Benzotrithiophene-Based Donor–Acceptor Copolymers with Distinct Supramolecular Organizations

Xin Guo, Sreenivasa Reddy Puniredd, Martin Baumgarten, Wojciech Pisula, and Klaus Müllen*

Max Planck Institute for Polymer Research, Ackermannweg 10, D-55128 Mainz, Germany

S *Supporting Information*

ABSTRACT: Two donor–acceptor copolymers, **P1** and **P2**, containing the novel donor component benzo[2,1-b:3,4-b′:5,6-c″]trithiophene were synthesized. Both polymers show small π-stacking distances (0.35 nm for **P1** and 0.37 nm for **P2**) due to the use of the disklike-shaped donor unit. However, they exhibit remarkable differences in supramolecular organization, film microstructure, and transistor performance. Indeed, **P1** reveals a distinct supramolecular organization in the bulk in comparison to conventional conjugated polymers, including **P2**. Interestingly, no charge carrier transport was observed for **P1** in field-effect transistors, while **P2** exhibited a hole mobility of up to 0.04 cm^2 V^{-1} s^{-1}. This variation in device behavior is attributed to the evidently different degree of curvature in the polymer backbone induced by the introduction of two additional thiophene units in **P2**.
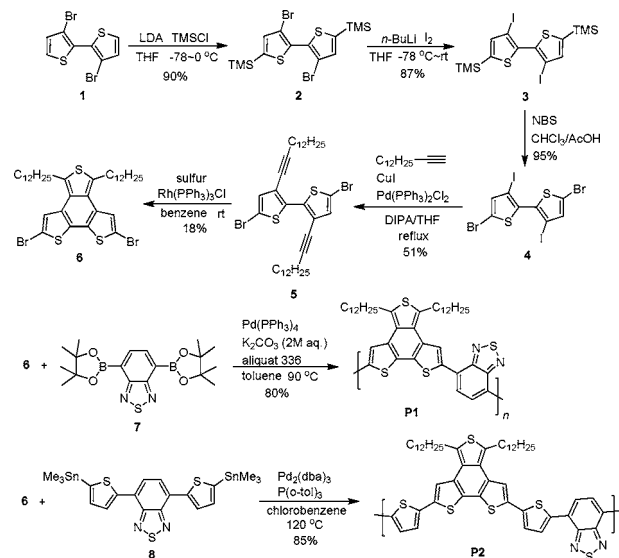
Donor–acceptor (D–A) copolymers have allowed for an effective strategy for tailoring the properties of conjugated polymers for applications in organic photovoltaics (OPVs) and organic field-effect transistors (OFETs).[1] The intra- and intermolecular interactions between donor and acceptor units can lead to self-assembly into ordered structures and strong π-stacking of polymer chains, both of which favor charge carrier transport. Typical donor units originate from electron-donating compounds such as benzo[1,2-b:4,5-b′]-dithiophene, cyclopenta[2,1-b:3,4-b′]dithiophene, dithieno-[3,2-b:2′,3′-d]silole, and dithieno[3,2-b:2′,3′-d]pyrrole, which have been copolymerized with strong acceptors such as 2,1,3-benzothiadiazole (BTZ) to yield high-performance organic semiconductors for organic electronics.[2] In addition to the application of these existing donors, it remains still a great challenge to explore D–A copolymers with new donor or acceptor structures to gain further understanding of the structure–property relationships and improve the performance of such polymers.

Benzotrithiophenes (**BTT**s) have emerged as a class of attractive building blocks for the design of various types of organic semiconductor materials in recent years.[3] Because of their electron-rich nature, **BTT**s would be expected to serve as donor units for the synthesis of narrow-band-gap D–A copolymers when combined with a suitable acceptor moiety. Furthermore, the coplanarity and extended π-conjugation of the **BTT** skeleton should promote intermolecular π-stacking, which would induce strong aggregation and enhanced packing in the solid state of the **BTT**-containing polymers. These features are particularly desirable for improving charge carrier transport in OFET devices. Three of seven **BTT** isomers, namely, benzo[1,2-b:3,4-b′:5,6-b″]trithiophene,[3b−f] benzo[1,2-c:3,4-c′:5,6-c″]trithiophene,[3g−i] and benzo[2,1-b:-3,4-b′:5,6-b″]-trithiophene,[3j−l] have been synthesized and studied intensively [see the structures in Figure S1 in the Supporting Information (SI)]. In particular, McCulloch and co-workers described a benzo[2,1-b:-3,4-b′:5,6-b″]trithiophene-containing D–A copolymer that showed potential for application in a bulk-heterojunction solar cell.[3l] However, the D–A copolymers containing other **BTT** isomers have not been synthesized to date, nor have their supramolecular organization and charge carrier transporting properties in particular been investigated.

Herein we report the synthesis of two new D–A copolymers, **P1** and **P2** (Scheme 1), containing a benzo[2,1-b:3,4-b′:5,6-

Scheme 1. Synthesis of Monomer 6 and BTT-Based D–A Copolymers P1 and P2

c″]trithiophene unit as a donor moiety. This donor unit possesses a higher HOMO level than all of the other **BTT** isomers and is a potential donor component for D–A copolymers, as described in our recent work.[4] It is worth noting that the dodecyl chains introduced at the 4- and 6-positions of this **BTT** donor for solubility lie almost in the same

Table 1. Properties of Copolymers P1 and P2

polymer	$M_n/M_w{}^a$	λ_{max}^{abs} (nm)			CV^e			OFET	
		soln^b	ε^c	film^d	E_{HOMO} (eV)	E_{LUMO} (eV)	E_g^{ec} (eV)	$\mu_{sat,h}$ (cm^2 V^{-1} s^{-1})^f	$I_{on}/I_{off}{}^g$
P1	19.5/38.6	547	11400	570	−5.42	−3.60	1.82	n.a.	n.a.
P2	31.0/95.2	645	33200	645, 705	−5.36	−3.45	1.91	0.04	∼10^4

^{a}In kg/mol, determined by GPC using polystyrene standards. ^{b}Measured in chlorobenzene solutions (1×10^{-5} M with respect to the repeating unit). ^{c}In M^{-1} cm^{-1} (per repeating unit), measured at λ_{max}^{abs} in solution. ^{d}Drop-cast from chlorobenzene solutions (5 mg/mL). ^{e}The energy levels and the electrochemical band gaps (E_g^{ec}) were determined by cyclic voltammetry (CV) measurements (for details, see the SI). ^{f}Maximum values of the hole mobility after annealing at 200 °C for 1 h. ^{g}Current on/off ratios.

plane as the conjugated core and stretch out along an angle of ca. 55° with respect to the C_2 symmetry axis, as shown in the single-crystal structure of the alkyl-substituted **BTT**.[4] This nature of our **BTT** donor is believed to make the alkyl chains of the corresponding polymers be located in the same plane with the polymer backbone and therefore to facilitate the $\pi-\pi$ interactions between the polymer chains much more than in other polymers with alkyl chains out of the main chains. As we have found, both copolymers show small π-stacking distances (0.35 nm for **P1** and 0.37 nm for **P2**). On the other hand, proceeding from **P1** to **P2** by inserting two thiophene units into the polymer backbone of **P2** significantly influences the chain conformation, the supermolecular organization, the film microstructure, and thus the charge carrier transport. This provides a deeper understanding of the structure−property relationships of **BTT**-based D−A copolymers.

The synthesis of dibrominated **BTT** monomer **6** with two dodecyl side chains is depicted in Scheme 1. Starting from 3,3′-dibromo-2,2′-bithiophene (**1**),[5] the important intermediate 5,5′-dibromo-3,3′-diiodo-2,2′-bithiophene (**4**) was prepared in an overall yield of 74% by protecting first the α-positions of **1** with trimethylsilyl groups to give **2**, then changing the bromo substituents at the 3- and 3′-positions to iodo substituents to give **3**, and finally performing the dibromination at the α-positions. Compound **4** was coupled with 1-tetradecyne in a yield of 51% by selective Sonogashira reaction to introduce the solubilizing alkyl chains. This precursor **5** was then treated with tris(triphenylphosphine)rhodium(I) chloride to produce the rhodium complex as an intermediate. The latter was converted into **6** by adding sulfur powder to form the third thiophene ring. Monomer **6** was carefully purified by column chromatography and recrystallization to ensure sufficient purity for polymerization. It is noteworthy that in this route, the dibromination is executed before the formation of the third thiophene ring. This avoids the need for direct dibromination of the alkyl-substituted **BTT** (an extremely electron-rich system) under harsh conditions as well as the complex purification process to remove monobromination impurities.

Polymer **P1** was synthesized by Suzuki coupling between monomer **6** and 4,7-bis(boronic acid pinacol ester)-2,1,3-benzothiadiazole (**7**),[2b] whereas polymer **P2** was synthesized by Stille coupling between monomer **6** and 4,7-bis(2-trimethylstannylthien-5-yl)-2,1,3-benzothiadiazole (**8**).[6] **P1** was obtained as a deep-purple solid with good solubility in common organic solvents such as tetrahydrofuran (THF), chloroform, and chlorobenzene. A number-average molecular weight (M_n) of 19.5 kg/mol with a polydispersity index (PDI) of 1.98 (Table 1) was measured by gel-permeation chromatography (GPC) in THF. In contrast, **P2** was a less soluble deep-blue solid that became soluble only in chlorinated solvents such as chlorobenzene and o-dichlorobenzene upon heating above 100 °C. The M_n of 31.0 kg/mol with a PDI of 3.07 was

measured by GPC in trichlorobenzene (TCB) at 135 °C. The higher molecular weight of **P2** relative to **P1** is a main reason for the poorer solubility of **P2**.

Quantum-chemical calculations (B3LYP/6-31G*) were performed to predict the minimum-energy conformations of the trimers of **P1** and **P2**. As illustrated in Figure 1, the alkyl
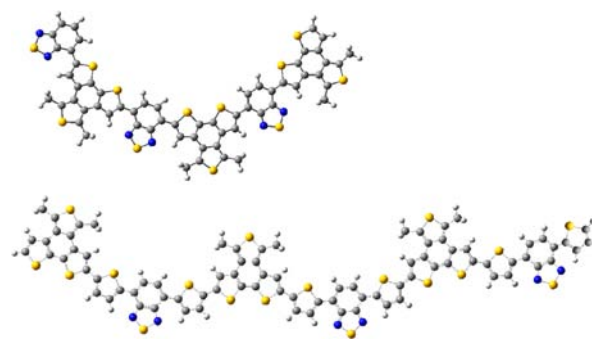

Figure 1. Minimum-energy conformations of methyl-substituted trimers of (top) **P1** and (bottom) **P2** optimized at the B3LYP/6-31G* level.

chains of both polymers turn toward the same side of the backbone, but the backbone of **P1** is more curved than that of **P2**, which should also somewhat contribute to the better solubility of the former. More importantly, the different degree of curvature in the polymer backbones also influences the supermolecular organization, the film microstructure, and the charge carrier mobility of the two polymers.

Both polymers display broad absorption bands, with maxima in solution at 547 and 645 nm for **P1** and **P2**, respectively (Figure S3 and Table 1). This can be attributed to the strong D−A interaction, indicating that **BTT** is a strong donor unit. The red shift of almost 100 nm in going from **P1** to **P2** is believed to originate from the insertion of the two thiophene units, which provide the extended conjugation and weaker electron-donating nature. In the solid state, the absorption maximum of **P1** is red-shifted and broadened, which can be ascribed to solid-state packing effects, whereas for **P2**, a strong shoulder at 705 nm appears, clearly suggesting the formation of a more aggregated conformation in the thin film. The optical band gaps estimated from the onset of the thin-film absorptions are 1.35 eV for **P1** and 1.53 eV for **P2**. In comparison with the optical band gap of the D−A copolymer derived from another **BTT** isomer, benzo[2,1-b:3,4-b':5,6-b'']trithiophene, and BTZ (1.75 eV),[31] **P1** shows a narrower optical band gap, indicating again the stronger electron-donating nature of our **BTT** donor unit.

The supramolecular organization of each polymer in the bulk was investigated by two-dimensional (2D) wide-angle X-ray scattering (WAXS). For this study, each polymer was extruded

into macroscopically aligned fibers that were mounted vertically toward the 2D detector. Polymer **P2** showed a characteristic 2D pattern for a conjugated polymer (Figure 2c).[3d] The small-
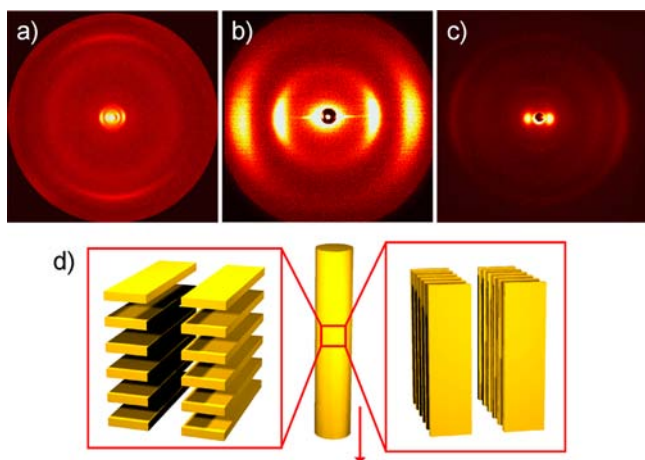

Figure 2. (a) WAXS and (b) SAXS patterns for **P1**. (c) WAXS pattern for **P2**. (d) Schematic illustrations of the polymer arrangements in the extruded fibers of (left) **P1** and (right) **P2**. The red arrow indicates the extrusion/orientation direction.

angle X-ray scattering (SAXS) reflections in the equatorial plane of the pattern are attributed to a chain-to-chain distance of 2.7 nm between the lamellar structures, which are aligned along the extrusion direction of the fiber (Figure 2d). The weak equatorial WAXS intensities are assigned to the π-stacking distance of 0.37 nm for the backbones within the lamellar stacks. Interestingly, the organization of **P1** in the fiber sample differs significantly. First, the chain-to-chain distance of 4.36 nm derived from the SAXS pattern (Figure 2b) is considerably larger than in **P2**, which is attributed to the more pronounced degree of curvature in the backbone of **P1**, as shown in Figure 1. The corresponding reflections are located on the equatorial plane, while surprisingly, the scattering intensities related to the π-stacking distance of 0.35 nm appear in the wide-angle meridional (Figure 2a). Therefore, the polymer chains are arranged perpendicular to the alignment direction of the sample (Figure 2d). This is very untypical for conjugated polymers with a high molecular aspect ratio, which is usually the driving force for alignment of the polymer backbone along the extrusion direction of the sample. Polymer **P1** shows an organization identical to that of discotic columnar systems, in which the π-stacking direction as well as the stacks characteristically are oriented along the alignment direction.[7] Therefore, the behavior of **P1** can be explained by the disklike shape of the **BTT** units, which pack on top of each other to form a columnar stack. However, in such a packing motif, the subunits of the same electron affinity have to pack on top of each other, and no D−A interactions between the conjugated backbones occur. We recently found such a D−D/A−A packing for a benzothiadiazole−cyclopentadithiophene polymer.[3f] In the case of **P2**, the molecular aspect ratio of the repeating unit is increased by extending the length by the two additional thiophene units within the backbone. This leads to the orientation of the polymer chains more parallel to the fiber axis.

Bottom-contact, bottom-gate FETs based on the polymers were prepared by drop-casting dichlorobenzene solutions with polymer concentrations of 2 mg/mL on hexamethyldisilazane-modified SiO_2 wafers at 100 °C. After solvent evaporation, the

films were additionally annealed at 200 °C for 1 h. Surprisingly, **P1** did not show any device performance even though good packing was found for the polymer in the bulk, with a π-stacking distance of only 0.35 nm. On the other hand, **P2** exhibited typical p-type transistor behavior with hole mobilities of up to 0.04 cm^2 V^{-1} s^{-1} and an average value of 0.01 cm^2 V^{-1} s^{-1} (Figure 3). The device performance was slightly improved
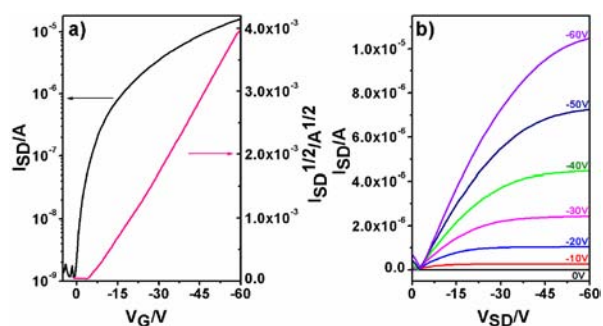

Figure 3. Characteristics of an FET of **P2**: (a) transfer curves at a source/drain bias (V_{SD}) of −60 V and (b) output characteristics at various gate biases (V_G).

by modification of the source and drain electrodes with benzenethiol, leading to an average mobility of 0.025 cm^2 V^{-1} s^{-1} for **P2** (Figure S6). In contrast to this, under these device conditions, polymer **P1** still lacked any field-effect response. To understand the difference in performance of the polymers, grazing-incidence WAXS (GIWAXS) measurements on the films were performed (Figure 4). Interestingly, the thin layer of
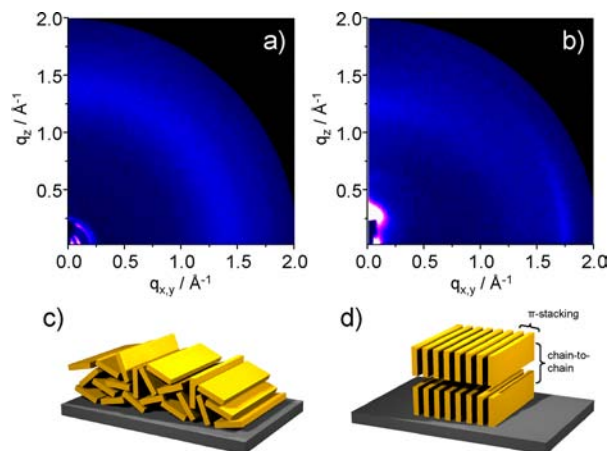

Figure 4. (a, b) GIWAXS patterns for thin films of (a) **P1** and (b) **P2** and (c, d) schematic illustrations of the polymer organization on the surface for (c) **P1** and (d) **P2** within one single domain.

P1 was highly disordered (even amorphous), as indicated by the lack of reflections (Figure 4a,c). It seems that solution casting of **P1** on a surface leads to high disorder, which inhibits charge carrier transport in the transistor. This is in agreement with our previous findings suggesting that polymers with a high degree of backbone curvature perform poorly in FET devices.[8] In contrast to this, **P2** was well-ordered in the film and arranged edge-on toward the surface, as assigned from the out-of-plane reflections for the chain-to-chain distance and the in-plane ones for the π-stacking correlation (Figure 4b,d). Equatorial integration along $q_z = 0$ gave a π-stacking distance of 0.36 nm for **P2** in the thin film, which is slightly smaller than that in

the bulk (Figure S7). Apart from the pronounced amorphous halo at 1.47 Å, which is related to the disordered alkyl side chains, the integration plot for **P1** also exhibits a weak shoulder at 1.72 Å (Figure S7). This peak is an indication of some π-stacking correlations between the backbones and thus minor ordering of **P1**.

In conclusion, we have presented two novel benzo[2,1-*b*:3,4-*b'*:5,6-*c''*]trithiophene-based D−A copolymers, **P1** and **P2**, that exhibit interesting supermolecular organization and promising OFET performance. The structural modification of **P1** by insertion of two thiophene units into the polymer backbone to give **P2** plays an important role in determining the chain conformation, the supermolecular organization, the film microstructure, and thus the charge carrier transport. Polymer **P1** did not show any field-effect response because of the pronounced disorder in the thin film, even though a distinctive supermolecular structure was observed with a good π-stacking distance of only 0.35 nm in the bulk. In stark contrast, polymer **P2** exhibited a hole mobility of 0.04 cm^2 V^{-1} s^{-1}, which is in agreement with the well-ordered film and the organization into lamellar structures with a π-stacking distance of 0.37 nm. It is expected that the charge carrier mobility can be further improved by increasing the molecular weight of the polymers or further optimization of the deposition techniques.[9] To the best of our knowledge, this is the first report of **BTT**-based D−A copolymers that exhibit distinctive supramolecular organization and reasonable field-effect behavior.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Synthetic details and characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

muellen@mpip-mainz.mpg.de

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

■ REFERENCES

(1) (a) Günes, S.; Neugebauer, H.; Sariciftci, N. S. *Chem. Rev.* **2007**, *107*, 1324. (b) Zhang, L.; Di, C.-a.; Yu, G.; Liu, Y. *J. Mater. Chem.* **2010**, *20*, 7059.

(2) (a) Hou, J.; Park, M.-H.; Zhang, S.; Yao, Y.; Chen, L.-M.; Li, J.-H.; Yang, Y. *Macromolecules* **2008**, *41*, 6012. (b) Zhang, M.; Tsao, H. N.; Pisula, W.; Yang, C.; Mishra, A. K.; Müllen, K. *J. Am. Chem. Soc.* **2007**, *129*, 3472. (c) Tsao, H. N.; Cho, D. M.; Park, I.; Hansen, M. R.; Mavrinskiy, A.; Yoon, D. Y.; Graf, R.; Pisula, W.; Spiess, H. W.; Müllen, K. *J. Am. Chem. Soc.* **2011**, *133*, 2605. (d) Beaujuge, P. M.; Pisula, W.; Tsao, H. N.; Ellinger, S.; Müllen, K.; Reynolds, J. R. *J. Am. Chem. Soc.* **2009**, *131*, 7514. (e) Hou, J.; Chen, H.-Y.; Zhang, S.; Li, G.; Yang, Y. *J. Am. Chem. Soc.* **2008**, *130*, 16144. (f) Zhou, E.; Nakamura, M.; Nishizawa, T.; Zhang, Y.; Wei, Q.; Tajima, K.; Yang, C.; Hashimoto, K. *Macromolecules* **2008**, *41*, 8302.

(3) (a) Jayasuriya, N.; Kagan, J. *J. Org. Chem.* **1989**, *54*, 4203. (b) Taerum, T.; Lukoyanova, O.; Wylie, R. G.; Perepichka, D. F. *Org. Lett.* **2009**, *11*, 3230. (c) Nicolas, Y.; Blanchard, P.; Levillain, E.; Allain, M.; Mercier, N.; Roncali, J. *Org. Lett.* **2004**, *6*, 273. (d) Proetzsch, R.; Bieniek, D.; Korte, F. *Tetrahedron Lett.* **1972**, *13*, 543. (e) Kashiki, T.; Kohara, M.; Osaka, I.; Miyazaki, E.; Takimiya, K. *J. Org. Chem.* **2011**, *76*, 4061. (f) Kashiki, T.; Shinamura, S.; Kohara, M.; Miyazaki, E.; Takimiya, K.; Ikeda, M.; Kuwabara, H. *Org. Lett.* **2009**, *11*, 2473. (g) Imamura, K.; Takimiya, K.; Aso, Y.; Otsubo, T. *Chem. Commun.* **1999**, 1859. (h) Patra, A.; Wijsboom, Y. H.; Shimon, L. J. W.; Bendikov, M. *Angew. Chem., Int. Ed.* **2007**, *46*, 8814. (i) Hart, H.; Sasaoka, M. *J. Am. Chem. Soc.* **1978**, *100*, 4326. (j) Nielsen, C. B.; Fraser, J. M.; Schroeder, B. C.; Du, J.; White, A. J. P.; Zhang, W.; McCulloch, I. *Org. Lett.* **2011**, *13*, 2414. (k) Schroeder, B. C.; Nielsen, C. B.; Kim, Y. J.; Smith, J.; Huang, Z.; Durrant, J.; Watkins, S. E.; Song, K.; Anthopoulos, T. D.; McCulloch, I. *Chem. Mater.* **2011**, *23*, 4025. (l) Nielsen, C. B.; Schroeder, B. C.; Hadipour, A.; Rand, B. P.; Watkins, S. E.; McCulloch, I. *J. Mater. Chem.* **2011**, *21*, 17642.

(4) Guo, X.; Wang, S.; Enkelmann, V.; Baumgarten, M.; Müllen, K. *Org. Lett.* **2011**, *13*, 6062.

(5) Lu, G.; Usta, H.; Risko, C.; Wang, L.; Facchetti, A.; Ratner, M. A.; Marks, T. J. *J. Am. Chem. Soc.* **2008**, *130*, 7670.

(6) Ong, K.-H.; Lim, S.-L.; Tan, H.-S.; Wong, H.-K.; Li, J.; Ma, Z.; Moh, L. C. H.; Lim, S.-H.; de Mello, J. C.; Chen, Z.-K. *Adv. Mater.* **2011**, *23*, 1409.

(7) (a) Pisula, W.; Feng, X.; Müllen, K. *Adv. Mater.* **2010**, *22*, 3634. (b) Laschat, S.; Baro, A.; Steinke, N.; Giesselmann, F.; Hägele, C.; Scalia, G.; Judele, R.; Kapatsina, E.; Sauer, S.; Schreivogel, A.; Tosoni, M. *Angew. Chem., Int. Ed.* **2007**, *46*, 4832.

(8) Rieger, R.; Beckmann, D.; Pisula, W.; Steffen, W.; Kastler, M.; Müllen, K. *Adv. Mater.* **2010**, *22*, 83.

(9) Tsao, H. N.; Müllen, K. *Chem. Soc. Rev.* **2010**, *39*, 2372.