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Importance of C₂ symmetry for the device performance of a newly synthesized family of fused-ring thiophenes

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Abstract

We investigated the relationship between molecular structure and field-effect hole mobility in a family of fused-ring polythiophene copolymers that we designed recently. The results suggest that a repeat unit that possesses a C₂ axis perpendicular to the conjugation plane is important to achieve a high-mobility. Our finding is supported by a review of literature data: Many polymer semiconductors showing a hole or electron mobility >0.1 cm²/V·s feature a repeat unit with C₂ symmetry; however exceptions have been found from some push – pull polymer structures.

Introduction

Polymer semiconductors are attracting a great deal of interest for applications in low-cost, large-area, and flexible active matrix display backplanes, radio-frequency identification (RFID) tags, and chemical/biological sensors.^{1–3} The development of regioregular poly(3-hexylthiophene) (P3HT)^{4a–4c} ushered in a new era in the design of soluble thiophene-based polymers with field-effect hole mobilities reaching the 0.1 cm²/V·s benchmark, making these materials competitive with amorphous silicon.^{4d}

Since then, the performance of polymer semiconductors has experienced great improvement,⁵ as various aspects of the repeat unit architecture are being intensively explored. For example, the reduction of the number of alkyl substituents on the thiophene backbone in poly(3,3'-diakyl-quarterthiophene)s (PQTs) was found to promote self-assembly and crystallization, resulting in a field-effect hole mobility up to 0.2 cm²/V·s after post-deposition annealing.⁶ Another particularly noteworthy example are poly(2,5-bis(alkyl-thiophen-2-yl)thieno[3,2-b]thiophenes) (pBTTT), which feature an unsubstituted unit that consists of two fused thiophene rings.⁷ The highly symmetric structure of the fused unit promotes the formation of crystalline regimes, so that the polymer main chains can assemble into large domains on crystallization from a liquid crystal phase. Field-effect hole mobilities of 0.2–0.6 cm²/V·s have been observed.⁷ A third example is poly(2,5-bis(thiophene-2-yl)-(3,7-ditridecanyltetrathienoacene) (P2TDC13FT4), with a field-effect hole mobility exceeding 0.3 cm²/V·s, which was achieved by increasing the rigidity of the thiophene monomer via the use of an alkyl-substituted core that consists of four fused thiophene rings.⁸

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Supporting Information Available: Synthesis, experimental procedures; characterizations and complete author list for reference ¹¹. This material is available free of charge via the Internet at <http://pubs.acs.org>.

Our current understanding of conjugated polymer design calls for a rigid and planar backbone, which will show extended π -conjugation along the main chain and promote close packing, allowing efficient intermolecular charge transfer.⁹ It also calls for alkyl side chains with appropriate length to ensure solubility, arranged at appropriate density to allow dense packing and at appropriate positions to yield a regioregular polymer and ensure minimal defects in conjugation.¹⁰ Additional design rules address stability, for example in terms of limiting the conjugation length to improve oxidative stability of *p*-type materials.¹¹

We recently reported a family of fused thiophene–bithiophene copolymers, as materials of interest for thin film transistor applications.¹² In particular, a comparison of the properties of P2TDC10FT3, P2TDC10FT4 and P2TDC10FT5 (see structures below) indicated that the polymer with the even numbered fused thiophene core exhibits a much smaller lamellar spacing than the polymers featuring odd numbered fused thiophene cores. As a result, transistors fabricated from polymer with the even numbered fused thiophene core (P2TDC10FT4) yielded much higher field-effect mobility than the other two P2TDC10FT3 and P2TDC10FT5.¹² In order to obtain further insight into structure vs. property relationships in polymeric semiconductors, we designed and synthesized two additional polymers in which we have kept the high mobility four-fold fused thiophene core and varied the co-component part to mono- or terthiophene. The chemical structure of these two new polymers, P1TDC13FT4 and P3TDC13FT4, is shown in Scheme 1. Together with P2TDC13FT4, a polymer with a bi-thiophene co-component reported earlier⁸, they constitute a new family of polymers that can help elucidate the role of symmetry of the polymer repeat unit on structure and device performance.

Experimental section

Polymer synthesis

Poly(α -thienyl)-(3,7-ditridecanyltetrathienoacene) (P1TDC13FT4) and poly(α -terthienyl)-(3,7-ditridecanyltetrathienoacene) (P3TDC13FT4) were synthesized following the Scheme 2. Detailed synthetic procedure was described below:

Compound 2 was synthesized and characterized by following reference¹³.

1,1'-[2,2':5',2''-terthiophene]-5,5''-diylbis[1,1,1-trimethylstannane] 3—Butyl lithium (6.8 mL, 16.9 mmol) was added dropwise to terthiophene (2.0 g, 8.1 mmol) in dry tetrahydrofuran (THF) (100 mL) at -78°C . The resulting mixture was slowly warmed up to room temperature and cooled to -78°C again before trimethyl tin chloride (169. mL, 16.9 mmol) was added. This mixture was stirred overnight and poured into saturated NaHCO_3 solution (100 mL). Organic was extracted with ethyl ether (2×100 mL) and washed with water (2×100 mL). The organic solution was dried over MgSO_4 . After removal of the solvent, the solid was stirred in methanol (60 mL) and filtrated. The solid was then heated in ethanol (150 mL) and the upper clear solution was collected. The target compound was collected via crystallization and yielded 1.7 gram of light yellow solid (36.8%). ^1H NMR: Solvent Methylene chloride, 7.28 (d, 2H), 7.11 (d, overlapped, 4H) and 0.39 (s, 18H).

Poly(α -thienyl)-(3,7-ditridecanyltetrathienoacene) (P1TDC13FT4)—2,6-dibromo-3,7-ditridecanyltetrathienoacene (0.61 g, 0.79 mmol) **4**⁸ and 2,5-ditrimethyltinthiophene (0.32 g, 0.79 mmol) **2** were dissolved into toluene (20 mL) in a flask. Dry nitrogen was bubbled through this flask for a few minutes. Tetrakis(triphenylphosphine) palladium(0) (0.046 g, 0.04 mmol) was added to this mixture. Then the flask was heated to 125°C under nitrogen overnight before the content was poured into a methanol (200 mL) and concentrated hydrochloric acid (10 mL) solution and stirred overnight at room temperature. The precipitate was filtered and extracted in a Soxhlet with acetone and hexane for 24 h each.

The collected polymer was dried in vacuum to yield 0.42 grams (76.4%). with molecular weights of M_n 16924, M_w 22690 using GPC (1,2-dichlorobenzene). The polymer had two major absorption peaks at $\lambda_1 = 545$ nm and $\lambda_2 = 589$ nm (thin film). Anal. Calc. for $C_{40}H_{58}S_5$ C, 68.71; H, 8.36; S, 22.93. Found C, 68.04; H, 8.87; S, 22.82

Poly(α -terthienyl)-(3,7-ditridecanyltetrathienoacene) (P3TDC13FT4)—2,6-dibromo-3,7-ditridecanyltetrathienoacene (0.32 g, 0.38 mmol) **4**⁸ and 1,1'-[2,2':5',2''-terthiophene]-5,5''-diylbis[1,1,1-trimethylstannane] (0.22 g, 0.38 mmol) were dissolved into toluene (20 mL) in a flask. Nitrogen was bubbled through this flask for a few minutes. Tetrakis (triphenylphosphine)palladium(0) (0.02 g, 0.19 mmol) was added to the mixture. Then the flask was heated to 125 °C under nitrogen overnight before the content was poured into methanol (200 mL) and concentrated hydrochloric acid (10 mL) solution and stirred overnight at room temperature. The precipitate was filtered and extracted in a Soxhlet <check spelling> with acetone and hexane for 24 h each. The collected polymer was dried in vacuum to yield 0.28 grams (77.8 %) with molecular weights of M_n 10174, M_w 11221 using GPC (1,2-dichlorobenzene). The polymer had two major absorption peaks at $\lambda_1 = 545$ nm and $\lambda_2 = 589$ nm (thin film). Anal. Calc. for $C_{48}H_{62}S_7$ C, 66.77; H, 7.24; S, 25.99 Found C, 66.01; H, 6.97; S, 26.82.

Characterization measurements

Polymers were characterized by elemental analysis using a CE Elantech FlashEA 1112 Series CNHS-O analyzer. Polymer molecular weights were evaluated via gel permeation chromatography (GPC) using a Waters Alliance 2690 separation module with a Styragel HT3 column (4.6 $\times$ 300mm, 10 μ m, 500–30,000 molecular weight range) and a Styragel HT6E column (4.6 $\times$ 300mm, 10 μ m, 5,000–10,000,000 molecular weight range) connected in series. Detection was completed by a Waters Model 2410 Refractive Index Detector and a Waters Model 996 Photodiode Array Detector. Calibrations were carried out with external polystyrene standards, Easi-Cal PS-2 A and B (Polymer Laboratories, Ltd.) at 0.1% w/v in toluene. The mobile phase was 1,2-dichlorobenzene with a flow rate of 0.5 mL/minute and a column temperature of 35 °C. Samples were prepared at a concentration of 1mg/mL in dichlorobenzene. Injection volume was 50 μ L.

Structure and crystallinity of polymer films were analyzed using X-Ray diffraction (XRD) with a Scintag diffractometer employing a Cu target ($\lambda = 1.5405$ Å). A θ -2 θ scan with a step size of 0.02° was set up between 2° and 12° with scan rate of 0.02 °/s. For X-Ray measurements polymers were spin cast from pentachloroethane solution (3 mg/mL) on HMDS treated SiO₂. These samples were further annealed at 150 °C for 10 minutes. Atomic Force Microscopy (AFM) was carried out in tapping mode on a Digital Instruments DI-3000.

Fabrication and Characterization of OFET Devices

Top-contact bottom-gate transistors using PmTDC13FT4 ($m = 1, 3$) as the organic semiconducting channel were fabricated in ambient conditions. Heavily doped Si<100> wafers were used as gate electrodes with a 300 nm thermally grown silicon dioxide layer as the gate dielectric. The substrates were cleaned by sonication in semiconductor grade acetone and isopropanol for 10 min in each solvent, and then given a 15 min air plasma treatment. Hexamethyldisilazane (HMDS, $\geq 99\%$) was used for surface modification of the gate dielectric layer. Prior to the SAM treatment, pre-cleaned Si/SiO₂ samples were baked at 200 °C for 15 min in N₂ for dehydration.

Solutions of polymers in pentachloroethane (3 mg/ml) were prepared by heating to 170 °C for 30 min with stirring to speed up dissolution. Polymer films were then deposited by spin-coating at 1500 RPM for 40 seconds. The films were baked at 150 °C in a vacuum chamber to remove

the solvent prior to thermal evaporation of top contacts. Gold contacts (50 nm) for source and drain electrodes were vacuum-deposited at a rate of 2.5 Å/s through a metal shadow mask that defined a series of transistor devices with a channel length (L) of 80 µm and a channel width (W) of 1 mm. Polymeric transistors were characterized in air using the Cascade Microtech Model 12861B probe station and Keithley 4200-SCS Semiconductor Characterization System.

When measuring current-voltage curves and transfer curves, the gate voltage (V_G) was scanned from +20 V to -80 V. The mobility was evaluated from the saturation regime with a source-drain voltage (V_{SD}) = -80 V using the following equation:

$$I_{DS,sat} = \frac{W}{2 \cdot L} \cdot \mu_i \cdot C_r \cdot (V_G - V_{TH})^2. \quad (1)$$

where I_{DS} is the drain current, C_r is the capacitance per unit area of the gate dielectric layer, V_G is the gate voltage, and V_{TH} is the threshold voltage. V_{TH} was determined from the intercept in the plot of $(I_{DS})^{1/2}$ vs. V_G .

Results and discussions

Molecular weight

Gel Permeation Chromatography (GPC) was used to characterize molecular weight of P1TDC13FT4 and P3TDC13FT4 using 1,2-dichlorobenzene as solvent.. Table 1 listed the results:

GPC results showed that P3TDC13FT4 gives narrower molecular weight distribution with polydispersity equal to 1.10. P3TDC13FT4 polymer also showed a smaller molecular weight which indicates P3TDC13FT4 polymer has slightly lower solubility in the toluene system. However, both polymers are soluble enough to be dissolved into pentachloroethane for device fabrications.

UV-vis study

UV-vis studies were conducted in order to understand whether the P1TDC13FT4 and P3TDC13FT4 backbones are twisted. Both polymers were dissolved into chloroform, and their UV-vis spectra were compared to that of the P2TDC13FT4 polymer (see Figure 1).⁸

P2TDC13FT4 and P3TDC13FT4 showed absorption maxima at 480 nm and 486 nm, respectively, while P1TDC13FT4 showed an absorption maximum at 545 nm. Since P2T and P3T polymer are linked by two and three single thiophene units with single bond, they can rotate freely in solution which results in shortening of the effective conjugation length. In the case of P1T, the rotational freedom is limited by the steric hindrance of the alkyl chains by the fused thiophene ring system. The absorption maximum at 545 nm indicates a longer effective conjugation length. However, in the solid state thin film UV-vis measurements for these three polymers yielded the same absorption maxima at 545 nm, with a shoulder peak at 589 nm for P1TDC13FT4 and P3TDC13FT4 polymers and 575 nm for P2TDC13FT4 polymer. These data indicate that conjugation along the polymer backbone is maintained, regardless if the polymer contains a single, bi- or tri- thiophene unit as a co-component. The shift of the shoulder absorption of P1T and P3T to lower energies suggests that P1T and P3T are slightly better conjugated than the P2TDC13FT4 polymer.

Structure characterization by X-ray diffraction and AFM

In analyzing the diffraction patterns, we assume the previously observed polymer packing with lamella formation parallel to the substrate. From the recorded diffraction patterns it is apparent

that the lamellar spacing varies between samples, even though the side chain length remained constant. The lamellar spacings were determined to be 19.4 Å, 18.7 Å, and 24.5 Å for P1TDC13FT4, P2TDC13FT4, and P3TDC13FT4, respectively. The P3TDC13FT4 lamellar spacing is the biggest in this series of polymers, suggesting that due to the lack of C2 symmetry and consequently the side chains of adjacent fused backbones pointing in different directions, close packing of vertically adjacent lamellae is inhibited (see Figure 2).

The P1TDC13FT4 has a similar lamellae spacing to P2TDC13FT4, which possesses C2 symmetry. This can be explained by considering the implication of a single thiophene ring between the fused thiophene backbones along the P1TDC13FT4 polymer chain and the increased freedom of rotation around those bonds. It may be energetically favorable for the fused backbone and thiophene ring to rotate in order to reduce the hindrance of two closely located side chains pointing in the same direction, thereby resulting in sidechains pointing in opposite directions and allowing close packing similar to P2TDC13FT4.

Using Scherrer analysis we determined the average lamellar stack heights to be 11.4, 9.0, and 7.2 lamellae, respectively, which confirms that P3TDC13FT4 film has the worst lamellar correlation, while P1TDC13FT4 and P2TDC13FT4 have similar ordering.

Additional features of the XRD measurement are the Laue oscillations close to the (100) peak in P2TDC13FT4 and P3TDC13FT4, arising from a finite number of lamellae in the film. The presence of these oscillations suggests higher film ordering in the case of P2TDC13FT4 and P3TDC13FT4 as compared to P1TDC13FT4, where only one oscillation can be seen. The Laue oscillations yield an alternative determination of the lamellar stack height. From the oscillations we are able to determine the lamellae stack height to be 8.5 and 5.8 lamellae for P2TDC13FT4 and P3TDC13FT4, respectively, which are similar to the results of the Scherrer analysis. The Laue oscillations are a direct measure of the average stack height variation, hence the P2 and P3 films seem to consist of a quite narrowly determined number of lamellae, while in the P1 film the number of lamellae in the film has a wider spread.

AFM was utilized to study the topography of the polymer films. In the case of P2TDC13FT4 and P3TDC13FT4, where more ordered lamellae are expected based on the XRD analysis, the topography reveals a terraced lamellae formation similar to PBTTT^{11a}. In contrast P1TDC13FT4, has a much rougher topography reminiscent of P3HT films, with no clearly discernable lamellar terraces. The average terrace diameter of the P2TDC13FT4 film is significantly higher than for P3TDC13FT4 producing smoother films which would be favorable for lateral charge transport. Through XRD and AFM analysis for these three polymers, the importance of C2 symmetry begins to emerge. Hindrance due to lack of C2 symmetry causes increased lamellae spacing, decreasing the π system delocalization as seen in the case of P3TDC13FT4. In contrast P1TDC13FT4 films have a rougher appearance and much less well-organized lamellae. This higher degree of disorder due to lack of C2 symmetry seems to be the limiting factor in the observed mobility. The P2 polymer with C2 symmetry seems to have gotten the best of both worlds with a small lamellar spacing and well-formed lamellar order yielding significantly higher mobility (see Figure 3).

Device performance

The OFET properties of the polymers were evaluated using top contact devices fabricated by spin-casting the room temperature pentachloroethane solution of the polymers on SiO₂ gate dielectrics, which were treated by hexamethyldisilazane (HMDS). Figures 4 and 5 show the typical current-voltage characteristics of polymeric OFET devices with a channel length (L) = 80 μ m, where I_{SD} , V_{SD} , and V_G represent source-drain current, source-drain voltage, and gate voltage, respectively. The saturation region field-effect mobility (μ) was calculated from the transfer characteristics of the OFETs using the slope derived from $(-I_{SD})^{1/2}$ versus V_G plots

between -100 to -60 V (Figures 4). The threshold voltages (V_{TH}) of different polymer OFETs were derived from the onset of the transfer curves.

The output curves (Figure 5) of polymers with different number of thiophene co-components show good saturation and linear behavior in the range of lower V_{SD} . The linearity of the output curves in the low V_{SD} regime (0 to -5 V) indicates that Au forms an ohmic contact with polymers. Mobility values, on/off ratios and threshold voltages of the polymer devices for P1TDC13FT4 and P3TDC13FT4 on HMDS treated SiO_2 surfaces are summarized in Table 2. All polymer devices showed very good reproducibility and low deviation values, which indicates the excellent uniformity of the polymer thin films. OFET characteristics of polymers on HMDS treated surfaces are shown in the figures. From the table, the P1TDC13FT4 polymer gave the higher mobility values than that of P3TDC13FT4 polymer. However, the 0.048 cm^2/Vs mobility values obtained from HMDS treated surfaces is about six-fold smaller than our reported value of 0.33 cm^2/Vs for P2TDC13FT4.⁸ On the other hand, P3TDC13FT4 polymers showed one order magnitude lower mobility values than P2TDC13FT4.

Symmetry and mobility

Combined with our previous device performance study, we have investigated the transport properties for two series of fused thiophene copolymers. In the first case, we characterized a family of P2TDC10FT3, P2TDC10FT4 and P2TDC10FT5, in a recently reported family of thienoacene copolymers.¹² In this report, we further characterized two more polymer P1TDC13FT4 and P3TDC13FT4 to compare with our previous published P2TDC13FT4 data. In the first series, the length of the fused core was systematically increased from three to four to five units, leading to an increase in the backbone rigidity, while the length of the alkyl side chains was kept constant to facilitate comparisons between the three polymers. In the second case, the four member fused core was kept, while the co-component part was changed from bithiophene to include single thiophene and terthiophene moieties. In the first series, devices made from the polymer with the four fused rings (P2TDC10FT4) showed a hole mobility of 0.087 cm^2/Vs , whereas devices made from the polymers with the three (P2TDC10FT3) and five (P2TDC10FT5) fused rings showed hole mobilities of 0.0017 and 0.0023 cm^2/Vs , respectively. Device made from P1TDC13FT4 and P3TDC13FT4 showed a hole mobility of 0.042 and 0.022 cm^2/Vs , respectively, which is about one order of magnitude lower than the 0.33 cm^2/Vs value achieved with P2TDC13FT4⁸.

The fact that the performance of P2TDC10FT5 is an order of magnitude lower than that of P2TDC10FT4 is surprising. In the context of semi-classical electron-transfer theory, the Marcus model of charge-transfer suggests an increase of the hopping rate with decreasing reorganization energies. Calculations with Gaussian 03 using BL3YP/6-31G** show that a five-fused-ring small molecule has lower reorganization energy than a four-fused-ring one (see the Supporting Information). Therefore, with all else being equal, a higher mobility would be expected in P2TDC10FT5.¹⁴ Moreover, one would expect that the increase in the length of the rigid core from four to five fused rings would lead to better packing and hence lead to a higher mobility. As opposed to this expectation, synchrotron x-ray scattering shows that both P2TDC10FT3 and P2TDC10FT5 show poor lamellar packing, in contrast with P2TDC10FT4 which shows good lamellae formation and in-plane order as well as a much smaller lamellar spacing.¹²

Our data show that packing and mobility depend on whether the number of fused rings or co-component is odd (low mobility) or even (high mobility). This variation affects not only the length of the rigid core, but also the relative location of the side chains with respect to the polymer backbone. In fact, the side chains in P2TDC10FT3 and P2TDC10FT5 are on the same side of the conjugated core, while in P2TDC10FT4 they are on opposite sides. This means that

the relative arrangement of side chains, rather than the length of the rigid core, dominates chain packing in the film.

In the second case of P1TDC13FT4 and P3TDC13FT4 polymers, we have kept the FT4 core, and thus avoided the direction change of the substituted alkyl groups. Changing the bithiophene co unit to single thiophene and terthiophene switched the even number of connecting thiophene moieties to odd numbers, and significant mobility decreases were observed. This decrease in mobility cannot be explained by a break-down of the extended conjugation since UV-Vis spectra of the P1TDC13FT4 and P3TDC13FT4 polymer thin films show almost no changes compared to that of P2TDC13FT4.⁸ The reason for this behavior becomes clear, if one thinks in terms of the symmetry of the repeat unit, as Fig. 6 aims to illustrate:

In the first case, upon spin coating, the polymer chains arrange parallel to the substrate. This process is, to first order, random, and will lead to a distribution of orientations of the side chains with respect to the substrate. If both side chains are on the same side of the backbone (a_1), the two possible configurations of side chains pointing towards the substrate and side chains pointing away from the substrate will be different. Similarly, an asymmetry in co-monomer unit (a_2) will yield two distinct configurations when the polymer chains arrange parallel to the substrate. However, if the side chains are arranged in such a fashion so that the repeat unit possesses a C_2 axis perpendicular to the conjugation plane (b), the two possible configurations will be equivalent. This will clearly aid in the packing of main chains. Moreover, we found that the packing of the main chains is intimately related to achieving high mobility.

It is interesting to raise the question whether the experimental results presented here would constitute a general design rule. Such a rule cannot possibly be suggested using examples from only a single polymer family. The literature seems, however, ripe with data that support this C_2 symmetry design rule. One example is a pair of thienothiophene copolymers, pBTtT and pBTCT, reported by McCulloch and Heeney et al.^{11,15}. The repeat unit of pBTtT shows C_2 group symmetry with the “anti” positioning of the sulfur atoms in the thieno[3,2-b]thiophene monomer. In contrast to pBTtT, pBTCT shows no C_2 symmetry yielding a mobility of only $0.03 \text{ cm}^2/\text{V}\cdot\text{s}$, over an order of magnitude lower than the reported mobility for pBTtT. Aside from PQT-12, pBTtT, and P2TDC13FT4, several polymer semiconductors that show hole mobility higher than $0.1 \text{ cm}^2/\text{V}\cdot\text{s}$ were reported recently, including PTzQTs-R,¹⁶ PQTBTz-C12,¹⁷ PETV12T¹⁸ and poly(4,8-dialkyl-2,6-bis(3-alkylthiophen-2-yl)benzo[1,2-*b*:4,5-*b'*]dithiophene)- a benzodithiophene copolymer.¹⁹ As shown in Table 3, the repeat units of these polymers show C_2 symmetry, supporting the C_2 rule proposed here.

Moreover, the recently reported *n*-type polymer poly{[N,N'-bis(2-octyldodecyl)-naphthalene-1,4,5,8-bis(dicarboximide)-2,6-diyl]-alt-5,5'-(2,2'-bithiophene)} {P(NDI2OD-T2)}, which shows a high electron mobility of $0.1\text{--}0.85 \text{ cm}^2/\text{V}\cdot\text{s}$,²⁰ also has a repeat unit that shows C_2 symmetry.

The question arises whether this C_2 rule is also applicable to small molecules. A quick review of structures in the Organic Field-Effect Transistors book by Bao and Locklin indicate that molecules with mobility larger than $1.0 \text{ cm}^2/\text{Vs}$ fulfilled the C_2 rule out of a set of more than 400 molecules.²⁵ Table 4 highlights such reported high mobility structures. However, since small molecules can rearrange during crystallization much easier than polymers, the C_2 symmetry rule is of higher importance for the latter class of materials.

We also need to note the exceptions from the C_2 rule. First of all, the prototypical conjugated polymer regioregular P3HT is the most marked exception. Tsao et al. reported a cyclopentadithiophene-benzothiadiazole polymer with mobility of $1.3 \text{ cm}^2/\text{V}\cdot\text{s}$ through a slow-dip coating process, while Guo et al. reported a PhBT polymer with mobility of $0.2 \text{ cm}^2/\text{V}\cdot\text{s}$.^{37,38} It should be noted that the slow-dip coating method used to forming films is similar

to crystal growing process and yields to films that are better ordered (hence have fewer defects) than spin coated ones.³⁹ Furthermore, Bao's group also reported a thienopirazine-fluorene copolymer with a maximum field-effect mobility of $0.2 \text{ cm}^2/\text{V}\cdot\text{s}$.⁴⁰ It should also be noted that these latter three exceptions are donor – acceptor structures. In these cases, the thin film formation process may strongly be influenced by dipole interactions and the charge carrier transport mechanism may be different from the symmetric molecules and polymers. This raises the tantalizing prospect that such functionalities and advanced deposition methods offer new ways to tune structure-property relationships.

Conclusion

The relationship between molecular structure and field-effect mobility was investigated in a family of fused-ring thiophene copolymers. The results strongly suggest a correlation between a repeat unit that possesses a C_2 axis perpendicular to the conjugation plane, a minimum attainable lamellar spacing, and a high field-effect mobility. Both our experimental results and combined literature survey supports this suggestion: Although a few notable exceptions to this rule have been identified, C_2 symmetry seems to pave the way to high mobility polymers.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1.
UV-vis of P1TDC13FT4, P2TDC13FT4 and P3TDC13FT4 in solution and solid state

Figure 2.
X-ray diffraction patterns of PnTDC13FT4 films ($n = 1, 2, 3$).

Figure 3. AFM images and associated height distribution functions of PnTDC13FT4 films ($n = 1, 2, 3$ from left to right). P2TDC13FT4 and P3TDC13FT4 show a clear lamellar structure with terraces, as also confirmed by the narrow height distributions featuring two prominent heights. The P1TDC13FT4 film features a much rougher surface.

Figure 4. Transfer characteristics of the annealed polymer devices on HMDS treated SiO_2/Si for P1TDC13FT4 and P3TDC13FT4 at $V_{SD} = -80$ V

Figure 5. Output curves of the annealed polymer devices on HMDS treated treated SiO_2/Si for (a) P1TDC13FT4 and (b) P3TDC13FT4 at different gate voltages.

Figure 6. Possible configurations of the repeat unit with respect to the substrate, for repeat units without (a_1 and a_2) and with (b) C_2 symmetry. Judging from the family of closely related conjugated polymers we have investigated, C_2 symmetry appears to enable a very small lamellar period and to promote high mobility.

Scheme 1.

Molecular structures of (a) P2TDC10FT_n ($n = 3, 4, 5$) polymers and (b) P_mTDC13FT₄ ($m = 1, 2, 3$)

Scheme 2.
Synthesis of P1TDC13FT4 and P3TDC13FT4 polymers

Table 1

GPC characterizations of P1TDC13FT4 and P3TDC13FT4

Polymer	Mn	Mw	Polydispersity
P1TDC13FT4	16924	22690	1.34
P3TDC13FT4	10174	11221	1.10

Table 2
Device Performance of P1TDC13FT4 and P3TDC13FT4 polymers on HMDS treated SiO₂/Si

Polymers	Maximum Mobility μ_{max} (cm ² /Vs)	Average mobility of 40 devices μ_{average} (cm ² /Vs)	Deviation (cm ² /Vs)	On/off ratio	V _i (V)
P1TDC13FT4	0.0479	0.0421	0.00532	10 ³ –10 ⁴	10
P3TDC13FT4	0.0269	0.0226	0.00171	10 ⁴ –10 ⁵	5
P2TDC10FT5	0.0023	0.0015	0.00053	10 ³ –10 ⁴	–9/12

Table 3

High performance semiconducting polymers and the symmetry of their repeating units.

Materials	Field-Eff
<p style="text-align: center;">PBTtT</p>
<p style="text-align: center;">PQT-12</p>
<p style="text-align: center;">P2TDC13FT4</p>	

Materials	Field-Eff
<p>The structure shows a polymer repeat unit with a central benzothiazole core. The 2 and 5 positions of the benzothiazole are connected to two thiophene rings. Each thiophene ring is further substituted with a C₁₂H₂₅ alkyl chain and another thiophene ring. The entire unit is enclosed in large parentheses with a subscript 'n'.</p> <p>PQTBTz-C12</p>
<p>The structure shows a polymer repeat unit with a central benzothiazole core. The 2 and 5 positions of the benzothiazole are connected to two thiophene rings. Each thiophene ring is substituted with an 'R' group and another thiophene ring. The entire unit is enclosed in large parentheses with a subscript 'n'.</p> <p>PTzQT-R</p>
<p>The structure shows a polymer repeat unit with a central trans-vinylene bridge. Each end of the bridge is connected to a thiophene ring, which is further substituted with a C₁₂H₂₅ alkyl chain and another thiophene ring. The entire unit is enclosed in large parentheses with a subscript 'n'.</p> <p>PETV12T</p>	

Materials	Field-Eff
<p style="text-align: center;">P(NDI2OD-T2)</p>	0.
<p style="text-align: center;">Benzodithiophene copolymer</p>	C

Materials	Field-Eff
<p style="text-align: center;">P3HT</p>
<p style="text-align: center;">PBTCT</p>
<p style="text-align: center;">F8T2</p>	0

Materials	Field-Eff
<p>The structure shows a polymer repeat unit enclosed in large parentheses with a subscript 'n'. The backbone consists of three fused aromatic rings: a fluorene unit (two benzene rings fused to a central five-membered ring) and a benzothiazole unit (a benzene ring fused to a five-membered ring containing two nitrogen atoms and one sulfur atom). Two octyl chains, labeled C_8H_{17}, are attached to the fluorene unit. The polymer chain continues through the fluorene and benzothiazole units.</p> <p style="text-align: center;">F8BT</p>
<p>The structure shows a polymer repeat unit enclosed in large parentheses with a subscript 'n'. The backbone consists of four thiophene rings connected by single bonds. A central silicon atom (Si) is bonded to two of the thiophene rings. Two n-hexyl chains, labeled $n-C_6H_{13}$, are attached to the silicon atom. The polymer chain continues through the thiophene rings.</p> <p style="text-align: center;">TS6T2</p>
<p>The structure shows a polymer repeat unit enclosed in large parentheses with a subscript 'n'. The backbone consists of a central nitrogen atom (N) bonded to two phenyl rings. The polymer chain continues through the phenyl rings.</p> <p style="text-align: center;">PTAA</p>	

Table 4

High Mobility Semiconducting Small Molecules

Materials	Field-E

Materials	Field-I