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Influence of Molecular Design on the Field-Effect Transistor Characteristics of Terthiophene Polymers

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Polymers containing thiophene backbones have demonstrated the highest p-type field-effect mobility of any solution-processed polymer to date. One drawback of this class of polymers, however, is that they can possess a relatively low ionization potential, which, in the presence of oxygen, often results in spontaneous p-type doping. As a result, the transistor properties can change with time, leading to low current modulation caused by high off currents. In this work, we have explored strategies to chemically modify the thiophene backbone structure, which leads to changes in both the backbone conformation and microstructure as well as the electronic energy levels of the molecular orbitals. A series of terthiophene polymers were synthesized, and their physical and electrical properties reported. The effects of changes in molecular structure on transistor performance and air stability are discussed.

Introduction

The advancement of organic transistor devices is creating a range of new applications, including low-cost RFID transponders tags, and organic TFT circuitry to complement flexible display modes such as electronic paper. Development of these emerging prototypes into widespread commercial applications relies on the availability of high-performance and high-purity materials as well as their compatibility with the additive, solution-based printing processes that are envisaged for product manufacture. A critical factor in this development is that devices exposed to the ambient environment sustain a high performance for the lifetime of the device. Recently there have been several publications demonstrating the long-term performance of poly(3-hexylthiophene) transistors in logic circuits.[1−7] However for applications such as organic TFTs in display backplanes, a higher on/off ratio is required. By assumption that no barrier encapsulation is included in the TFT device structure, achieving these low off currents requires that the semiconductor does not oxidatively dope on exposure to oxygen either during fabrication or operation.

Discussion

The centrosymmetric terthiophene, shown in Figure 1 as Polymer 1, has a highly crystalline morphology,[8] characterized by adjacent thiophene rings on each polymer chain orienting in a coplanar conformation, thus allowing good overlap of the π-conjugated system along the length of the backbone. The planar mainchains assemble cofacially with respect to neighboring chains, while the regularly spaced side chains extend from the backbone, allowing a high degree of interdigitization within each polymer layer. This stable conformation has small cofacial distances (about 3.8 Å), giving rise to efficient charge carrier hopping. The extended, planar, electron-rich, conjugated thiophene system not only contributes to the high charge carrier mobility exhibited by this polymer but also to its low highest-occupied molecular orbital (HOMO) energy level and therefore low ionization potential (IP). It has been shown[9] that materials with IPs in this range (4.5−5.0 eV) are susceptible to oxidative doping, and therefore transistors exposed to ambient atmosphere will, over time, p-dope due to interaction with oxygen. There is evidence to support that this doping is reversible, especially in the absence of photoexcitation, and that the transistor properties can be recovered on removal of oxygen from the semiconductor layer by either subjecting to vacuum or treatment with a reducing agent such as hydrazine.[10] When doped, the transistor electrical properties change. Typically the off current is substantially higher than in the undoped state, and thus the current modulation is reduced. There is a strong desire therefore to prepare polythiophenes capable of achieving low off currents, and consequently, strategies to increase the IP of polythiophenes were employed.

The HOMO energy level of terthiophene polymers can be modified[11,12] at the molecular level by controlling both

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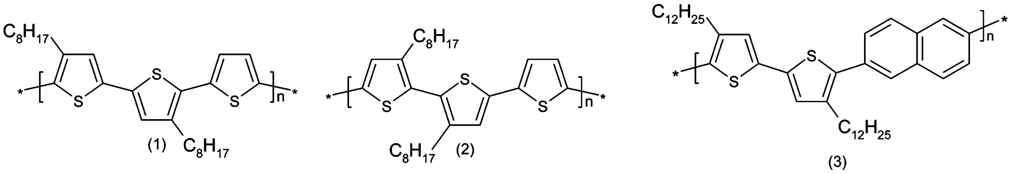
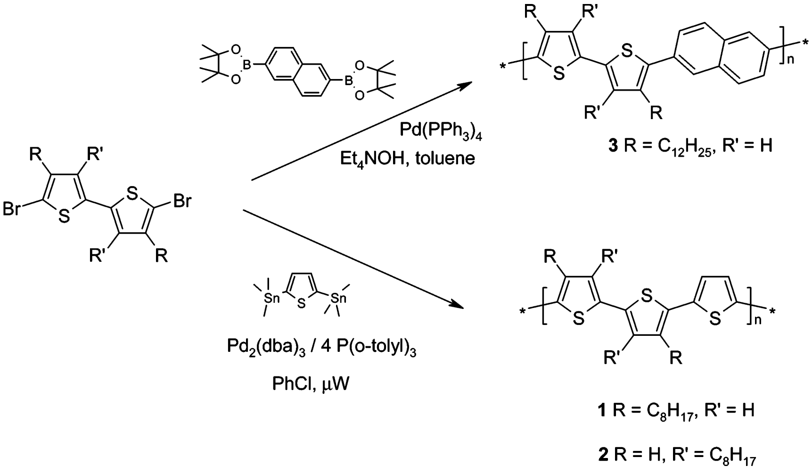


Figure 1. Structure of terthiophene polymers utilized in the studies.

Scheme 1. Representative Syntheses of Polyterthiophenes via Suzuki or Stille Cross-Coupling Reactions



the extent of conjugation along the polymer chain and the electron density of the conjugated system. Controlling the extent of conjugation can be achieved by either sterically forcing a twist between adjacent thiophene rings, thereby reducing the π orbital overlap, or by introducing a non- or less-conjugated unit as a component of the polymer backbone, thus limiting the conjugation length. Twisting adjacent thiophene rings can be achieved through steric interactions between nearby substituents, for example, head-to-head 3-alkyl linkages on adjoining thiophene rings. Obviously stopping conjugation can be achieved through the inclusion of a nonconjugated comonomer. This however, may introduce additional undesired conformational effects in that an sp^3-hybridized unit will bend the backbone out of plane. Inclusion of a conjugated monomer, in which the resonant quinoidal form is highly unfavored, will reduce the conjugation without disturbing the backbone planarity.

Three terthiophene polymers which illustrate these principals are included in this study, as shown in Figure 1.

The polymers were synthesized by palladium-catalyzed cross-coupling reactions, utilizing an A + B co-polymerization strategy (Scheme 1). For the naphthalene-containing polymer, a Suzuki-type polymerization between 2,6-bis(tetramethyldioxaborolato) naphthalene and a dibromo dialkylbithiophene proved effective. However for the all thiophene systems, attempted Suzuki reactions of thiophene bis(boronic) esters under similar conditions afforded low molecular weight oligomers, possibly due to problems with deboronation.[13] For this reason, the Stille reaction with 2,5-bis(trimethylstannyl)thiophene was preferred. In this case, reactions were performed under microwave heating to afford polymers in very short reaction times that typically had higher molecular weights than conventional heating.[14,15] The lower molecular weights obtained for the naphthalene polymers are attributed to the low solubility of the growing chain. A longer (dodecyl) chain was used to attain sufficient solubility to at least achieve a M_n value of about 9000.

The physical properties and electrical performance of all polymers were measured and collected in Table 1. Polymer 1 was observed to have an IP measurement of 5.0 eV, as determined by a UV photoelectron spectroscopic method,[16] and an absorption maximum at 463 nm in solution and 550 nm in the solid state as can be seen in Figure 2. This long wavelength absorption, coupled with a large bathochromic shift in the solid state, is consistent with a highly conjugated polymer exhibiting a crystalline morphology. As these values are very similar to the highly planar poly(3-hexylthiophene), it is believed that the tail-to-tail coupling of the alkyl group in Polymer 1 does not perturb the conjugation along the backbone to any extent.

Polymer 1 also has a relatively high melting point and a large crystallization enthalpy, as reported in Table 1, due to the well-organized side chain packing structure.

The air stability of the polymer was determined by exposing a field effect transistor device to ambient air and measuring the device I−V characteristics over an extended time period. As can be seen in Figure 3a, there is an immediate and rapid change in off current on exposure to air, accompanied by a slight positive shift in turn-on voltage as seen in Figure 3b. This is consistent with oxygen doping. After several days, both the off current and transfer characteristics stabilized and an on/off ratio of about 10^2 could

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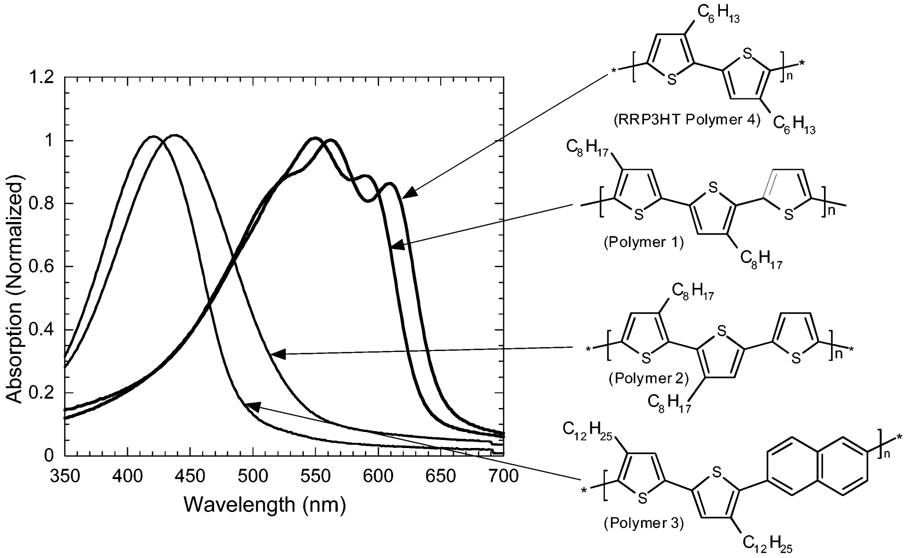

Figure 2. Thin-film UV−vis absorption spectra of thiophene polymers. Absorption spectrum of regioregular P3HT is shown for comparison.

Table 1. Properties of Terthiophene Polymers

polymer	MW (avg)	T_m (°C)	cryst. enth. (J/g)	absorption max (toluene) (nm)	absorption max (solid state) (nm)	IP (eV)	charge-carrier mobility (cm^2/Vs)[a]	on/off ratio[b]
1	13 000	170	14	463	550	5.0	3×10^{-2}	2×10^2
2	30 000			430	438	5.6	1×10^{-5}	1×10^3
3	9 000	125	5	401	426	5.4	6×10^{-4}	4×10^4
4	22 000	212	20	450	560	4.8	2×10^{-2}	1×10^1

[a] Field-effect mobility is quoted for dry nitrogen measurements in a glovebox before exposure to air. [b] On/off ratio is reported for measurements in ambient air, several days after initial exposure, when on and off currents have stabilized. Polymer 4 did not show stable performance in ambient atmosphere; on/off ratio was constantly dropping to approximately a value of <10 after several days exposure to air (¥).

be obtained. A charge carrier mobility of 3×10^{-2} cm^2/Vs was derived for measurements in a dry nitrogen atmosphere. The very high on current (up to 10^{-2} A) obtained from this polymer was in part due to the large W/L ratio of the transistor structure where L is the transistor channel length and W is the channel width.

By comparison of polymers 1 and 2, it can be clearly seen that in the case of Polymer 2 there are head−head steric interactions between the 3-alkyl chains on neighboring thiophene rings that do not occur in Polymer 1. The impact of this effect is most likely to force a twisting of the backbone in Polymer 2, resulting in a less planar structure with reduced $\pi-\pi$ overlap between thiophene rings and, hence, a larger band gap and lower HOMO level. Increase in the band gap manifests as a hypsochromic shift in the UV spectra, as can be seen in Figure 2, and a corresponding increase in the IP value to 5.6 eV. The lack of spatial ordering of the side chains in Polymer 2 also prevents crystallization, and in contrast to the Polymers 1 and 3, which have tail−tail thiophene linkages, this polymer is amorphous. This lack of solid-state aggregation is further confirmed by the similarity of the solution and solid-state UV spectra. Both the reduced conjugation, and lower macroscopic organization contribute to a low p-type field-effect mobility of 1×10^{-5} cm^2/Vs obtained from transistor devices. In accordance with its low IP value, the transistor properties of Polymer 2, when measured in ambient air, were much more stable than Polymer 1. On prolonged exposure to air, a small positive turn-on voltage shift was observed, as can be seen in Figure 3e; however, the on/off ratio remained quite stable, and a value of 10^3 was obtained.

The substitution of the central thiophene unit with naphthalene (Polymer 3) resulted in an increase in IP to 5.4 eV when compared to Polymer 1. This can be attributed to both lower electron density of the naphthalene unit as well as its highly aromatic nature. Incorporation of naphthalene has the effect of limiting the extent of conjugation through the backbone, as, although it possesses a conjugated electronic structure, the quinoidal form of the molecule is unfavored (the resonance stabilization of naphthalene is 255 vs 121 kJ mol^{-1} for thiophene).[17] Although the 2,6 linkage introduces a “crank-shaft”-like geometry to the polymer backbone, crystallization still occurs. The enthalpy of crystallization is less than the other thiophene polymers, and the melting point is also lower, as can be seen in Table 1. This may also be in part due to the larger aliphatic side groups, which as previously discussed were necessary to incorporate to ensure solubility. The charge carrier mobility of 6×10^{-4} cm^2/Vs obtained for this polymer was unremarkable; however, the transistor characteristics appeared to be quite stable on prolonged exposure to air. There was a slight positive shift in turn-on voltage as shown in Figure 3h; however, the off current remained very low with a very small increase from 14 pA after 10 min exposure to air to about 70 pA after 43 days in air. The subthreshold slope (4.3 V/decade) remained practically the same within the duration of the experiment.

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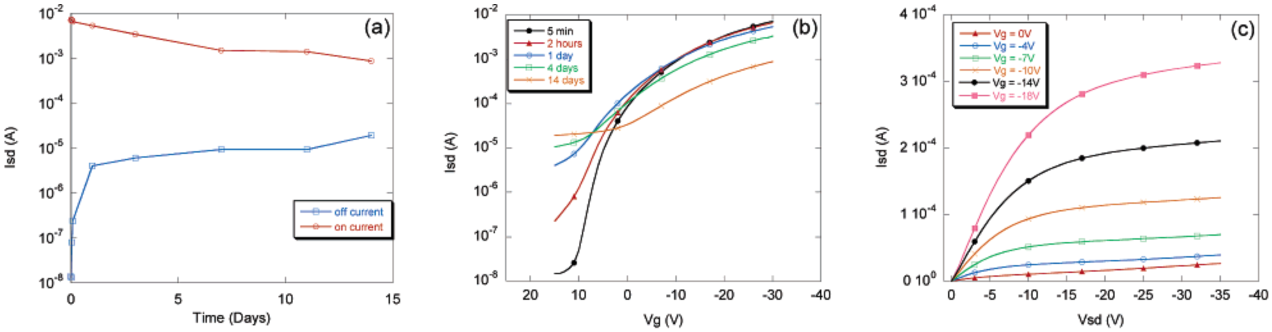
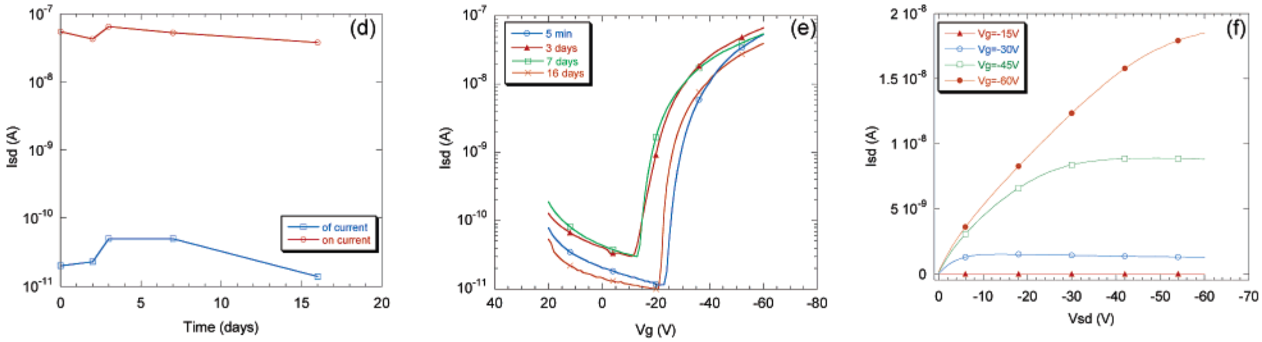
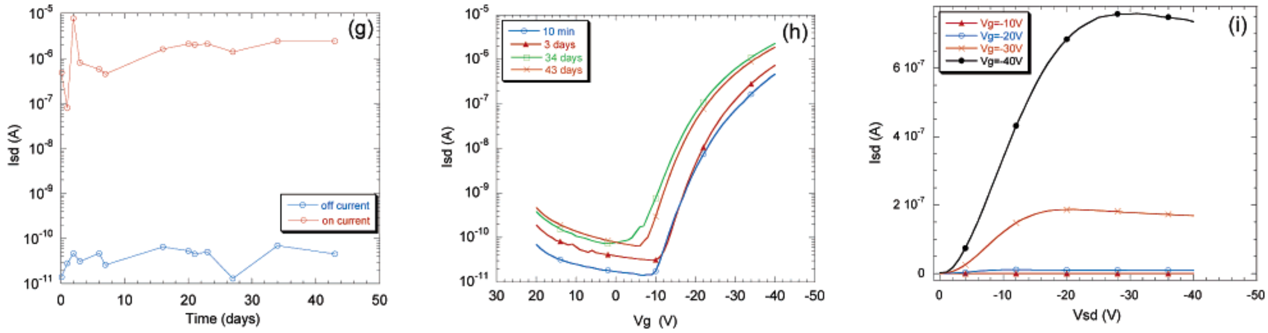


Polymer 1. (a) ON/OFF ratio; (b) transfer characteristics; (c) output characteristics



Polymer 2. (d) ON/OFF ratio; (e) transfer characteristics; (f) output characteristics



Polymer 3. (g) ON/OFF ratio; (h) transfer characteristics; (i) output characteristics

Figure 3. On/off currents and transistor characteristics of terthiophene polymer FETs on prolonged exposure to air.

It is possible that, by increasing the molecular weight[18] of this polymer and optimizing the transistor device fabrication, much higher mobilities can be achieved.

The IP value of 5.6 eV obtained for Polymer 2 appears to be inconsistent with both its optical band gap and electrical properties when compared to Polymer 3 with an IP value of 5.4 eV. Polymer 2 has a smaller band gap, and field-effect transistor (FET) output characteristics show ohmic contact behavior (Figure 3f). Transistor output curves of Polymer 3 (Figure 3i), on the contrary, indicate significant nonohmic contact behavior as evidenced by nonlinear current increase at low Vsd, although different channel length devices where not investigated.

Experimental Section

All starting materials and reagents were purchased from Aldrich Chemicals or Lancaster Chemicals and used as received with the exception of tetrakis(triphenylphosphine)palladium(0) and tris(dibenzylideneacetone)palladium(0) (Strem Chemicals). The precursors, 5,5′-dibromo-4,4′-dialkylbithiophene,[19] 5,5′-dibromo-3,3′-dialkylbithiophene,[20] 2,5-bis(trimethylstannyl)thiophene,[21] and 2,6-bis(tetramethyl-1,3,2-dioxaborolato) naphthalene[22] were synthesized following published procedures. ^{1}H NMR spectra were recorded at 50 °C on a Bruker AV-300 (300 MHz), using the residual solvent resonance of $CDCl_3$ or trimethylsilane as an internal reference and are given in ppm. Polymer molecular weight determinations were carried out in chloroform solution on an Agilent 1100 Series HPLC using two Polymer Laboratories Mixed B columns in series, and the system was calibrated against narrow-weight PL polystyrene calibration standards. HOMO energy levels were directly determined by an ambient photoelectron spectroscopy method with a Riken-Keiki AC-2 spectrometer.[16] The absorption maxima were collected by a Perkin-Elmer Lambda 9 UV−vis spectrophotometer.

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Thermal properties of the polymers were obtained with a TA Q1000 differential scanning calorimeter. Thin-film organic field-effect transistors were fabricated under dry nitrogen in a glovebox, on highly doped silicon substrates with 230 nm thick thermally grown silicon oxide (SiO_2) insulating layer, where the substrate served as a common gate electrode. Transistor source-drain gold electrodes were photolithographically defined on the SiO_2 layer giving a device channel length $L = 10\ \mu$m and channel widths of $W = 2$ cm (used to determine the electrical characteristics of polymers 2 and 3) and 31.2 cm (used to determine the electrical characteristics of polymer 1). Prior to organic semiconductor deposition, FET substrates were treated with a silylating agent hexamethyldisilazane. Thin semiconductor films, typically 30−60 nm (measured by n KLA Tencor Alpha-Step 500 profilometer), were then deposited by spin-coating polymer solutions in chloroform (0.4−1 wt %) on FET substrates. The transistor samples were then annealed and field-effect mobilities measured and reported in Table 1. Devices were then transferred into ambient air and their electrical properties measured and reported in parts a−i of Figure 3. The devices were stored in the absence of light, and measured under yellow light (wavelengths < 500 nm removed by filtration).

FET characterization was carried out using a computer-controlled Agilent 4155C semiconductor parameter analyzer. The scans were obtained using a delay of 0.2 s, 1 s hold time, and a voltage scan of step size of 0.5 V.

Field-effect mobility was calculated in the saturation regime ($V_d > (V_g - V_0)$) using eq 1

$$\left(\frac{dI_d^{\,sat}}{dV_g}\right)_{V_d} = \frac{WC_i}{L}\mu^{sat}(V_g - V_0) \qquad (1)$$

where W is the channel width, L the channel length, C_i the capacitance of insulating layer, V_g the gate voltage, and V_0 the turn-on voltage. Turn-on voltage (V_0) was determined as the onset of source-drain current (parts b, e, and h of Figure 3).

Poly(3,3′′-dioctylterthiophene) (1). A 20-mL glass vial was charged with 5,5′-dibromo-4,4′-dioctylbithiophene (987 mg, 1.80 mmol), 2,5-bis(trimethylstannyl)thiophene (738 mg, 1.80 mmol), $Pd_2(dba)_3$ (33 mg, 4 mol % Pd), P(*o*-tol)$_3$ (44 mg, 8 mol %), and chlorobenzene (16 mL). The glass vial was purged with nitrogen and securely sealed. The glass vial was placed into a microwave reactor (Emrys Creator, Personal Chemistry Ltd) and heated at 180 °C for 15 min with stirring. After it was cooled to room temperature, the reaction mixture was precipitated into a mixture of methanol (300 mL) and concentrated HCl (30 mL) and stirred for 1 h. The polymer was filtered off, washed with methanol, and dried under vacuum. The polymer was washed (via Soxhlet extraction) with methanol for 24 h and acetone for 18 h. The polymer was dissolved in chloroform and filtered through basic alumina. The filtrate was precipitated from methanol (300 mL), and polymer was collected by centrifugation and dried under vacuum to yield **1** as a dark red solid (800 mg, 94%). $M_n = 13\,000$. $M_w = 29\,000$. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.10 (s, 2H, Ar*H*), 7.01 (s, 2H, Ar*H*), 2.80 (t, $^3J = 7.5$ Hz, 4H, ArCH_2), 1.72 (m, 4H, CH_2), 1.29−1.42 (m, 20H, CH_2), 0.91 (t, $^3J = 6.0$ Hz, 6H, CH_3). Anal. Calcd. for $(C_{28}H_{38}S_3)_n$: C, 71.1; H, 8.5; S, 20.4. Found: C, 70.2; H, 7.3; S, 20.7.

Poly(4,4′′-dioctylterthiophene) (2). A 20-mL glass vial was charged with 5,5′-dibromo-3,3′-dioctylbithiophene (260 mg, 0.48 mmol), 2,5-bis(trimethylstannyl)thiophene (195 mg, 0.48 mmol), $Pd_2(dba)_3$ (9 mg, 4 mol % Pd), P(*o*-tol)$_3$ (12 mg, 8 mol %), and chlorobenzene (9 mL). The glass vial was purged with nitrogen and securely sealed. The glass vial was placed into a microwave reactor (Emrys Creator, Personal Chemistry Ltd) and heated at 180 °C for 15 min with stirring. After cooling to room temperature, the reaction mixture was precipitated into a mixture of methanol (100 mL) and concentrated HCl (10 mL) and stirred for 1 h. The polymer was filtered off, washed with methanol, and dried under vacuum. The polymer was washed (via Soxhlet extraction) with methanol for 6 h and acetone for 16 h. The polymer was dissolved in chloroform and filtered through basic alumina. The filtrate was precipitated from methanol (100 mL) and polymer was collected by centrifugation and dried under vacuum to yield **2** as a bright-red solid (155 mg, 65%). $M_n = 30\,000$. $M_w = 73\,000$. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.09 (s, 2H, Ar*H*), 7.07 (s, 2H, Ar*H*), 2.57 (t, $^3J = 7.5$ Hz, 4H, ArCH_2), 1.62 (m, 4H, CH_2), 1.22−1.41 (m, 20H, CH_2), 0.89 (t, $^3J = 6.0$ Hz, 6H, CH_3). Anal. Calcd. for $(C_{28}H_{38}S_3)_n$: C, 71.1; H, 8.5; S, 20.4. Found: C, 71.1; H, 7.9; S, 20.6.

Poly(4,4′′-didodecylbithiophene-*co*-2,6-naphthalene) (3). A three-necked flask was charged with 5,5′-dibromo-3,3′-didodecylbithiophene (950 mg, 1.44 mmol), 2,6-bis(tetramethyl-1,3,2-dioxaborolane)naphthalene (547 mg, 1.44 mmol), tetrakis(triphenylphosphine)palladium(0) (34 mg, 2 mol %), and toluene (30 mL) and purged with nitrogen. The solution was stirred at room temperature for 5 min. A solution of 20% w/v tetraethylammonium hydroxide (5 mL) was added. The reaction mixture was heated to 100 °C and stirred for 48 h. The reaction mixture was precipitated from methanol (400 mL). The polymer was filtered off, washed with water and then methanol, and dried under vacuum. The polymer was washed (via Soxhlet extraction) with methanol for 20 h and *iso*-hexane for 16 h. The polymer was dissolved in chloroform, reprecipitated from methanol (400 mL), filtered off, and dried under vacuum to yield **3** as a bright-yellow solid (700 mg, 77%). $M_n = 9\,000$. $M_w = 22\,000$. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.85−7.97 (m, 4H, Ar*H*), 7.65 (d, $^3J = 8.5$ Hz, 2H, Ar*H*), 7.15 (s, 2H, Ar*H*), 2.71 (t, $^3J = 7.5$ Hz, 4H, ArCH_2), 1.70 (m, 4H, CH_2), 1.19−1.42 (m, 36H, CH_2), 0.89 (t, $^3J = 6.0$ Hz, 6H, CH_3). Anal. Calcd. for $(C_{42}H_{58}S_2)_n$: C, 80.2; H, 9.6; S, 10.2. Found: C, 78.5; H, 8.6; S, 10.2.

Conclusions

In summary, the HOMO energy level, and hence the IP, of terthiophene polymers was effectively manipulated through molecular modifications of the polymer backbone, which resulted in a perturbation of the π electron conjugation. These perturbations had a marked influence on both charge carrier mobility and stability to ambient air. Steric twisting of the thiophene backbone was observed to substantially raise the polymer IP, resulting in high on/off ratios being obtained on prolonged exposure to air. The corresponding loss of close intermolecular aggregation of the thiophene backbone however had a severely detrimental effect on charge-carrier mobility. Similarly, reducing the efficiency of π conjugation along the backbone through incorporation of the naphthalene group also increased the polymer IP. In this case, some degree of intermolecular $\pi-\pi$ aggregation remained, and the reduction in charge carrier mobility was not as large.

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