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ARTICLE

High-Performance Polythiophene Thin-Film Transistors Processed with Environmentally Benign Solvent

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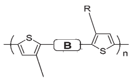
ABSTRACT: Solution processable organic thin-film transistors (OTFTs) have attracted great attention recently due to their high potentials to dramatically reduce the manufacturing cost for large-area and flexible electronic devices. However, most high performance polymeric semiconductors require chlorinated solvents for their device fabrications, which is not an environmentally friendly manufacturing process. In this article, we describe a facile approach to tuning the solubility characteristics of a high mobility polythiophene system by strategic structure modification and demonstrate significantly improved solution properties in environmentally benign solvents with high field-effect mobility up to 0.18 $cm^2 V^{-1} s^{-1}$. To our best knowledge, this is one of the highest mobility values reported so far for solution-processed OTFTs fabricated from polymeric semiconductors in nonchlorinated solvents. Furthermore, the molecular orientations and structural properties of newly developed polythiophenes were evaluated by both single crystal data of their building blocks and X-ray diffraction (XRD) of their thin films.

Introduction

Printed organic thin-film transistors represent an appealing low-cost alternative to their amorphous silicon counterparts for applications in large-area, flexible and ultra low-cost electronics.[1−17] This emerging technology requires stable organic semiconductors which can be readily solution-processed in an environmentally friendly solvent to enable low-cost mass-manufacturing of thin-film transistor (TFT) arrays/circuits under ideally ambient conditions. However, most solution processable high performance organic semiconductors such as polythipophenes and their derivatives suffer from either extreme sensitivity to air or requiring chlorinated solvents for their device fabrications to achieve optimal OTFT performances.[18−27]

Earlier, we reported the design principle for high-performance polythiophene semiconductors for OTFTs based on structure **1**.



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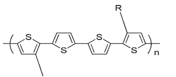

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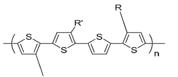

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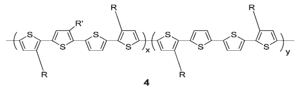

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In this structural design, the long pendant alkyl side-chains would impart solution processability and self-assembly capability to the system, while the intervening bridge, **B**, serves to provide stability against photoinduced oxidative doping. Using this design principle, a high-performance polythiophene semiconductor, poly(3,3‴-dialkylquaterthiophene) (**2, PQT**), with enhanced air stability was developed. Excellent field effect transistor (FET) properties have been achieved in OTFTs using this polythiophene semiconductor system (**2**, R = *n*-$C_{12}H_{25}$) fabricated entirely at ambient conditions.[19] However, like most high-performance solution-processable polymeric semiconductors, **2** self-assembles readily even in solution and exhibits a great tendency to gel out of solution at room temperature. This has presented some practical difficulties in OTFT fabrications until the recent development of structurally ordered PQT nanoparticles, which effectively resolves the gelling complications.[28] Nevertheless, this approach still requires the use of chlorinated solvents for its device fabrication to achieve the optimum performance, thus severely limiting its general applicability in manufacturing environments.[5] In this article, we describe a facile approach to tuning the solution properties of high mobility polythiophene **2** (**PQT**) system of this nature. Our results reveal that both significantly improved solution processability in environmentally benign solvents such as xylene and high field-effect mobility up to 0.18 $cm^2 V^{-1} s^{-1}$ can be simultaneously achieved via judicial structure modification, thus circumventing a general and formidable challenge currently besetting solution-processable polymeric semiconductors for low-cost TFT array/circuit manufacturing.

The strong self-assembly ability of **2** stems from the strategically regioregular placement of long pendant side-chains, R's, along its backbone, which promotes intermolecular side-chain interdigitation leading to extensive lamellar ordering in solution. We envisioned that this facile self-organization in solution could be greatly suppressed or even eliminated by slight perturbation to the structural regioregularity of **2** via incorporation of a small substituent (e.g., methyl) in the intervening thienylene moiety as in polythiophene **3** (*R* = long *n*-alkyl; R′ = CH_3) or copolythiophene **4** (*R* = long *n*-alkyl; R′ = CH_3), in which the structural regioregularity of long side-chains, R's, of parent polythiophene **2** could still preserve. It was anticipated that this weak structural

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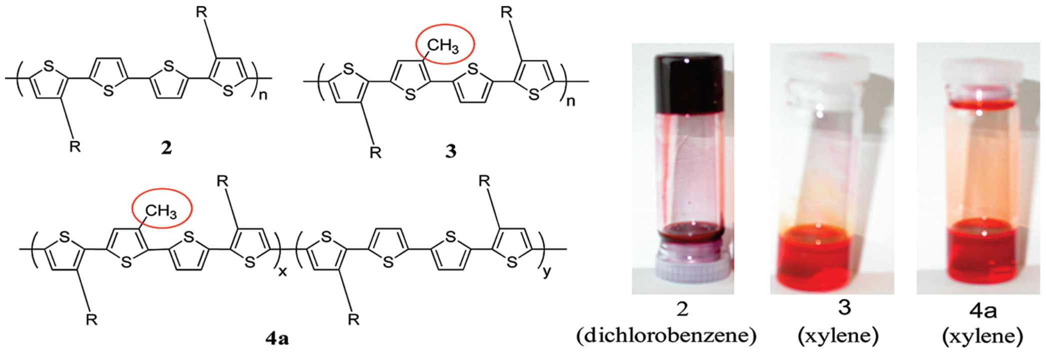
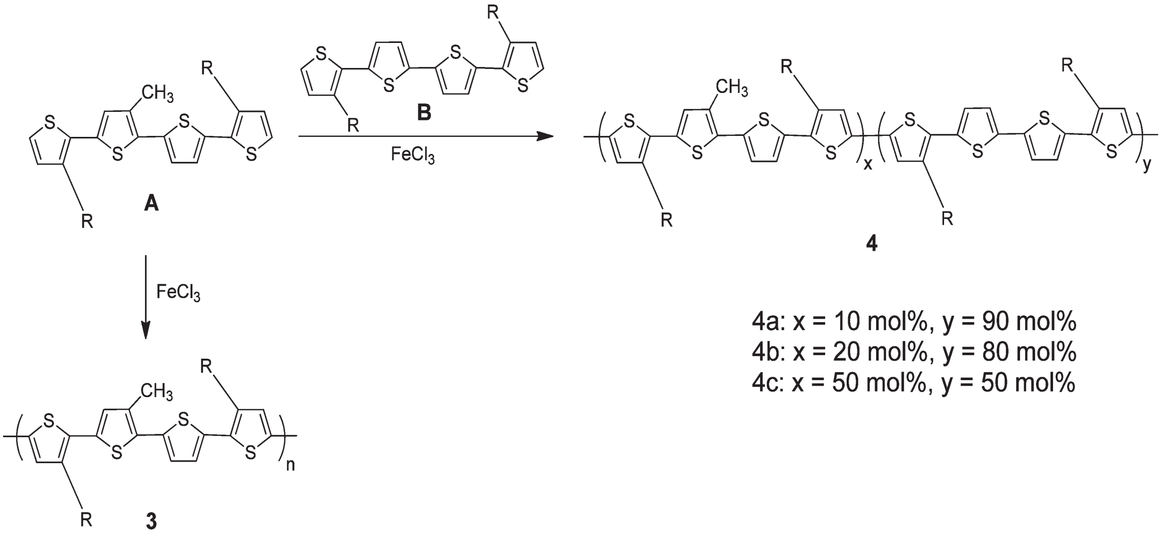


Figure 1. Coating solution stability of **2** (**PQT**) in dichlorobenzene (0.3 wt %), **3** (**PQT-CH$_3$**) and copolythiophene **4a** (x = 10 mol %, y = 90 mol %) in xylene (1.0 wt %).

Scheme 1. Syntheses of Polythiophene 3 and Copolythiophene 4



perturbation, while rendering the polythiophene system disordered when in solution, could be overcome in a great extent by the strong self-assembly tendency associated with the regioregularity of long pendant side-chains via intermolecular interdigitation when in solid state such that highly ordered semiconductor channels could be created in TFTs.

Results and Discussion

Polythiophene **3** (R = $C_{12}H_{25}$; R′ = CH_3), PQT-CH$_3$, was prepared readily by FeCl$_3$-mediated oxidation coupling polymerization of 3,3‴-didodecyl-3′-methylquaterthiophene (**A**) in good yields; while **4** (R = $C_{12}H_{25}$; R′ = CH_3) was prepared by copolymerization of 3,3‴-didodecyl-3′-methylquaterthiophene (**A**) and 3,3‴-didodecylquaterthiophene (**B**) in various stoichiometries under analogous conditions (Scheme 1). The final content of monomer A in the copolymer **4** was calculated from NMR data. The resutls showed that the copolymers have a similar molar ratio as the feeding ratio of the monomers, which is anticipated by the similar reactivity of the monomers.

As expected, **3** (**PQT-CH$_3$**) showed much better solubility in organic solvents than **2** (PQT) not only in chlorinated solvents but also in nonchlorinated environmentally benign solvents such as THF, toluene and xylene at room temperature. More specifically, a hot solution of **2** (**PQT**) in dichlorobenzene with 0.3 wt % was gelled upon cooling to room temperature within several minutes due to its poor solubility, on the other hand, a much more concentrated solution of **3** (**PQT-CH$_3$**) up to 2.0 wt % in dichlorobenzene was very stable without gelling at room temperature. Furthermore, a comparison of their solubility in a nonchlorinated solvent such as *o*-xylene was also examined. The solubility of **2** (**PQT**) in *o*-xylene was very poor, which could not be dissolved in *o*-xylene even with very low concentration of 0.1 wt %, while a 10 times more concentrated solution of **3** (**PQT-CH$_3$**) in *o*-xylene (1.0 wt %) was stable at room temperature in a period of over 2 weeks. It should be noted that such a 1−2 wt % concentration is sufficient for OTFT fabrications.[3,19,21,22] It is interesting that such a dramatic solubility improvement in organic solvents can be achieved by this strategic structure modification. As a result, copolythiophene **4** showed much better solubility in common organic solvents than PQT. As shown in Figure 1, a hot coating solution of **2** (**PQT**) in dichlorobenzene with 0.3 wt % was gelled upon cooling to room temperature within several minutes due to its poor solubility, while the coating solutions prepared from polythiophene **3** and copolymer **4a** even in a nonchlorinated solvent such as *o*-xylene were much more stable at room temperature for much longer time (e.g., a couple of hours for copolymer **4a** and a few weeks for polymer **3**), providing sufficient time for their device fabrications. In general, the solution stability of the new polymers increases with the increase of mole ratio of monomer **A**.

Nevertheless, the ability to order in their thin-films has been preserved even with y approaching zero as in the case of **3** (i.e., **4**, $y = 0$). This can be readily understood from the single-crystal data of the corresponding quaterthiophene monomers as depicted in Figure 2. As can be noted, the two pendant dodecyl side-chains in methyl-substituted didodecylquaterthiophene in the single crystal structure assume a coplanar conformation, which is similar to its unsubstituted didodecyl-quaterthiophene counterpart.[29] Thus, it is reasonable to assume that the conformational structures of

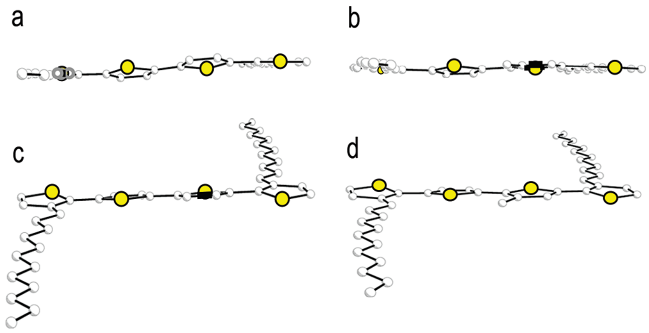


Figure 2. Single crystal structures of **monomer B** (a, c) and **monomer A** (b, d) (a, b: view along outer thiophene plane; c, d: view along inner thiophene plane.).

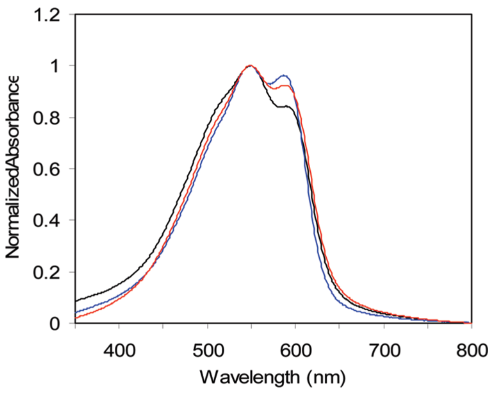


Figure 3. UV−vis absorption spectra of thin films spin-cast from **2** (blue), **3** (black), and **4a** (red).

3 (**PQT-CH$_3$**) and copolythiophene **4** would be similar to that of **2** (**PQT**) in their solid states. Therefore, the ability of forming lamellar structural order of polythiophene **2** (**PQT**)[19] has been preserved for both **3** (**PQT-CH$_3$**) and copolythiophene **4**(**a**−**c**) in their thin films, which leads to the high mobility. The significantly improved solubility characteristics of **3** (**PQT-CH$_3$**) and copolythiophene **4**(**a**−**c**) in common organic solvents could be attributed to the random nature of their compositions with respect to the regiochemistry of the methyl substituent.

UV−visible absorption spectra of thin films spin-cast from solution of **2** (**PQT**), **3** (**PQT-CH$_3$**), and copolythiophene **4a** (x = 10 mol %) in chlorobenzene on glass slides (Figure 3) have shown that all of the polythiophenes exhibited well-defined vibronic splitting characteristic of high structural ordering at $\lambda_{\max} \sim 510$ nm (shoulder), 548 nm, and 587 nm, indicating that the thin-film spectral properties of polythiophene **3**(**PQT-CH$_3$**) and copolythiophene **4** are similar to those of polythiophene **2** (**PQT**) with 3D lamellar π−stacking structural ordering in the thin film.[19,28]

The structural order of **3** (**PQT-CH$_3$**) and copolythiophene **4a** in their thin films were further established by X-ray diffraction (XRD) studies. XRD of a 0.2 μm thin film spin-cast from **3** and **4a** on an octyltrichlorosilane (OTS-8)-modified silicon wafer showed very similar three distinctive diffraction peaks after annealing. The diffraction peaks of the annealed thin films are at $2\theta = 5.2°$ (100), 10.8° (200), and 16.2° (300) for **3** and at $2\theta = 5.3°$ (100), 10.6° (200), and 16.0° (300) for **4a**, respectively, as shown in Figure 4. These diffraction peaks correspond to *d* spacing for the interchain distance between two neighboring polythiophene chains within the lamellar structure, which showed essentially similar lamellar structural orders of polythiophene **2** (**PQT**).[19,28] Comparing to **4a**, the slightly increased *d* spacing of **3** might be due to the present of methyl group.

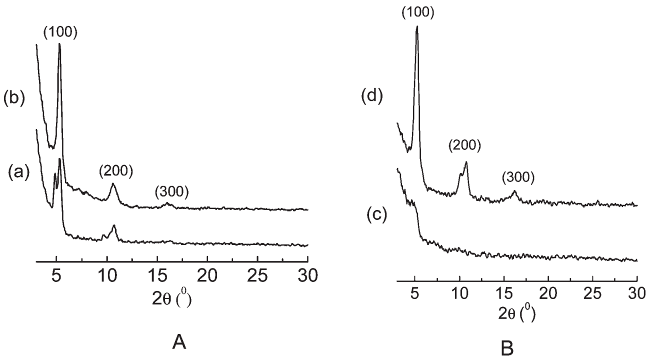


Figure 4. (A) XRDs of **4a**: (a) 0.2 μm thin film without annealing; (b) 0.2 μm thin film annealed at 140 °C. (B) XRDs of **3**: (c) 0.2 μm thin film without annealing; (d) 0.2 μm thin film annealed at 120 °C.

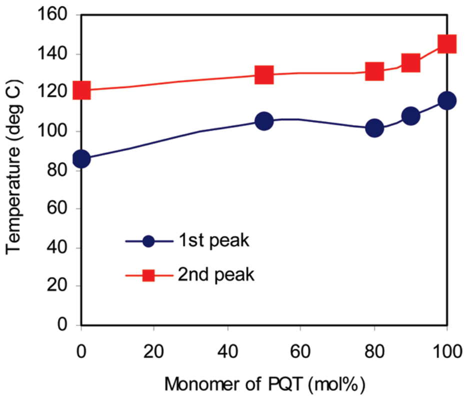


Figure 5. Phase transition temperatures of **2** (**PQT**), **3** (**PQT-CH$_3$**), and **4**(**a**−**c**) on heating.

Thermal properties of **2** (**PQT**), **3** (**PQT-CH$_3$**) and **4**(**a**−**c**) were characterized by DSC measurements and their phase transition temperatures on heating are shown in Figure 5. Two endothermic peaks were observed on heating curves for all of them, indicating liquid crystalline properties of these polymeric semiconductors. The first peak on heating can be assigned to melting of the long alkyl side chain, and the second peak can be assigned to melting of the polythiophene backbone. In general, the phase transition temperature increases slightly with the increase of the monomer content of **2** (**PQT**). The slight variation might be due to the difference of molecular weight.

Electronic properties of thin-film transistors fabricated from **3** (**PQT-CH$_3$**) and **4**(**a**−**c**) as a semiconductor layer were evaluated from both dichlorobenzene and *o*-xylene solvents, and their mobilities in both solvents were at the similar level. The results of OTFTs fabricated from **3** (**PQT-CH$_3$**) and **4**(**a**−**c**) in *o*-xylene by spin coating were compared with those OTFTs fabricated from semiconductor **2** (**PQT**) in dichlorobenzene, as it was not soluble in *o*-xylene at room temperature. All the fabrication and characterization of organic thin-film transistors (OTFTs) were done under ambient conditions without taking any precautions to isolate the materials and devices from exposure to air, moisture, and light. Bottom-gate TFT devices were built by spin-coating solutions of **2**, **3**, and **4**(**a**−**c**) on n-doped silicon wafer as the gate electrode with a 110 nm thermal silicon oxide (SiO$_2$) as the dielectric layer. The dielectric surface was modified with octyltrichlorosilane as reported before for better compatibility with polythiophene semiconductor.[30] The values of mobility and current On/Off ratio for the OTFTs were summarized in Table 1 and illustrated in Figure 6. The results show that mobility increases with increasing the composition of polythiophene **2** (**PQT**). The

Table 1. Summary of Enthalpy Data, OTFT Mobility, and Current on/off Ratio with 2 (PQT), 3 (PQT-CH$_3$), and 4(a−c) as a Semiconductor Layer

polythiophenes	M_w/M_n	solvent	enthalpy (J/g)	Mobility (cm^{2}V^{-1}s^{-1}), (Current On/Off) before annealing	after annealing
2 (**PQT**)	22.9K/17.3K	dichlorobenzene	7.30	0.03−0.047 (10^6)	0.10−0.2 (10^7)
4a (x = 10 mol %)	30.6K/17.4K	*o*-xylene	5.53	0.024−0.035 (10^6)	0.10−0.18 (10^7)
4b (x = 20 mol %)	21.5K/10.9K	*o*-xylene	5.42	0.021−0.03 (10^6)	0.05−0.07 (10^6)
4c (x = 50 mol %)	21.6K/10.9K	*o*-xylene	4.77	0.025−0.035 (10^6)	0.03−0.05 (10^6)
3 (**PQT-CH$_3$**)	29.2K/14.8k	*o*-xylene	1.79	0.015−0.022 (10^6)	0.015−0.03 (10^6)

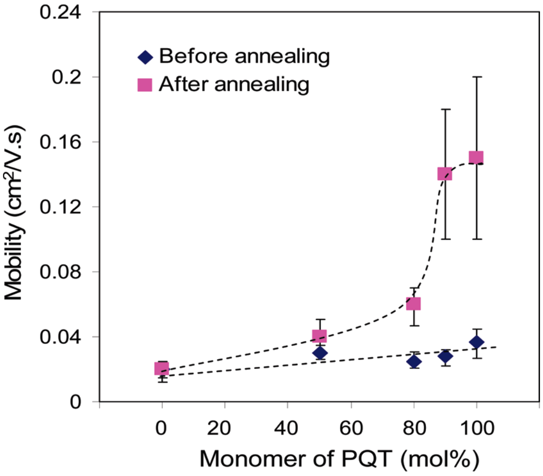


Figure 6. Mobility as a function of the molar percentage of the monomer for **2** (PQT) in the copolythiophene.

result is consistent with their enthalpy values which were obtained from DSC measurement. Also shown in Table 1, the enthalpy value decreased with increasing the content of monomer **A**, indicating a gradually decreased crystallinity with increasing the content of monomer **A**. The incorporation of methyl group does cause a slight perturbation of solid state crystallinity. However, even with 100 mol % of monomer **A**, polymer **3** (**PQT-CH$_3$**) not only showed excellent stability in coating solution for over several weeks, but also reached a reasonable field-effect mobility up to 0.03 cm^2 V^{-1}s^{-1}, which is consistent with our assumption that by strategically attaching a small substituent, the methyl group, in PQT system, the structural regioregularity of long side-chains of **PQT** would not be significantly disturbed and, therefore both polymer **3** and copolymer **4(a−c)** can still form ordered molecular structures and give good mobility values.

Furthermore, it was observed that the OTFTs fabricated from the solution of copolythiophene **4a** in xylene showed high TFT performance with mobility up to 0.18 cm^2 V^{-1} s^{-1} and current on/off >10^7 (Figure 7), which reached similar mobility of **2** (**PQT**) fabricated in dichlorobenzene. The results demonstrated that the solubility characteristics of high performance semiconductor **2** (**PQT**) system of this nature were significantly improved, and in the same time a small amount of steric perturbation effect in solid state has little effect on charge carrier mobility. Therefore, an optimum TFT performance, fabricated from an environmentally benign solvent, was obtained by this strategic judicial structure modification.

Conclusion

In conclusion, we have developed a facile approach to tuning the solubility characteristics of a high mobility polythiophene system, **2** (**PQT**), of this nature. The results demonstrated that significantly improved solution processability in an environmentally benign solvent with high field effect mobility could be simultaneously obtained through the judicial structure modification. Solution processed OTFTs comprised with newly developed **3** (**PQT-CH$_3$**) and copolythiophene **4(a−c)** were fabricated using an environmentally benign solvent and excellent TFT characteristics with high field-effect mobility up to 0.18 cm^2 V^{-1} s^{-1} and current On/Off ratio up to 10^7 were obtained. Thus, they are suitable for OTFT applications in low-cost solution process manufacturing environments.

Experimental Procedures

All the synthetic works, material characterizations, and OTFT device fabrications were done at Xerox Research Centre of Canada, excepting that X-ray diffraction analyses were done at McMaster University, Ontario, Canada.

Instrumentation and Measurements. NMR spectra were obtained in CDCl$_3$ with a Bruker DPX 300 NMR spectrometer with tetramethylsilane as an internal reference. Absorption spectra were measured on a Varian Cary-5 UV−vis−NIR spectrophotometer for the thin films of polymeric semiconductors. Gel permeation chromatography (GPC) was conducted using a Waters 2690 separation module to obtain molecular weights and molecular weight distributions (relative to polystyrene standards). Thermal properties of polymeric semiconductors were measured using a differential scanning calorimeter (DSC) (TA Instruments, DSC2910) with a scanning rate of 10 °C/min. The film X-ray diffractions were performed at room temperature on a Rigaku MiniFlex diffractometer using Cu Kα radiation (λ = 1.5418 Å) with a $\theta-2\theta$ scans configuration. Single crystal X-ray diffractions were performed on a Bruker Smart 6000 CCD 3-circle D8 diffractometer with a Cu RA X-ray source (λ = 1.5418 Å) at room temperature. OTFTs were characterized using a Keithley SCS-4200 characterization system under ambient conditions.

Synthesis. All the chemicals were purchased from Sigma-Aldrich and used without further purification. Polythiophene **2** (**PQT**) was synthesized according to the synthetic method reported in the literature.[19]

5,5′-Bis(3-dodecyl-2-thienyl)-3-methyl-2,2′-dithiophene (Monomer A). A solution of 2-bromo-3-dodecylthiophene (15.36 g, 46.36 mmol) in anhydrous tetrahydrofuran (30 mL) was added slowly over a period of time (~20 min) to a magnetically stirred suspension of magnesium turnings (1.69 g, 69.52 mmol) in anhydrous tetrahydrofuran (10 mL) under an inert argon atmosphere. The resulting mixture was stirred at room temperature for 2.5 h, and then at 50 °C for 30 min before cooling down to room temperature. Then, the freshly prepared Grignard solution was added slowly via a cannula to a mixture of 5,5′-dibromo-3-methyl-2,2′-dithiophene (6.27 g, 18.54 mmol) and [1,3-bis-(diphenylphosphinoethane]dichloronickel(II) (0.48 g, 0.91 mmol) in anhydrous tetrahydrofuran (50 mL) and the resulting mixture was refluxed for 48 h under inert argon atmosphere. Subsequently, the reaction mixture was diluted with ethyl acetate (200 mL), washed with water and dried with magnisium sulfate. After the solvent was removed by using a rotary evaporator, the resulting dark brown crude solid was purified by column chromotography on silica gel with hexane. The final product was obtained from recrystallization in a mixture of methanol and isopropanol, giving 5,5′-bis(3-dodecyl-2-thienyl)-3-methyl-2,2′-dithiophene as an orange yellow crystalline solid (8.61 g, 68% yield).

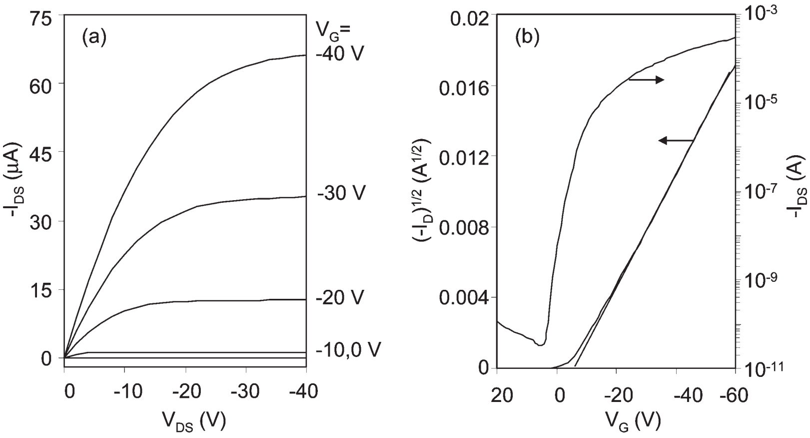


Figure 7. I−V characteristics of exemplary copolymer **4a** TFT device with 90-μm channel length and 5000-μm channel width: (a) output curves at different gate voltages; (b) transfer curve at linear regime.

^{1}H NMR ($CDCl_3$): δ 7.19 (m, 2H), 7.10 (dd, 2H), 6.96(m, 2H), 6.93 (s, 1H), 2.80 (t, 4H), 2.45 (s, 3H), 1.67 (q, 1.65, 4H), 1.27 (bs, 36H), 0.89 (m, 6H). Mp: 34 °C. Anal. Found: C, 71.99; H, 9.06, S, 20.24.

Polythiophene 3 (PQT-CH$_3$). A solution of 5,5′-bis(3-dodecyl-2-thienyl)-3-methyl-2,2′-dithiophene (monomer A, 1.0 g, 1.47 mmol) in chlorobenzene (20 mL) was added slowly to a well stirred mixture of $FeCl_3$ (1.0 g, 6.16 mmol) and chlorobenzene (10 mL), and the resulting mixture was stirred at 60 °C under an argon atmosphere for 48 h. After the resulting mixture was cooled to room temperature, it was diluted with methylene chloride (50 mL) and washed with water (~200 mL) three times. The combined organic layer was stirred in an aqueous ammonia solution (150 mL, 7.5 wt %) for 1 h and then washed with water (~200 mL) three times. The washed organic layer was poured into methanol (~300 mL) with good stirring and the crude product was collected by filtration. Then, the crude product was purifed by Soxhlet extraction with methanol, hexane, and chlorobenzene, respectively. After the soxhlation, the resuting product in chlorobenzene solution was precipitated in methanol (~300 mL) and collected by filtration, giving the final product as a dark red solid (0.57 g, 57%) with following molecular weight properties: M_w 29.2K and M_n 14.8K. ^{1}H NMR ($CDCl_3$): δ 7.13 (m, 2H), 7.03(m, 2H), 6.96 (s, 1H), 2.80 (t, 4H), 2.47 (s, 3H), 1.70 (q, 4H), 1.28 (bs, 36H), 0.89 (m, 6H).

Copolythiophene 4a (x = 10 mol %). A solution of mixed 5,5′-bis(3-dodecyl-2-thienyl)-2,2′-dithiophene (monomer B, 500 mg, 0.75 mmol) and 5,5′-bis(3-dodecyl-2-thienyl)-3-methyl-2,2′-dithiophene (monomer A, 57 mg, 0.084 mmol) in 10 mL of chlorobenzene was added slowly to a well stirred mixture of $FeCl_3$ (500 mg, 3.08 mmol) in 5 mL of chlorobenzene. The resulting mixture was stirred at 60 °C under an argon atmosphere for 48 h. After the polymerization, the resulting mixture was cooled to room temperature, diluted with methylene chloride (~50 mL) and washed with water (~200 mL) three times. The collected organic layer was stirred with an aqueous ammonia solution (150 mL, 7.5 wt %) for 1 h and then washed with water (~200 mL) three times. The collected organic layer was poured into methanol (~300 mL) with good stirring and the crude product was collected by filtration. The crude product was purified by Soxhlet extraction with methanol, heptane, and chlorobenzene, respectively. After the soxhlation the resulting product in chlorobenzene solution was precipitated in methanol (~300 mL), collected by filtration and then dried in a vacuum oven. The content of monomer A in the copolymer was determined from NMR results by integration of the peak area of the methyl group in monomer A at 2.47 ppm (chemical shift) and the ethylene groups attached to the thiophene atoms in both monomer A and monomer B at 2.80 ppm (chemical shift). The result is consistent with the starting monomer ratio. The final product as dark red solid with a yield of 86% (0.48 g) showed the following molecular weight properties: M_w = 30.6K and M_n = 17.4K. ^{1}H NMR ($CDCl_3$): δ 7.16 (m, 2H), 7.07(m, 1.6H), 7.04 (s, 1H), 6.98 (s, 0.1H), 2.80 (t, 4H), 2.47 (s, 0.3H), 1.71 (q, 4H), 1.28 (bs, 36H), 0.89 (t, 6H).

Copolythiophene 4b (x = 20 mol %) and 4c (x = 50 mol %) were prepared in a manner similar to that described in **4a**. The content of monomer A in the copolymer **4b** and **4c** is 19.7 mol % and 50.4 mol %, respectively, calculated from NMR results using the same method as described for copolymer 4a. The results are consistent with the starting monomer ratios as well. The molecular weights of **4b** and **4c** were M_w = 21.5K (M_n = 15.4K) and M_w = 21.6K (M_n = 10.9K), respectively. The yields of **4b** and **4c** were 79% and 68% respectively. ^{1}H NMR ($CDCl_3$) for **4b**: δ 7.16 (m, 2H), 7.08(m, 1H), 6.97 (s, 0.2H), 2.80 (t, 4H), 2.47 (s, 0.6H), 1.71 (q, 4H), 1.28 (bs, 36H), 0.89 (m, 6H). ^{1}H NMR ($CDCl_3$) for **4c**: δ 7.13 (m, 2H), 7.03 (bS, 2H), 6.96 (s, 0.5H), 2.80 (t, 4H), 2.47 (s, 1.5H), 1.71 (q, 4H), 1.28 (bs, 36H), 0.89 (m, 6H).

OTFT Fabrication and Evaluation. All the fabrication and characterization of organic thin-film transistor device (OTFTs) were done under ambient conditions without taking any precautions to isolate the material and device from exposure to air, moisture, and light. Bottom-gate TFT devices were built on n-doped silicon wafer as the gate electrode with a 110 nm thermal silicon oxide (SiO_2) as the dielectric layer. The SiO_2 surface was modified with octyltrichlorosilane (OTS-8) by immersing a cleaned silicon wafer substrate in 0.1 M OTS-8 in toluene at 60 °C for 20 min. The wafer was subsequently rinsed with toluene and isopropanol, and then dried with an air stream. Semiconductor layer was first deposited on the OTS-8-modified SiO_2 layer by spin coating a semiconductor solution in *o*-xylene (1.0 wt %) for **3** (**PQT-CH$_3$**) and **4**(**a**−**c**), and the semiconductor layer of **2** (**PQT-12**) was deposited by spin coating its solution in dichlorobenzene (0.3 wt %) at 1000 rpm for 120 s, and vacuum-dried to give a 20−50 nm-thick semiconductor layer. Subsequently, the gold source and drain electrodes were deposited by vacuum evaporation through a shadow mask, thus creating a series of TFTs with various channel length (L) and width (W) dimensions. All the devices were annealed by heating the dried TFT devices in a vacuum oven at 120−140 °C for 15 to 30 min and then cooled down to room temperature. Patterned transistors with channel length of 90 or 190 μm and channel width of 1 or 5 mm were used for $I-V$ measurements. The mobilities in the saturated regimes were extracted from the following equation:

$$\text{saturated regime } (V_D > V_G): I_D = C_i\mu(W/2L)(V_G - V_T)^2$$

Here I_D is the drain current, C_i is the capacitance per unit area of the gate dielectric layer, and V_G and V_T are respectively the gate voltage and threshold voltage. V_T of the device was determined from the relationship between the square root of I_D at the saturated regime and V_G of the device by extrapolating the measured data to $I_D = 0$.

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Supporting Information Available: Figure showing the NMR spectrum of copolymer **4c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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