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Synthesis and Thin-Film Transistor Performance of Poly(4,8-didodecylbenzo[1,2-b:4,5-b′]dithiophene)

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The synthesis of novel regioregular poly(4,8-didodecylbenzo[1,2-b:4,5-b′]dithiophene) and its use as a semiconductor in organic thin-film transistors (OTFTs) are described. The polymer was prepared from 2,6-dibromo-4,8-didodecylbenzo[1,2-b:4,5-b′]dithiophene by a dehalogenative coupling polymerization. A field-effect mobility of ~0.012 cm^2 V^{-1} s^{-1} and a current on/off ratio of ~2.5 × 10^5 have been obtained with OTFTs using this polymer semiconductor.

Introduction

The promise of fabricating low-cost organic electronics using liquid patterning and deposition techniques has propelled phenomenal research interest in organic thin-film transistors (OTFTs).[1−10] One of critical active components of OTFTs is the semiconductor which essentially dictates the transistor performance. Polymer semiconductors have received special attention for OTFTs by virtue of their solution processablility and good film-forming property—the former renders them compatible with inexpensive common liquid deposition techniques (e.g., spin coating, inkjet printing, etc.)[3−6] while the latter renders them compatible with plastic substrates to enable flexible electronic design.[7−10] However, most of the current polymer semiconductors suffer from lack of air stability and/or low mobility, thus posing significant challenges in their use for practical applications. Only a few polymer semiconductors offer functionally useful field-effect transistor (FET) mobility of ≥0.01 cm^2 V^{-1} s^{-1}. Among them, regioregular poly(3-hexythiphene) (P3HT) was shown to provide a mobility of ~0.1 cm^2 V^{-1} s^{-1} when fabricated in an inert atmosphere.[11] It was found that for P3HT, the higher the degree of its head-to-tail regiochemistry, the higher the mobility. However, the mobility of P3HT was significantly lower when device fabrication was carried in ambient conditions. A more stable polymer semiconductor, poly(9,9′-*n*-dioctylfluorene-*alt*-bithiophene) (F8T2), exhibited mobility ≥0.01 cm^2 V^{-1} s^{-1} when the polymer was properly aligned in the liquid-crystalline phase.[12] A higher mobility polymer semiconductor is regioregular poly(3,3‴-dialkyl-quaterthiophene) (PQT), which gave a mobility of 0.1−0.2 cm^2 V^{-1} s^{-1} even when the OTFTs were fabricated in air.[13] Since then, several structural analogues of PQT[14−17] and F8T2[18,19] with high mobility were reported. Analysis of the FET performance of polymer semiconductors shows that polymer regioregularity is crucial to establishing high crystal orders which are necessary for achieving high mobility.[8,20−22] In this paper, we report the

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(1) See the special issue on organic electronics: Jenekhe, S. A. *Chem. Mater.* **2004**, *16*, 4381−4846.
(2) Dimitrakopoulos, C. D.; Malenfant, P. R. L. *Adv. Mater.* **2002**, *14*, 99−117.
(3) Sirringhaus, H. *Adv. Mater.* **2005**, *17*, 2411−2425.
(4) Garnier, F.; Hajlaoui, R.; Yassar, A.; Srivastava, P. *Science* **1994**, *265*, 1684−1686.
(5) Bao, Z. *Adv. Mater.* **2000**, *12*, 227−230.
(6) Gelinck, G. H.; Huitema, H. E. A.; van Veenendaal, E.; Cantatore, E.; Schrijnemakers, L.; van der Putten, J. B. P. H.; Geuns, T. C. T.; Beenhakkers, M.; Giesbers, J. B.; Huisman, B.-H.; Meijer, E. J.; Benito, E. M.; Touwslager, F. J.; Marsman, A. W.; van Rens, B. J. E.; de Leeuw, D. M. *Nat. Mater.* **2004**, *3*, 106−110.
(7) Sirringhaus, H.; Tessler, N.; Friend, R. H. *Science* **1998**, *280*, 1741−1744.
(8) Sirringhaus, H.; Brown, P. J.; Friend, R. H.; Nielen, M. M.; Bechgaard, K.; Langeveld-Voss, B. M. W.; Spiering, A. J. H.; Janssen, R. A. J.; Meijer, E. W.; Herwig, P.; de Leeuw, D. M. *Nature* **1999**, *401*, 685−688.
(9) Huitena, H. E. A.; Gelinck, G. H.; van der Putter, J. B. P. H.; Kuijk, K. E.; Hart, C. M.; Cantatore, E.; Herwig, P. T.; van Breemen, A. J. J. M.; de Leeuw, D. M. *Nature* **2001**, *414*, 599.
(10) Sirringhaus, H.; Kawase, T.; Friend, R. H.; Shimoda, T.; Inbasekaran, M.; Wu, W.; Woo, E. P. *Science* **2000**, *290*, 2123−2126.
(11) Bao, Z.; Dodabalapur, A.; Lovinger, A. J. *Appl. Phys. Lett.* **1996**, *69*, 4108−4110.
(12) Sirringhaus, H.; Wilson R. J.; Friend, R. H.; Inbasekaran, M.; Wu, W.; Woo, E. P.; Grell, M.; Bradley, D. D. C. *Appl. Phys. Lett.* **2000**, *77*, 406−408.
(13) Ong, B. S.; Wu, Y.; Liu, P.; Gardner, S. *J. Am. Chem. Soc* **2004**, *126*, 3378−3379.
(14) Heeney, M.; Bailey, C.; Genevicius, K.; Shkunov, M.; Sparrowe, D.; Tierney, S.; McCulloch, I. *J. Am. Chem. Soc.* **2005**, *127*, 1078−1079.
(15) Wu, Y.; Liu, P.; Gardner, S.; Ong, B. S. *Chem. Mater.* **2005**, *17*, 221−223.
(16) Murphy, A. R.; Liu, J.; Luscombe, C.; Kavulak, D.; Frechet, J. M. J.; Kline, R. J.; McGehee, M. D. *Chem. Mater.* **2005**, *17*, 4892−4899.
(17) McCulloch, I.; Bailey, C.; Giles, M.; Heeney, M.; Love, I.; Shkunov, M.; Sparrowe, D.; Tierney, S. *Chem. Mater.* **2005**, *17*, 1381−1385.
(18) Lim, E.; Jung, B.-J.; Lee, J.; Shim, H.-K.; Lee, J.-I.; Yang, Y. S.; Do, L.-M. *Macromolecules* **2005**, *38*, 4531−4535.
(19) Yasuda, T.; Fujita, K.; Tsutsui, T.; Geng, Y.; Culligan, S. W.; Chen, S. H. *Chem. Mater.* **2005**, *17*, 264−268.
(20) Ong, B. S.; Wu, Y.; Liu, P. *Proc. IEEE* **2005**, *93*, 1412−1419.
(21) Ong, B. S.; Wu, Y.; Liu, P.; Gardner, S. *Adv. Mater.* **2005**, *17*, 1141−1144.
(22) Zhao, N.; Botton, G. A.; Zhu, S.; Duft, A.; Ong, B. S.; Wu, Y.; Liu, P. *Macromolecules* **2004**, *37*, 8307−8312.

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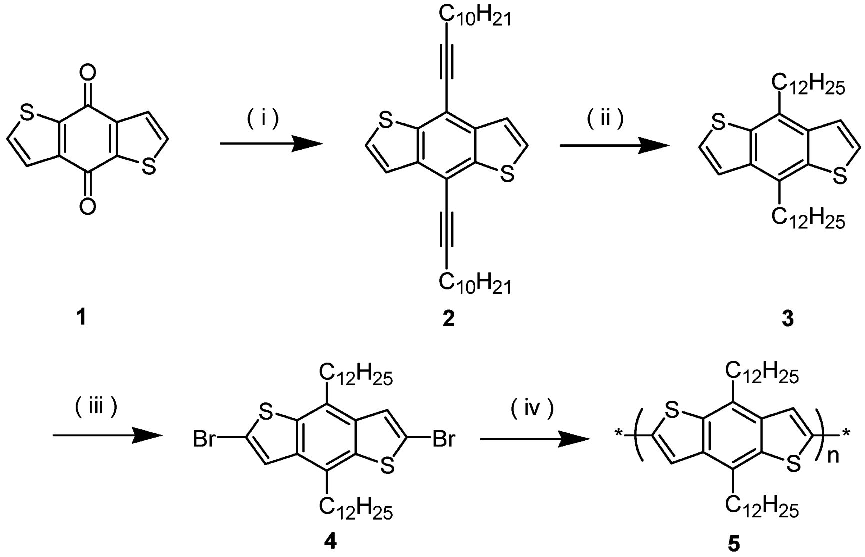
Scheme 1. Synthesis of Poly(4,8-didodecylbenzo[1,2-b:4,5-b′]dithiophene) 5



(i): $C_{10}H_{21}$—≡—H + iso-PrMgCl; $SnCl_2$/HCl (ii): NBS/AcOH/CH_2Cl_2

(iii): H_2 / Pd/THF (iv): Zn/$NiCl_2$/PPh_3/2,2'-Dipyridil/DMAc/Toluene

synthesis of a novel class of regioregular polymer semiconductors, poly(benzodithiophene)s, which are obtainable by direct polymerization of their corresponding benzodithiophene monomer and present no regiochemical complications generally associated with the use of polymer semiconductors for OTFT fabrication.

Benzodithiophenes have been used as vacuum-evaporated small-molecule semiconductors in OTFTs.[23−26] The parent structure has a near-planar molecular plane which would be conducive to establishing a close molecular $\pi-\pi$ stacking order for efficient charge carrier transport to afford high FET mobility.[23,24] However, these are small molecular semiconductors which generally form brittle thin films and may not be suitable for use in fabricating flexible integrated circuits. On the other hand, we believe that polymers based on the benzodithiophene building blocks, which have rarely been investigated,[27,28] might serve as interesting semiconductors for flexible OTFT circuits on plastic substrates. We selected poly(4,8-didodecylbenzo[1,2-b:4,5-b′]dithiophene) as our target polymer semiconductor for its solution processability from the presence of a relatively long alkyl chain and self-assembly capability from the regioregular placement of alkyl chains along the polymer backbone. Regioregularity of polymer side chains would help promote intermolecular side chain interdigitation as previously demonstrated in PQT.[13,20]

Results and Discussion

The synthesis of poly(4,8-didodecylbenzo[1,2-b:4,5-b′]-dithiophene) **5** is schematically presented in Scheme 1. Alkynylmagnesium chloride, as generated in situ from an alkyne and isopropylmagnesium chloride, was allowed to react with benzo[1,2-b:4,5-b′]dithiophene-4,8-dione **1** at 50 °C, followed by reduction with $SnCl_2$ under acidic conditions to give the corresponding dialkynyl-substituted intermediate **2** in about 65% yield. Hydrogenation of **2** was readily accomplished with hydrogen gas in the presence of a catalytic amount of Pd/C, giving 4,8-didodecylbenzo[1,2-b:4,5-b′]-dithiophene **3** in 60% yield. The latter was converted to the dibromo derivative **4** in 50% yield with *N*-bromosuccinimide (NBS) and purified by recrystallization from acetone. Subsequent dehalogenative polymerization using the catalyst system, zinc/triphenylphosphine/2,2′-dipyridil, anhydrous nickel(II) chloride, afforded poly(4,8-didodecylbenzo-[1,2-b:4,5-b′]dithiophene) **5**. The undesired oligomer materials and residual catalyst were removed by Soxhlet extraction from the crude product with heptane, and pure poly(4,8-didodecylbenzo[1,2-b:4,5-b′]dithiophene) **5** was isolated by extraction with chlorobenzene (46% yield). MALDI-TOF measurement of the final polymer product gave a molecular weight of about 2100.

The X-ray single-crystal structure of the monomer of poly-(4,8-didodecylbenzo[1,2-b:4,5-b′]dithiophene), **3**, is presented in Figure 1. The X-ray data showed a close face-to-face $\pi-\pi$ stacking of monomer molecules in the direction normal to molecular plane (Figure 1 in the Supporting Information) and extensive intermolecular side chain interdigitation in the direction of the molecular plane with an interchain distance of ~21.1 Å. This interchain distance was very close to that of the molecular packing in a solution-cast thin film of parent poly(4,8-didodecylbenzo[1,2-b:4,5-b′]dithiophene **5** as determined by small angle XRD [$d = 23.9$ Å at (100), 11.8 Å at (200), and 7.9 Å at (300)] (Figure 2). These results suggested that the polymer also assumed a similar molecular packing as that of its monomer. The clear appearance of three orders of XRD peaks indicated that the solution-cast film of **5** was highly crystalline. On the basis

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(23) Katz, H. E.; Bao, Z.; Gilat, S. L. *Acc. Chem. Res.* **2001**, *34*, 359−369.
(24) Laquidanum, J. G.; Katz, H. E.; Lovinger, A. J.; Dodabalapur, A. *Adv. Mater.* **1997**, *9*, 36−37.
(25) Katz, H. E. *J. Mater. Chem.* **1997**, *7*, 369−376.
(26) Laquindanum, J. G.; Katz, H. E.; Lovinger, A. J. *J. Am. Chem. Soc.* **1998**, *120*, 664−672.
(27) Shiraishi, K.; Yamamoto, T. *Synth. Met.* **2002**, *130*, 139−147.
(28) Pomerantz, M.; Wang, J. P.; Seong, S.; Starkey, K. P.; Nguyen, L.; Marynick, D. S. *Macromolecules* **1994**, *27*, 7478−7485.

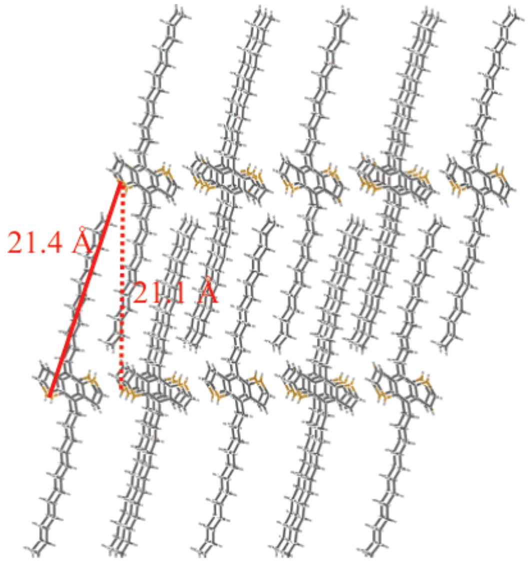

Figure 1. Crystal packing of 4,8-didodecylbenzo[1,2-b:4,5-b′]dithiophene **3** showing the $\pi-\pi$ stacking and intermolecular side chain interdigitation.

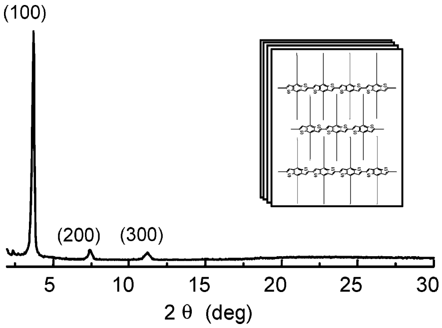

Figure 2. XRD of poly(4,8-didodecylbenzo[1,2-b:4,5-b′]dithiophene) **5** showing the interlayer diffraction peaks at 2θ: 3.72(100), 7.44(200), and 11.20(300). Inset: schematic representation of the lamellar ordering of **5**.

of single-crystal structure and thin-film XRD data, it was reasonable to envisage that poly(4,8-didodecylbenzo[1,2-b:4,5-b′]dithiophene **5** exhibited a high molecular order in its solution-cast thin film as schematically presented by the inset in Figure 2.

The thermal properties of **5** were evaluated by differential scanning calorimetry (DCS) and thermogravimetric analysis (TGA). The DSC of **5** (Figure 3A) showed in the first heating cycle a sharp peak at ~140 °C attributable to the melting of side chains and a broad peak at ~280 °C due to the melting of polymer backbones. The high rigidity of the backbone of **5** was responsible for the observed high melting points. On cooling, only a sharp backbone crystallization peak at ~260 °C appeared, while no thermal transition due to side chain crystallization was observed. The lack of side chain crystallization was attributed to the low molecular weight of the polymer. Good thermal stability of this rigid polymer was manifested in its TGA profile (Figure 3B) with an onset decomposition temperature of ~450 °C, demonstrating its thermal stability approaching that of triphenylamine.[29]

The optical absorption spectral properties of monomer **3** and polymer **5** and photoluminescence (PL) emission spectra of **5** are shown in Figure 4. The monomer **3** displayed typical acene-like absorptions with a very strong $\pi \rightarrow \pi^*$ (HOMO to LUMO) transition at $\lambda_{\max} = 347$ nm. This is significantly blue shifted compared to that of anthracene at $\lambda_{\max} = 376$ nm, suggesting a lesser extent of π-delocalization. As expected, **5** exhibited significant red shifts in absorption relative to that of its monomer **3** as a result of extended π-conjugation. In hot chlorobenzene solution, the absorptions appeared at $\lambda_{\max} = 446$ and 469 nm, a red shift of ~120 nm from those of **3**. When the solution was cooled to room temperature, a shoulder appeared at $\lambda_{\max} = 481$ nm, which was attributable to molecular aggregation.[15,30] In the solid state as a thin film, **5** showed a broad absorption with weak

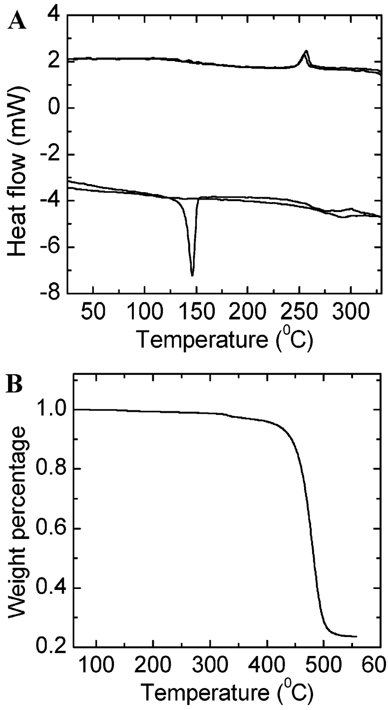

Figure 3. DSC (A) and TGA (B) of poly(4,8-didodecylbenzo[1,2-b:4,5-b′]dithiophene) **5** at a heating rate of 10 °C/min in nitrogen.

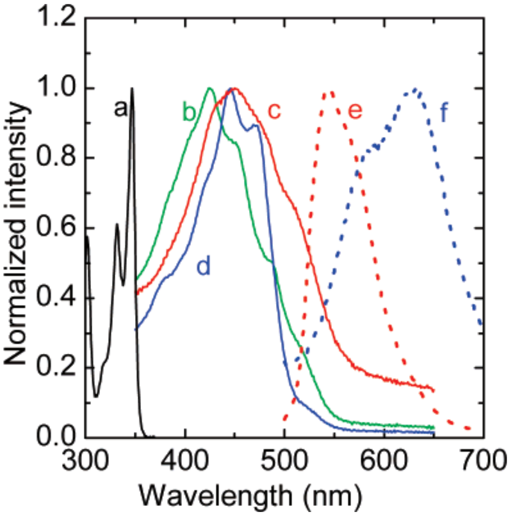

Figure 4. Spectral properties of 4,8-didodecylbenzo[1,2-b:4,5-b′]dithiophene **3** and poly(4,8-didodecylbenzo[1,2-b:4,5-b′]dithiophene) **5**: (a) absorptions of **3** in methylene chloride (black solid line); (b) absorptions of **5** in chlorobenzene at 25 °C (green solid line); (c) absorptions of a solution-cast thin film of **5** (red solid line); (d) absorptions of **5** in chlorobenzene at 110 °C (blue solid line); (e) photoluminescence of **5** in chlorobenzene at 25 °C (red dotted line); (f) photoluminescence of **5** in thin film (blue dotted line).

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(29) Sonntag, M.; Kreger, K.; Hanft, D.; Strohriegl, P. *Chem. Mater.* **2005**, *17*, 3031−3039.

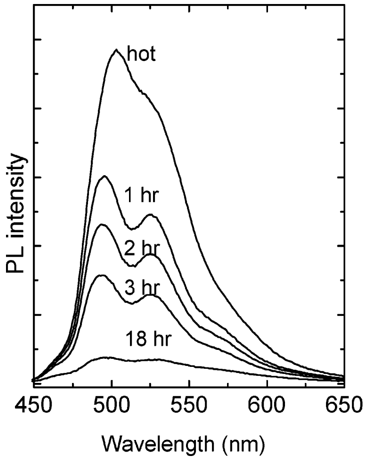

Figure 5. Photoluminescence behaviors of poly(4,8-didodecylbenzo[1,2-b:4,5-b′]dithiophene **5** in dichlorobenzene solution, showing the reduction of photoluminescence intensity with time as the hot solution (110 °C) was cooled to room temperature.

vibronic fine structure, but its solid-state photoluminescence emission peak at $\lambda_{max} = 633$ nm was significantly red shifted from that of its solution ($\lambda_{max} = 545$ nm), indicative of a higher molecular assembly in the solid state. The reduction in photoluminescence emissions of **5** in solution with decreasing temperature (Figure 5) was a manifestation of molecular self-assembly of **5** as the temperature was lowered, leading to quenching of its photoluminescence.

To characterize the FET performance, bottom-gate top-contact OTFT test devices with **5** as the semiconductor were built on a silicon wafer in the following manner. The devices were prepared in ambient conditions without taking any special precautions to exclude air, moisture, and ambient light. A heavily n-doped silicon wafer with a 200 nm thermal silicon dioxide (SiO_2) was used as the substrate/gate electrode, with the top SiO_2 layer serving as the gate dielectric. The SiO_2 surface was first cleaned with oxygen plasma and then modified with a self-assembled monolayer of octyltrichlorosilane (OTS-8).[15] The semiconductor layer was deposited on top of OTS-8-modified SiO_2 surface by spin coating a hot solution of **5** in chlorobenzene (0.5 wt %) at 1000 rpm for 30 s, vacuum-dried, and annealed at 140 °C for 10 min in vacuo. Subsequently, a series of gold source/drain electrode pairs were deposited by vacuum evaporation through a shadow mask with different channel length/width features, thus forming an array of OTFTs of various dimensions. The resulting OTFT devices were characterized using a Keithley SCS-4200 in a black metal box in air. The FET mobility of the OTFTs was extracted using the following equation in the saturation regime from the gate sweep:

$$I_D = \mu C_i (V_G - V_T)^2 (W/2L)$$

where I_D is the drain current, μ is the field-effect mobility, C_i is the capacitance per unit area of the gate dielectric layer (SiO_2, 200 nm, $C_i = 15$ nF/cm^2), and V_G and V_T are, respectively, the gate voltage and threshold voltage. V_T was derived from the relationship between the square root of I_D at the saturated regime and V_G by extrapolating the measured data to $I_D = 0$. W and L are, respectively, channel width and length.

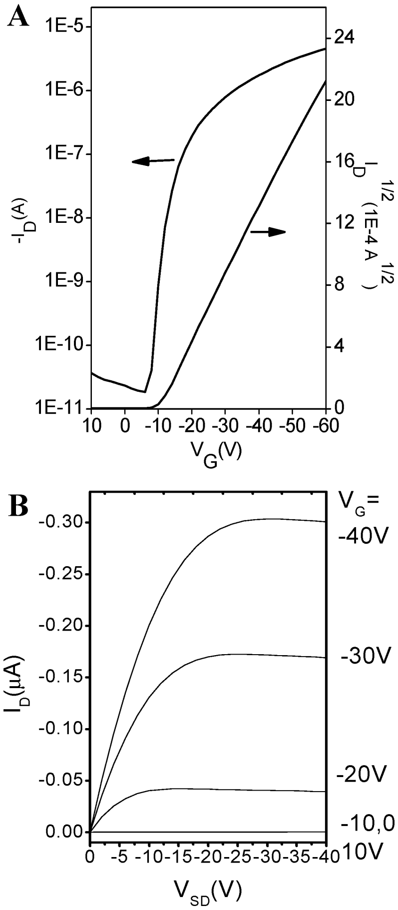

Figure 6. Transfer (A) and output (B) characteristics of an illustrative OTFT with poly(4,8-didodecylbenzo[1,2-b:4,5-b′]dithiophene) **5** as the semiconductor [channel length = 190 μm; channel width = 5000 μm; $V_{SD} = -60$ V in transfer (A)].

The OTFTs with **5** as the semiconductor exhibited a characteristic p-type FET performance as manifested in the transfer and output curves (Figure 6). The devices provided consistent FET behaviors which follow closely the conventional transistor models in both the linear and saturated regimes. The output curves displayed clear saturation with no observable contact resistance, with the extracted mobility from the saturated regimes being up to 1.2×10^{-2} cm^2 V^{-1} s^{-1} and the current on/off ratio of over 1.0×10^5. This mobility was an order of magnitude higher than that of the devices before annealing (to 9.0×10^{-4} cm^2 V^{-1} s^{-1}), suggesting that annealing might have improved semiconductor ordering and removed trapped oxygen leading to enhanced FET performance.[13,15] A slight negative turn-on voltage at −8 V was however observed. These results were among the best reported for solution-processed polymer OTFTs fabricated and evaluated without protection against exposure to ambient air, light, and moisture. We believe that the FET performance of this class of polymer semiconductors can be further improved through process and structural optimizations such as increased molecular weight.[31]

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(30) Balakrishnan, K.; Datar, A.; Oitker, R.; Chen, H.; Zuo, J.; Zang, L. *J. Am. Chem. Soc.* **2005**, *127*, 10496−10497.

(31) Kline, R. J.; McGehee, M. D.; Kadnikova, E. N.; Liu, J.; Frechet, J. M. J.; Toney, M. F. *Macromolecules* **2005**, *38*, 3312−3319.

In conclusion, we have shown that poly(4,8-didodecylbenzo[1,2-b:4,5-b′]dithiophene) **5**, obtained via dehalogenative coupling polymerization, is a solution processable polymer semiconductor which exhibits an ability to self-assemble into lamellar structural order upon deposition on a substrate under appropriate conditions. It has provided functionally desirable FET performance characteristics when used as a semiconductor in OTFTs.

Experimental Section

Materials and Instruments. All materials were purchased from Aldrich and used as received without purification. The NMR spectra were recorded at room temperature using a Bruker DPX 300 NMR spectrometer. Molecular weight was recorded on a Micromass TofSpec 2E (MALDI-TOF mass spectrometer). Thermal properties of the polymer were measured using a differential scanning calorimeter (DSC) and thermogravimetric analysis (TGA). (TA Instrument, DSC2910) with a scanning rate of 10 °C/min. Absorption spectra were obtained on a VARIAN CARY 5 UV−vis−NIR spectrophotometer both as solid films on glass and in 1,2-dichlorobenzene solution. Photoluminescence spectra were recorded on a JOBIN YVON−SPEX FluoroMax-2 (ISA Instruments. S. A., Inc.). X-ray diffraction was performed at room temperature on a Rigaku MiniFlex diffractometer using Cu Kα radiation ($\lambda = 1.5418$ Å) with a $\theta - 2\theta$ scans configuration. OTFTs were characterized using a Keithley SCS-4200 characterization system under ambient conditions.

Synthesis. *Benzo[1,2-b:4,5-b′]dithiophene-4,8-dione* ***1*** was prepared according to the literature procedure.[32]

4,8-Didodecynbenzo[1,2-b:4,5-b′]dithiophene 2. To a solution of dodecyne (13.6 g, 81.7 mmol) in THF (20 mL) in a 100 mL flask equipped with a condenser under an argon atmosphere was added dropwise 36 mL (72 mmol) of a 2 M solution of isopropylmagnesium chloride in THF at room temperature. An exothermic reaction occurred upon addition. After addition, the reaction mixture was heated at 50 °C for 95 min and cooled to room temperature. Benzo[1,2-b:4,5-b′]dithiophene-4,8-dione **1** (3 g, 13.6 mmol) was added, and the mixture was heated at 50 °C for 1 h before cooling down to room temperature. Subsequently, a solution of 20 g of $SnCl_2$ in 50 mL 10% aq HCl solution was added in a dropwise fashion followed by a further heating at 60 °C for 1 h. After the reaction, the solvent was removed by vacuum evaporation and the residue was purified by passing through a silica gel flash column using toluene as an eluent. Recrystallization of the crude product collected from flash chromatography from hexane gave 4.72 g (67% yield) of a dark green crystal after drying in vacuo.

^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 7.48 (d, $J = 5.8$ Hz, 2H), 7.47 (d, $J = 5.8$ Hz, 2H), 3.20 (t, 4H), 1.82 (m, 4H), 1.28 (bs, 36H), 0.88 (t, 6H).

^{13}C NMR ($CDCl_3$, 300 MHz, ppm): δ 140.59, 138.63, 127.95, 123.64, 112.59, 100.82, 32.34, 30.02, 29.99, 29.76, 29.60, 29.32, 29.20, 23.11, 23.36, 14.54.

4,8-Didodecylbenzo[1,2-b:4,5-b′]dithiophene 3. To a solution of 4,8-didodecynbenzo[1,2-b:4,5-b′]dithiophene **2** (4.72 g, 9.1 mmol) in THF (150 mL) in a round-bottomed flask was added 10% Pd/C (0.96 g, 0.9 mmol). The mixture was stirred under a hydrogen atmosphere at room temperature for 16 h. The solvent was removed by vacuum evaporation, and the residue was passed through a silica gel flash column with toluene as eluent to remove the catalyst residue. The crude product obtained from flash chromatography was purified by column chromatography on silica gel using hexane as an eluent. Recrystallization of the product isolated from column chromatography from 2-propanol afforded 2.5 g (60% yield) of white needle crystals after drying in vacuo.

(Caution: hydrogen gas reacts violently with Pd/C and may cause fire in the presence of oxygen.)

^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 7.48 (d, $J = 5.8$ Hz, 2H), 7.47 (d, $J = 5.8$ Hz, 2H), 3.20 (t, 4H), 1.82 (m, 4H), 1.28 (bs, 36H), 0.88 (t, 6H).

^{13}C NMR ($CDCl_3$, 300 MHz, ppm): δ 137.73, 136.26, 129.39, 126.24, 122.27, 33.92, 30.40(×2), 30.08(×3), 29.99, 29.94, 29.76.

2,6-Dibromo-4,8-didodecylbenzo[1,2-b:4,5-b′]dithiophene 4. To a well-stirred solution of 4,8-didodecylbenzo[1,2-b:4,5-b′]dithiophene **3** (1.12 g, 2 mmol) in CH_2Cl_2 (30 mL) and acetic acid (7.5 mL) in a 200 mL three-necked flask under an argon atmosphere was added powdered NBS (0.71 g, 4.0 mmol) in small portions over a period of about 5 min in the absence of light. The resulting reaction mixture was stirred for 24 h. After the reaction, the white precipitate formed was isolated by filtration, washed with water and methanol, and recrystallized once from 2-propanol and once from acetone to provide 0.68 g (50% yield) of white needle crystals after drying in vacuo.

^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 7.43 (s, 2H), 3.01 (t, 4H), 1.55 (m, 4H), 1.28 (bs, 36H), 0.90 (t, 6H).

^{13}C NMR ($CDCl_3$, 300 MHz, ppm): δ 139.0, 135.9, 128.0, 125.1, 115.3, 33.8, 32.3, 30.28, 30.07, 29.96, 29.7, 23.11, 14.5.

Poly(4,8-didodecylbenzo[1,2-b:4,5-b′]dithiophene 5. A mixture of 2, 6-dibromo-4,8-didodecyl-benzo[1,2-b:4,5-b′]dithiophene **4** (0.355 g), triphenylphosphine (0.0666 g), zinc powder (100 mesh) (0.137 g), 2,2′-dipyridil (5.4 mg), and anhydrous nickel(II) chloride (4.6 mg) in a 25 mL flask was degassed to 2.1×10^{-2} torr and then refilled with argon gas. This procedure was repeated twice before addition of dimethylacetamide (DMAc) (2 mL), and the resulting mixture was heated at 80 °C for 25 min. Subsequently, the reaction mixture was diluted with 8 mL of toluene, and heating was continued at 80 °C for 24 h. After cooling to room temperature, the reaction mixture was poured into an ice-cold mixture of methanol/37% aq HCl solution (200 mL/20 mL). The precipitated solid was filtered, washed with methanol, and then stirred in a mixture of methanol/36% aq ammonia solution (200 mL/20 mL) for 30 min. The oligomers and residual catalyst were extracted from the crude product by Soxhlet extraction with heptane for 24 h, and the pure product was extracted with chlorobenzene for 6 h. Removal of the solvent from the chlorobenzene extraction gave 0.12 g (yield: 46%) of pure poly(4,8-didodecylbenzo[1,2-b:4,5-b′]-dithiophene **5** which was suitable for use as a semiconductor in OTFT evaluation. Molecular weight (main peak in MALDI-TOF): 2098.419 (see Figure 2 in the Supporting Information).

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Supporting Information Available: Figure of MALDI-TOF of **5**, monomer **3** crystal packing, and single-crystal data. This material is available free of charge via the Internet at http://pubs.acs.org.

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(32) Beimling, P.; Koβmehl, G. *Chem. Ber.* **1986**, *119*, 3198−3203.