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Monodisperse Co-oligomer Approach toward Nanostructured Films with Alternating Donor−Acceptor Lamellae

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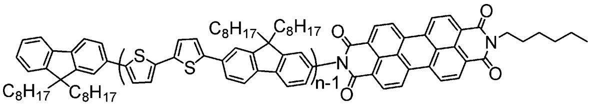
Limited by short exciton diffusion length (~10 nm) of organic semiconductors, nanostructured films with electron−donor (D) and electron−acceptor (A) bicontinuous phases with nanometer-scale interspacing for efficient charge separation and transport are highly desirable for preparation of high-performance polymer solar cells (PSCs).[1] PSCs are usually fabricated with blends of D and A materials, and it is rather difficult to realize the aforementioned film morphology. Block copolymers intrinsically prefer composition-dependent nanophase separation due to the incompatibility between different blocks.[2,3] Accordingly, several D−A block copolymers with fullerene[4] or perylene diimide (PDI)[5,6] as the A component have been prepared for achieving nanostructured D−A heterojunctions. However, due to the polydispersity and rigid nature of conjugated polymers, disordered naonostructures with domain sizes larger than 20 nm were often obtained.[6] Consequently, the efficiencies of the resulting PSCs were lower than 0.5%,[6] and design and synthesis of materials toward well-defined nanostructured D−A heterojunctions remain great challenges.[7]

Monodisperse conjugated oligomers are characterized by a uniform chemical structure as well as a tunable molecular length around 10 nm;[8] therefore, they are ideal scaffolds for well-defined nanostructures with a length scale equal to or less than the exciton diffusion length of organic semiconductors. Herein, three D−A co-oligomers, **F3T4-hP**, **F4T6-hP**, and **F5T8-hP** as shown in Chart 1, with different molecular lengths were designed and synthesized to illustrate this concept. These co-oligomers can form highly ordered films comprising alternating D−A lamellar nanostructures with the period depending on the molecular length. As a result, single-molecular organic solar cells with an external quantum efficiency (EQE) up to 46% at 410−500 nm and a power conversion efficiency (PCE) up to 1.50% have been demonstrated. These results represent the best performance for single-molecular solar cells to date.

As shown in Chart 1, oligo(fluorene-*alt*-bithiophene)s (**OFbT**s) are selected as D segments not only because they are typical *p*-type organic semiconductors but also because their liquid crystalline property may provide an additional driving force for the formation of ordered films via post-treatment.[9] PDIs are recognized as good A-materials,[10,11] and their strong $\pi-\pi$ interactions qualify them as great building blocks for functional supramolecular architectures.[12] All three co-oligomers are smectic liquid crystals as characterized by differential scanning calorimetry (DSC, Figure S5 in Supporting Information (SI)) and small-angle X-ray scattering (SAXS, Figure 1). At room temperature, the lamellar *d*-spacings from first-order diffractions are 5.59, 7.42, and 8.95 nm for **F3T4-hP**, **F4T6-hP**, and **F5T8-hP**, respectively, which are close to their molecular lengths of 5.89, 7.91, and 9.37 nm, respectively.

Chart 1. Chemical Structures of **F3T4-hP**, **F4T6-hP**, and **F5T8-hP** and Their Corresponding Phase Transitions upon Heating[a]



n = 3, **F3T4-hP** G 66.4 S_{X2} 212.3 S_{X1} 215.7 I
4, **F4T6-hP** G 83.4 S_{X3} 194.8 S_{X2} 204.7 S_{X1} 233.5 I
5, **F5T8-hP** G 90.4 S_X 189.5 N 248.5 I

[a] Symbols: *G*, glassy; *S*, smectic; *N*, nematic; *I*, isotropic.

Thin films of the co-oligomers with thickness of ~70 nm on poly(3,4-ethylene dioxythiophene):poly(styrene sulfonate) (PEDOT:PSS)-covered indium−tin−oxide (ITO) glass substrates were floated with water to microgrids for transmission electron microscopy (TEM) characterization. In prinstine films, lamellar nanostructures were only observed for **F5T8-hP** (Figure S7, SI). This may be ascribed to its having the strongest D−A segregation and the longest molecular length.[2] After thermal annealing at 210 °C for 2 min, dark-bright stripes appeared in the films for all three co-oligomers (Figure 2a−c). However, the order of the films is still relatively low, as indicated by weak selected area electron diffractions (SAED, insets of Figure 2a−c). Solvent−vapor annealing has been found to be a promising method to generate highly ordered block copolymer films with few defects in large area.[13] Here, the film order of the co-oligomers can be significantly improved with CH_2Cl_2 vapor annealing. As shown in Figure 2d−f, the persistent lengths of the lamellae increase from 50−150 nm for thermal annealed films to 100−400 nm for solvent-vapor annealed films, and the (002) and (003) diffraction rings in SAED become distinct. The periods of the lamellae are 5.6, 7.4, and 8.9 nm for **F3T4-hP**,

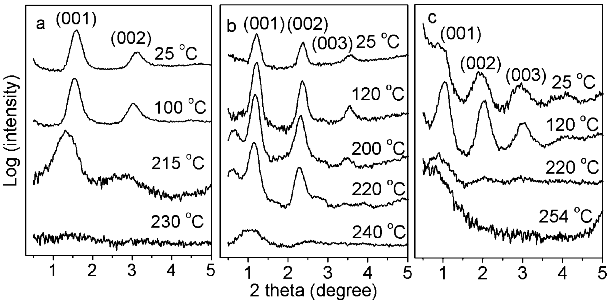


Figure 1. SAXS of **F3T4-hP** (a), **F4T6-hP** (b), and **F5T8-hP** (c) powders at different temperatures. Temperatures are labeled to the right.

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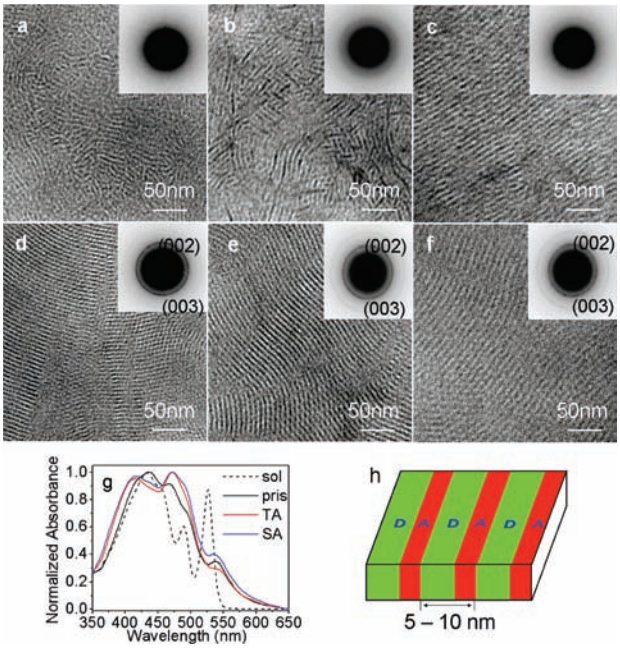

Figure 2. TEM images and SAED patterns (inset) of **F3T4-hP** (a,d), **F4T6-hP** (b,e), and **F5T8-hP** (c,f) thin films after thermal annealing (a−c) or solvent-vapor annealing (d−f). Solution (sol, 1×10^{-6} M in chloroform) and film (pristine, pris; thermal annealed, TA; solvent-vapor annealed, SA) absorption spectra of **F3T4-hP** (g). Schematic illustration of the lamellar nanostructures in films (h).

F4T6-hP, and **F5T8-hP**, respectively, which are consistent with SAXS. Meanwhile, UV−vis absorption spectra of the co-oligomers indicate that **PDI** units are face-to-face stacked (H-aggregation) in films. With **F3T4-hP** as an example (Figure 2g), the relative intensity of the 0−0 absorption band of **PDI** at 535 nm in films is significantly reduced compared to that in solution, which is characteristic of H-aggregation.[14,15] These results clearly indicate that the co-oligomers have formed alternating D−A lamellar nanostructures with the period depending on the molecular length, as shown in Figure 2h.

To demonstrate the advantage of the films with the highly ordered alternating D−A lamellar nanostructures, photovoltaic devices based on the co-oligomers were fabricated with the device structure of ITO/PEDOT:PSS (50 nm)/co-oligomers (70 nm)/**epPDI** (3 nm)/LiF (1 nm)/Al (100 nm), in which **epPDI** (*N*,*N*′-bis(1-ethylpropyl)-3,4,9,10-perylenetetracarboxyl diimide) was used as a hole-blocking layer and could result in the higher fill factor (FF) and short-circuit current density (I_{SC}) (Figure S8, SI). It was found that the device performance measured in ambient conditions under AM 1.5 solar simulation at 100 mW/cm^2 was enhanced with increasing film order or molecular length (Table S1, SI). The device based on a solvent−vapor annealed film of **F5T8-hP** gave the best device performance, with a PCE up to 1.50% (open-circuit voltage (V_{OC}) = 0.87 V; I_{SC} = 4.49 mA/cm^2; FF = 0.38, Figure 3a). Both D and A blocks contributed to photocurrent, as indicated by the resemblance of the EQE profile and film absorption spectrum of **F5T8-hP** (Figure 3b). An EQE of ∼46% and an internal quantum efficiency (IQE) of ∼60% (Figure S10, SI) at 410−500 nm were achieved. To the best of our knowledge, the performance of the device based on the solvent−vapor annealed **F5T8-hP** film is the highest in single-molecular organic solar cells to date,[16] and it is also much higher than that of the devices based on D−A blends and copolymers with **PDI**s as the A materials.[5,6,10,11,17] All these indicate that the nanostructured films can tansport both electrons and holes efficiently. In contrast, the devices based on the blends of **OFbT**s and **epPDI** gave much inferior device performance, as shown in Table S1 (SI).

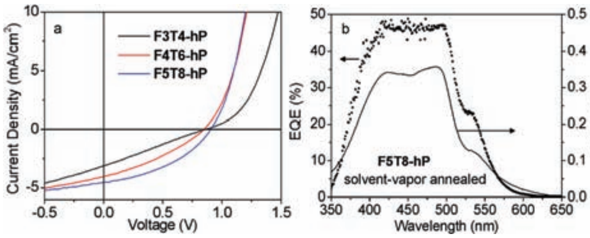

Figure 3. $I-V$ characteristics of solar cells based on solvent vapor annealed thin films of the co-oligomers (a), and EQE curve of the device based on solvent vapor annealed **F5T8-hP** film and UV−vis absorption spectrum of the corresponding film (b).

In conclusion, we have demonstrated that highly ordered films comprising well-defined and tunable alternating D−A lamellar nanostructures could be prepared with monodisperse D−A co-oligomers. These films can tansport charge carriers efficiently and, therefore, can be used in fabrication of high-performance single-molecular optoelectronic devices.

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Supporting Information Available: Detailed experimental procedures, characterization of all co-oligomers, and detailed device data. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Günes, S.; Neugebauer, H.; Sariciftci, N. S. *Chem. Rev.* **2007**, *107*, 1324.
(2) Bates, F. S.; Fredrickson, G. H. *Annu. Rev. Phys. Chem.* **1990**, *41*, 525.
(3) Scherf, U.; Gutacker, A.; Koenen, N. *Acc. Chem. Res.* **2008**, *41*, 1086.
(4) (a) de Boer, B.; Stalmach, U.; van Hutten, P. F.; Melzer, C.; Krasnikov, V. V.; Hadziioannou, G. *Polymer* **2001**, *42*, 9097. (b) van der Veen, M. H.; de Boer, B.; Stalmach, U.; van de wetering, K. I.; Hadziioannou, G. *Macromolecules* **2004**, *37*, 3673. (c) Barrau, S.; Heiser, T.; Richard, F.; Brochon, C.; Ngov, C.; van de Wetering, K.; Hadziioannou, G.; Anokhin, D. V.; Ivanov, D. A. *Macromolecules* **2008**, *41*, 2701. (d) Lee, J. U.; Cirpan, A.; Emrick, T.; Russell, T. P.; Jo, W. H. *J. Mater. Chem.* **2009**, *19*, 1483.
(5) (a) Lindner, S. M.; Thelakkat, M. *Macromolecules* **2004**, *37*, 8832. (b) Lindner, S. M.; Hüttner, S.; Chiche, A.; Thelakkat, M.; Krausch, G. *Angew. Chem., Int. Ed.* **2006**, *45*, 3364. (c) Sommer, M.; Lindner, S. M.; Thelakkat, M. *Adv. Funct. Mater.* **2007**, *17*, 1493. (d) Sommer, M.; Lang, A. S.; Thelakkat, M. *Angew. Chem., Int. Ed.* **2008**, *47*, 7901.
(6) Zhang, Q. L.; Cirpan, A.; Russell, T. P.; Emrick, T. *Macromolecules* **2009**, *42*, 1079.
(7) Mativetsky, J. M.; Kastler, M.; Savage, R. C.; Gentilini, D.; Palma, M.; Pisula, W.; Müllen, K.; Samorì, P. *Adv. Funct. Mater.* **2009**, *19*, 2486.
(8) Müllen, K.; Wegner, G. *Electronic Materials: The Oligomer Approach*; Wiley-VCH: Weinheim, New York, 1998.
(9) Zhang, X. J.; Qu, Y.; Bu, L. J.; Tian, H. K.; Zhang, J. P.; Wang, L. X.; Geng, Y. H.; Wang, F. S. *Chem.−Eur. J.* **2007**, *13*, 6238.
(10) Dittmer, J. J.; Lazzaroni, R.; Leclère, P.; Moretti, P.; Granström, M.; Petritsch, K.; Marseglia, E. A.; Friend, R. H.; Brédas, J. L.; Rost, H.; Holmes, A. B. *Sol. Energy Mater. Sol. Cells* **2000**, *61*, 53.
(11) Schmidt-Mende, L.; Fechtenkötter, A.; Müllen, K.; Moons, E.; Friend, R. H.; MacKenzie, J. D. *Science* **2001**, *293*, 1119.
(12) Würthner, F. *Chem. Commun.* **2004**, *14*, 1564.
(13) Kim, S. H.; Misner, M. J.; Xu, T.; Kimura, M.; Russell, T. P. *Adv. Mater.* **2004**, *16*, 226.
(14) Kasha, M.; Rawls, H. R.; Ashraf El-Bayoumi, M. *Pure Appl. Chem.* **1965**, *11*, 371.
(15) Seibt, J.; Marquetand, P.; Engel, V.; Chen, Z.; Dehrn, V.; Würthner, F. *Chem. Phys.* **2006**, *328*, 354.
(16) Nishizawa, T.; Lim, H. K.; Tajima, K.; Hashimoto, K. *Chem. Commun.* **2009**, *18*, 2469.
(17) (a) Rajaram, S.; Armstrong, P. B.; Kim, B. J.; Fréchet, J. M. J. *Chem. Mater.* **2009**, *21*, 1775. (b) Guo, X. Y.; Bu, L. J.; Zhao, Y.; Xie, Z. Y.; Geng, Y. H.; Wang, L. X. *Thin Solid Films* **2009**, *517*, 4654. (c) Shin, W. S.; Jeong, H. H.; Kim, M. K.; Jin, S. H.; Kim, M. R.; Lee, J. K.; Lee, J. W.; Gal, Y. S. *J. Mater. Chem.* **2006**, *16*, 384. (d) Li, J. L.; Dierschke, F.; Wu, J. S.; Grimsdale, A. C.; Müllen, K. *J. Mater. Chem.* **2006**, *16*, 96.

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