology for bulk heterojunction solar cells

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A series of novel donor–acceptor (D–A) liquid crystalline conjugated cooligomers, i.e. F3T4-epP, F4T6-epP and F5T8-epP, which comprise oligo(fluorene-alt-bithiophene)s (OFbTs) with the different lengths as the donor segments and a perylene diimide (PDI) derivative as the acceptor segment, were designed and synthesized. The cooligomers can form the films with the desired ideal morphology for bulk heterojunction (BHJ) polymer solar cells (PSCs). That means the films comprise ordered alternating D–A lamellae perpendicular to the substrates. Most importantly, the periods of the nanostructures can be tuned by varying molecular length and post-treatment condition. For F3T4-epP and F4T6-epP, the periods are close to the single and double molecular lengths upon thermal and solvent vapor annealing, respectively. However, only the nanostructures with the period close to the single molecular length were formed for F5T8-epP for both annealing processes. Solar cells based on above nanostructured films were fabricated to demonstrate the advantages of the ideal morphology for BHJ solar cells. It was found that the power conversion efficiency (PCE) of the devices was dependent on the molecular length and the order of the films. Solvent vapor annealed films exhibited the highest order therefore gave the best device performance. A PCE of 1.75% was demonstrated with the solvent vapor annealed films of F5T8-epP. This performance represents the best among the solar cells based on the single molecular materials.

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1. Introduction

The photophysical and optoelectronic properties of conjugated materials are considerably influenced by the nanostructures [1], which are particularly important for optoelectronic devices such as organic solar cells [2–4]. For example, the ideal film morphology for the bulk heterojunction (BHJ) solar cells demands that electron-donor (D) and electron-acceptor (A) components to be interspersed by ~10 nm and form two separate straight phases aligned perpendicular to electrodes for efficient charge separation and transport [2]. It is a great challenge to achieve this type of morphology by the blending method. Compared with the blends of D and A materials, D–A block copolymers are easier to form the well-defined nanostructures due to phase separation of D and A blocks [5–10]. However, most D–A block copolymers are characterized by the wide distribution of molecular weight owing to synthetic methods, and as a result, disordered nanostructures with the domain sizes larger than 20 nm are often obtained [11]. The power conversion efficiency (PCE) of solar cells based on D–A block copolymers alone is often lower than 0.5% [5–9].

Monodisperse conjugated oligomers are featured by the uniform chemical structures [12,13]. Moreover, their molecular length can be well-controlled at the length scale of ~10 nm. Therefore, they are imperative as the ideal building blocks for well-defined nanostructures [5]. However, monodisperse D–A conjugated cooligomers that have been studied by many groups for solar cells so far often exhibited much low efficiency probably due to the poor film morphology [14–21], and only one example showed PCE over 1% [21]. We think that the self-assembly ability is crucial for D–A cooligomers to form the films with well-defined morphology such as aforementioned BHJ nanostructures since phase separation tendency of cooligomers is weaker compared to that of copolymers, and pristine films are usually characterized by low order, especially in large area. Recently, we found that liquid crystalline conjugated cooligomers were capable of self-assembling into ideal BHJ-like lamellar nanostructures for high performance solar cells based on a single molecular material [22]. However, it is a great challenge to control the nanostructures and then optoelectronic properties of conjugated materials [23], and how to manipulate above
nanostructures remains as an unsolved problem. For understanding the self-assembly process and to develop the way for modulating the self-assembly structures of this type of D–A conjugated cooligomers, herein we synthesized three new cooligomers, i.e. F3T4-epP, F4T6-epP and F5T8-epP (Fig. 1), which contained oligo(fluorene-alt-bithiophene)s (OFBTs) as the D segments and perylene diimide (PDI) substituted by branched 1-ethylpropyl as the A segment. Their liquid crystalline property, self-assembly behavior, and optoelectronic properties were investigated in detail. It was found that all three cooligomers could self-assemble into D–A lamellar nanostructures identical to the ideal ones required by the ideal BHJ solar cells. Meanwhile, the periods of the nanostructures were dependent on the molecular length and post-annealing process. Solar cells with PCE up to 1.75% have been demonstrated based on the films comprising above nanostructured films. This performance represents the best among the solar cells based on single molecular materials [10,21,22].

2. Experimental section

2.1. Materials

Toluene was distilled over sodium/benzophenone. N,N-dimethyl formamide (DMF) was distilled over CaH₂ under reduced pressure. Compounds epPDI, 1, 2, 4 and F3TH4 (comprising 3 fluorene and 4 thiophene units, identical to the OFBT segment in F3T4-epP) were synthesized according to the procedures reported in the literatures [24–26]. Other reagents were obtained from commercial resources and used without further purification.

2.2. Compound 3

A mixture of N-(1-ethylpropyl)perylene-3,4:9,10-tetracarboxylylic-3,4-anhydride-9,10-imide (1, 0.87 g, 1.89 mmol), 9,9-dicyanfluorene-2-yl-amine (2, 1.00 g, 2.06 mmol), imidazole (20 g) and zinc acetate (0.26 g) were stirred at 160 °C for 24 h under argon. After cooling to room temperature, the mixture was washed with water, 10% HCl and then diluted KOH aqueous solution. The crude product was dried at 80 °C under vacuum, and then purified with column chromatography on silica gel with CH₂Cl₂ as eluent to yield 1.51 g (86%) product as a dark-red solid. 1H NMR (300 MHz, CDCl₃): δ = 8.79–8.67 (m, 8H), 7.88 (d, J = 8.55 Hz, 1H), 7.65 (d, J = 8.61 Hz, 1H), 7.55 (s, 2H), 7.36–7.35 (m, 2H), 5.15–5.09 (m, 1H), 2.32–2.29 (m, 2H), 2.04–1.97 (m, 6H), 1.26 (m, 20H), 0.98 (t, J = 7.42 Hz, 6H), 0.86 (t, J = 6.92 Hz, 6H), 0.70 (m, 4H). MS (MALDI-TOF, reflecton mode): m/z (%) calcd for C₉₈H₇BrN₂O₄ (928.36), found: 929.54 (100) [M+H]⁺.

2.3. Synthesis of the cooligomers

General procedure for the synthesis of the cooligomers is exemplified by the synthesis of F3T4-epP: In absence of light, a solution of compound 3 (0.60 g, 0.65 mmol), compound 4a (0.91 g, 0.65 mmol), and Pd(PPh₃)₄ (7.5 mg, 6.5 × 10⁻⁵ mol) in anhydrous DMF/toluene (5 mL, v/v = 1:4) was stirred at 85 °C for 24 h. The mixture was cooled to room temperature and then poured into a large amount of ethanol. The precipitate was collected by filtration and then purified with column chromatography on silica gel with dichloromethane as eluent and further purified with preparative gel permeation chromatography (PGPC) to afford a dark-red solid (0.74g, 51%). 1H NMR (300 MHz, CDCl₃): δ = 7.88–7.65 (m, 8H), 7.87 (d, J = 8.55 Hz, 1H), 7.77 (d, J = 7.92 Hz, 1H), 7.71–7.68 (m, 4H), 7.66 (d, J = 1.26 Hz, 1H), 7.63–7.56 (m, 8H), 7.35–7.29 (m, 9H), 7.23–7.18 (m, 3H), 5.14–5.11 (m, 1H), 2.30–2.26 (m, 2H), 2.05–1.98 (m, 14H), 1.20–1.01 (m, 60H), 0.94 (t, J = 7.5 Hz, 6H), 0.84–0.77 (m, 10H), 0.68 (m, 12H) ppm; 13C NMR (75 MHz, CDCl₃): δ = 163.5, 152.2, 152.0, 151.8, 151.6, 150.9, 144.0, 143.8, 140.9, 140.6, 140.3, 140.2, 136.6, 136.4, 134.8, 134.3, 133.9, 133.2, 130.5, 132.3, 131.7, 130.7, 126.3, 127.3, 127.2, 126.9, 126.6, 126.3, 124.7, 124.5, 123.7, 123.6, 123.5, 123.1, 123.0, 122.9, 120.5, 120.4, 120.2, 120.1, 120.0, 119.8, 55.5, 55.4, 55.2, 40.4, 40.2, 31.9, 31.8, 30.1, 30.0, 29.2, 25.1, 23.9, 23.8, 22.6, 14.1, 11.4 ppm. Elemental analysis (%): 3057.61 (100) [C₁₃₂H₁₄₈N₂O₄S₄].

Fig. 1. Chemical structures of epPDI, F3T4 and D–A cooligomers F3T4-epP, F4T6-epP and F5T8-epP.
tetramethylsilane (TMS) as an internal standard. Elemental analysis was carried out on a FlashEA1112 elemental analysis system. MALDI-TOF mass spectra were recorded on a Bruker/AutoflexIII Smartbeam MALDI Mass Spectrometer with anthracene-1,8,9-triol as the matrix. Cyclic voltammetry was performed on a CHI660a electrochemical analyzer with a three-electrode cell in a solution of 0.1 mol L⁻¹ tetrabutylammonium hexafluorophosphate (Bu4NPF6) in anhydrous CH2Cl2 at a scanning rate of 50 mV s⁻¹. A platinum (Pt) electrode with a diameter of 2 mm, a Pt wire and a saturated calomel electrode (SCE) were used as the working, the counter and the reference electrodes, respectively. UV–vis absorption spectra were recorded on a Shimadzu UV3600 spectrometer. Polarizing optical microscopy (POM) observation was conducted on an Olympus BX51 polarizing optical microscope equipped with a LTS 350 hot stage and a TMS 94 temperature programmer (Linkam). Optical micrographs were taken from an Olympus digital camera. Differential scanning calorimetry (DSC) measurements were performed on a TA Q100 thermal analyzer at scanning rate of 10 °C min⁻¹. Small angle X-ray scattering (SAXS) was recorded on a Bruker Nanostar instrument operated at 40 kV and 35 mA.

2.5. Transmission electron microscopy (TEM) characterization

To prepare cooligomer films for TEM observations, 50 nm poly(3,4-ethylenedioxythiophene):poly(styrene sulphonate) (PEDOT:PSS) was first spin-cast on precleaned glass slides. After heating the substrates at 120 °C for 30 min, 70 nm cooligomer layers were spin-coated from 16 mg/mL chlorobenzene solutions in N2 filled glovebox. The films were then heated at 150 °C for 5 min or put in CH2Cl2 atmosphere for 20 min. Finally, films were floated with water to micro-grids and dried at ambient conditions. TEM was performed on a JEOL JEM-1011 transmission electron microscope operated at an acceleration voltage of 100 kV. Selected area electron diffraction (SAED) was taken with camera length of 160 cm and Au (111) diffraction as the external standard.

2.6. Device fabrication and measurement

Cooligomer films for electronic devices were prepared in the same way as those for TEM observation, except for different substrates. For organic solar cells, 50 nm PEDOT:PSS-coated indium–tin–oxide (ITO) glass was used as the substrate. After the preparation of cooligomer films, epPDI hole blocking-layer (3 nm), LiF (1 nm) and Al electrode (100 nm) were thermally evaporated successively in vacuum. The active area of the unit cell is 14 mm². Solar cell devices were sealed in the glovebox before measured in ambient. The current density–voltage (I–V) measurements of devices in the dark or under AM 1.5G solar simulation at 100 mW cm⁻² were conducted using a computer-controlled Keithley 236 source meter. EQE was measured with a lock-in amplifier after illumination with monochromatic light from a xenon lamp, and was calibrated against a multicrystalline Si solar cell with a known spectral response. For hole-only devices, cooligomer films were cast on PEDOT:PSS-coated ITO glass. Then MoO3 (10 nm) and Al (100 nm) were thermally evaporated successively in vacuum. For electron-only devices, 100 nm Al was first thermally evaporated on ITO glass in vacuum. After cooligomer films had been cast and annealed, another 100 nm Al was thermally deposited. All the devices were tested in ambient under dark using a computer-controlled Keithley 236 source meter.
3. Results and discussion

3.1. Molecular design concept, synthesis and characterization

As shown in Fig. 1, F3T4-epP, F4T6-epP and F5T8-epP contain OFbTs and PDI as the D and A segments, respectively. The liquid crystalline property of OFbT segments [24] and strong $\pi-\pi$ interaction of PDI unit [27] are expected to endow the D–A conjugated co-oligomers desired self-assembly properties. From the literatures, the substituent on the imide-N of PDI has primary importance to the longitudinal and transverse offset between neighboring PDI molecules in solid state but little influence on the electronic energy levels of PDI because N-atoms locate on the nodes of the highest occupied molecular orbital (HOMO) and the lowest

**Fig. 3.** The first cooling and the second heating DSC traces of F3T4-epP, F4T6-epP and F5T8-epP at a heating/cooling rate of 10 °C min⁻¹ in N₂ (a), and SAXS of F3T4-epP (b), F4T6-epP (c) and F5T8-epP (d) powders at different temperatures upon cooling from isotropic state. G = glass; S = smectic liquid crystalline state; I = isotropic state. Inset of (a) shows the enlarged glass transitions of F4T6-epP and F5T8-epP.

**Fig. 4.** TEM images of F3T4-epP (a, d, g), F4T6-epP (b, e, h) and F5T8-epP (c, f, i) thin films: pristine (a–c), thermal annealed at 150 °C for 5 min (d–f) and CH₂Cl₂ vapor annealed for 20 min (g–i). Insets on top-right corner are corresponding SAED patterns of the films.
be no ground-state electronic interactions as expected. From the photoluminescence spectra (Fig. 2b), F3T4-epPDI and F5T8-epPDI were both highly fluorescent; whereas the photoluminescence of F3T4-epP was strongly quenched. This phenomenon was also observed for F4T6-epP and F5T8-epP, and indicated the efficient charge transfer between OFbT and PDI segments.

### 3.3. Electrochemical properties

Cyclic voltammograms were measured in CH2Cl2 solution (10−3 M) to estimate the HOMO and LUMO levels of F3T4-epP, F4T6-epP, and F5T8-epP. As shown in Fig. 5A, two or three reversible or quasi-reversible redox waves between 0.8 and 1.5 V, and two reversible redox waves between ~0.5 and ~0.9 V were observed. The redox waves in the positive and negative potential regions are identical to those of corresponding OFbT oligomers [24] and PDI derivatives [29], respectively. This again indicates the absence of electronic interaction between OFbT and PDI segments. The HOMO/LUMO energy levels were estimated to be −5.27/−3.90 eV for F3T4-epP, −5.27/−3.91 eV for F4T6-epP and −5.26/−3.91 eV for F5T8-epP. The difference of the HOMO and LUMO is as high as 1.37–1.35 eV, which implies that the solar cells based on these cooligomers will have the high open circuit voltages (VOC) [30,31].

### 3.4. Liquid crystalline properties

The thermotropic liquid crystalline properties of F3T4-epP, F4T6-epP, and F5T8-epP were studied by POM, DSC, temperature-dependant SAXS, and wide angle XRD. Fig. 3a shows the DSC cooling and heating scans with the assignment of the phases. All cooligomers exhibit a glass transition, a mesophase—mesophase transition and a mesophase—isotropic state transition. Transition temperatures and the entropies of the transitions are listed in Table S1. The glass transition temperatures (Tg) of the cooligomers increase with the increase of the length of OFbT segments, which are 69.9, 83.4 and 90.9 °C for F3T4-epP, F4T6-epP and F5T8-epP, respectively. Tg of F3T4-epP was determined by the modulated DSC measurements (Fig. S6). F3T4-epP, F4T6-epP and F5T8-epP can form glassy smectic liquid crystalline phase at room temperature with the layer d-spacings of 5.70, 7.06 and 8.53 nm for F3T4-epP, F4T6-epP and F5T8-epP, respectively, which are comparable to their molecular lengths (Fig. 3b-d). Only broad halos at about 20° were observed in wide angle XRD of all the three cooligomers (Fig. S7a), which further proves the formation of smectic liquid crystalline phase at room temperature. This characteristic is promising for realizing D–A alternating nanophase separation toward ideal BHJ film morphology. Nematic mesophase was also observed at higher temperature for F4T6-epP and F5T8-epP, as indicated by temperature-dependant SAXS [Fig. 3c and d] and POM photos (Fig. S8).
3.5. Thin film nanostructures and self-assembly process

Thin films with the thickness of ~70 nm were spin-cast on PEDOT:PSS-coated glass slides for film morphology characterizations by TEM. The as-cast or pristine films of F3T4-epP, F4T6-epP and F5T8-epP were all featureless (Fig. 4a–c). After thermal annealing at 150 °C for 5 min, dark–bright stripes emerged in F3T4-epP, F4T6-epP and F5T8-epP films with the periods of 5.7, 7.0 and 8.0 nm (Fig. 4d–f), respectively, which are consistent with their layer d-spacings at room temperature (Fig. 3b–d). However, the SAEDs were all weak, which indicates the lower order of the thermal annealed films. Since solvent vapor (CH2Cl2 vapor) annealing could significantly improve the order of D–A cooligomer films as previous report [22], solvent vapor annealed films of F3T4-epP, F4T6-epP and F5T8-epP were also investigated (Fig. 4g–i). The film order of all three cooligomers was indeed improved as indicated by the distinct and sharp SAED rings. Unexpectedly, different from those of D–A cooligomers with identical molecular lengths but with n-hexyl as the substituent on the N-atom in PDI segment [22], the periods of the lamellar structures of F3T4-epP and F4T6-epP were no longer relevant to their single molecular lengths, but 10.8 and 12.5 nm, respectively, which are close to their double molecular lengths. In contrast, the period of F5T8-epP lamellar structure (8.3 nm) was still comparable to its single molecular length. All above results indicate that the nanostructures of this type of D–A conjugated oligomers depend on the molecular length, alkyl substituents and annealing process.

Single crystal analysis can give the solid information of the molecular packing. Fortunately, micro-sized ribbon-like single crystals of F3T4-epP were successfully grown from solvent slow evaporation of CH2Cl2 solutions for TEM study. As shown in Fig. 5, a representative crystal exhibited straight dark–bright stripes with a period of 9.8 nm. Clearly, the period of F3T4-epP is much longer than the molecular length, but close to the double molecular length. This phenomenon is consistent with the thin film TEM characterizations. We also monitored the SAXS patterns of the powders of F3T4-epP, F4T6-epP and F5T8-epP upon the same solvent vapor treatment. Consistent with the thin film TEM characterizations, the primary peak of F3T4-epP (Fig. S10a) and F4T6-epP (Fig. S10b) presents at 0.87° (10.2 nm) and 0.64° (13.7 nm), respectively. Meanwhile, the broad diffraction peaks in the range of 15°–25° were observed in the wide angle XRD of the solvent annealed powders (Fig. S7b), implying that the thin films after solvent vapor annealing should be semi-crystalline. Upon heating, the lamellar nanostructures again transferred to those with the periods relevant to the single molecular lengths. This indicates that these two types of nanostructures can be switched between each other. For F5T8-epP (Fig. S10c), only diffraction peaks relevant to the single molecular length were observed.

The SAED patterns of the single crystals are shown in the inset of Fig. 5. The (004) diffraction points along the direction perpendicular to the crystal growth direction are originated from the periods related to the double molecular length. Along the meridian of SAED pattern (also the crystal growth direction), the diffraction spot (040) corresponding to the d-spacing of 0.34 nm (Taking the SAED pattern of ab plane as shown in Fig. S11 into account, this diffraction spot is indexed as (040)), is ascribed to the π–π stacking of PDI planes, which means that the self-assembling of F3T4-epP under the solvent vapor annealing is driven by the π–π interaction, just like other PDI derivatives reported in the literatures [27,28,32]. The presence of the π–π interaction of PDI segment also indicates that OFbT and PDI segments in F3T4-epP crystals packed in a head-to-head fashion to form the lamellar nanostructures comprising alternating D and A phases. The (004) and (040) diffraction spots were also observed in the SAED of the solvent vapor annealed film of F3T4-epP (Fig. S12), indicating that the solvent vapor annealed film of F3T4-epP shares the same structure as solution-grown single crystals.

To clearly elucidate the packing behavior of the D–A molecules, thin film UV–vis absorption spectra of F3T4-epP, F4T6-epP and F5T8-epP were measured and compared with the solution ones. The absorption spectra of F3T4-epP, F4T6-epP and F5T8-epP in solution (5 × 10⁻⁶ mol/L in CHCl3), pristine, thermal annealed and solvent vapor annealed films are shown in Fig. 6. From solution to film, the 0–0 transition absorption band of the PDI band at about 527 nm red-shifted by ~10 nm and the relative intensity was reduced compared to those in solutions, while the relative intensity of the 0–1 transition absorption band at about 490 nm increased. This suggests that the PDI segment already aggregated in a face-to-face

Table 1: Solar cell performances of F3T4-epP, F4T6-epP, and F5T8-epP with a device structure of ITO/PEDOT:PSS (50 nm)/cooligomer (70 nm)/epPDI (3 nm)/LiF (1 nm)/Al (100 nm).*

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* pris – pristine; TA – thermal annealed; SA – solvent vapor annealed.
fashion (H-aggregation) in film [33,34]. After thermal and solvent vapor annealing, the absorption bands of OFTθ segments all blue-shifted, indicative of H-aggregation of whole molecule. All above results imply that the films formed by the current D–A cooligomers comprising ordered alternating D–A lamellae.

Unraveling how the lamellar nanostructures are formed is very important for understanding the self-assembly behavior of the D–A cooligomers. Accordingly, the films of F3T4-epP and F4T6-epP with different solvent vapor annealing time were studied by TEM. For F3T4-epP (Fig. 7a–e) and F4T6-epP (Fig. 7f–j), the phenomenon was identical in the first 5 min. The lamellar nanostructures presented in 2 min with the periods of 5.7 and 7.0 nm, respectively, corresponding to the single molecular lengths. However, after 5 min, the self-assembly process still went on, and the lamellar nanostructures with the periods of 10.8 and 12.5 nm, which are close to the double molecular lengths of F3T4-epP and F4T6-epP, respectively, began to grow. Films were full of the double-molecular-length lamellar nanostructures in 20 min.

3.6. Photovoltaic properties

Photovoltaic devices based on the cooligomers were fabricated with the device structure of ITO/PEDOT:PSS (50 nm)/D–A cooligomer (70 nm)/epPDI (3 nm)/LiF (1 nm)/Al (100 nm), in which epPDI was used as a hole blocking-layer and can result in the higher fill factor (FF) and short-circuit current density (JSC) [22]. All devices were encapsulated before measurement. Table 1 shows the average device performance data from 15 devices, and the representative current density–voltage (J–V) curves and external quantum efficiency (EQE) profiles are displayed in Fig. 8. The fluctuation of the device performance of F5T8-epP is included in the SI (Fig. S13). As shown in Table 1, both FF and JSC increased with an increase of the film order or molecular length, resulting in the improved device performance (Table 1 and Fig. 8). For example, PCE of F5T8-epP increased from 0.20% for the pristine film to 1.15% for the thermal annealed film and then 1.75% for the solvent vapor annealed film, consistent with the increase of the film order. This improvement of the device performance should be attributed to the enhanced film order therefore the charge carrier transport property. The devices based on the solvent vapor annealed films of F3T4-epP, F4T6-epP and F5T8-epP exhibited PCEs of 0.42, 1.32 and 1.75%, respectively. The increase of the PCE with the increasing molecular length may reflect the importance of the length scale of the D and A phases. As shown in Fig. 8b, both D– and A-blocks contributed to photocurrent as indicated by resembling EQE profiles and film absorption spectra of the cooligomers. Meanwhile, an EQE of ~60% at 410–500 nm were achieved with F5T8-epP. According to the literature, VOC of BHJ solar cells can be estimated by the formula 1/e (|HOMO|\text{donor} − |LUMO|\text{acceptor}) − 0.3 V [31]. As shown in Table 1, all the devices showed VOC of ~0.9 V, which is close to the value (~1.0 V) estimated from HOMO/LUMO values of the cooligomers according to the formula. It should be pointed out that the PCE of the devices based on the solvent vapor annealed films of F5T8-epP represents the best among the solar cells based on the single molecular materials [21,22]. More recently, Hashimoto et al. reported a poly(3-hexylthiophene) (P3HT) D–A block copolymers, which exhibited a PCE of 1.70%. The absorption onset of F5T8-epP is ~100 nm blue-shifted compared to P3HT, however, the PCE as high as 1.75% was still achieved. This further solidifies the importance of the film morphology on the performance of BHJ solar cells. Considering that the weight percentages of PDI acceptor segment in F3T4-epP, F4T6-epP and F5T8-epP are as low as 23.5%, 18.3% and 15.0%, respectively, the hole and electron mobilities of solvent vapor annealed films were also measured by hole and electron-only devices. With a device structure of ITO/PEDOT:PSS (50 nm)/cooligomer (70 nm)/MoO3 (10 nm)/Al (100 nm), the hole mobilities were measured to be 3.6, 3.9 and 4.4 × 10⁻⁵ cm² V⁻¹ s⁻¹ for F3T4-epP, F4T6-epP and F5T8-epP, respectively, while the electron mobilities of F3T4-epP, F4T6-epP and F5T8-epP were 4.2, 1.5 and 1.4 × 10⁻⁵ cm² V⁻¹ s⁻¹, respectively, as measured with a device structure of Al (100 nm)/cooligomer (70 nm)/Al (100 nm). Although the longer cooligomer F5T8-epP contains PDI segment as low as 15%, reasonable hole and electron mobilities were still achieved. This further proves the advantages of the well-defined nanostructures in the fabrication of BHJ solar cells.

4. Conclusion

A series of novel monodisperse D–A conjugated cooligomers, i.e. F3T4-epP, F4T6-epP and F5T8-epP, were synthesized. F3T4-epP, F4T6-epP and F5T8-epP are mesomorphism and can self-assemble into the films comprising ordered alternating D–A lamellae with the period relative to the single molecular length upon thermal annealing. However, upon solvent vapor annealing, F3T4-epP and F4T6-epP exhibited unique behavior and self-assembled into D–A lamellar nanostructures with the period close to the double molecular length. Solar cells based on the nanostructured films were fabricated, and a PCE of 1.75% was demonstrated with the solvent vapor annealed films of F5T8-epP. Our study provides an approach for realizing the ideal film morphology required by BHJ solar cells. Most importantly, the nanostructures of the films can be modulated by tuning either molecular length or post-treatment condition.

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Appendix. Supplementary material

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.polymer.2011.07.029.

References