The backbone rigidity and its influence on the morphology and charge mobility of FBT based conjugated polymers†

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A series of three PVTh4FBT polymers containing different alkyl side chain placement was synthesized. The thermochromic behaviors and DFT calculations indicated that the backbone coplanarity and rigidity of the PVTh4FBT polymers can be effectively modulated by adjusting the side chain position and density. Higher ordered and better oriented edge-on lamellar packing was formed by P1, which possesses the most rigid backbone among the three polymers and pre-aggregates in the solution. P1 also delivered the highest hole mobility (0.26 cm² V⁻¹ s⁻¹) among the three analogues because its thin-film morphology is in favor of charge transport.

Introduction

Solution-processed organic field-effect transistors (OFETs) have attracted substantial research attention for their potential application as low-cost components in large-area flexible electronics. Significant advances in molecular design and device physics have led to polymer-based OFETs with a charge mobility (μ) of over 1.0 cm² V⁻¹ s⁻¹. Based on the Marcus theory, low reorganization energies (λreorgS) and high degrees of intermolecular electronic coupling are conducive for conjugated molecules to reach high μ values. By fusing the neighboring aromatic units, chemical rigidification inhibits inter-annular rotation. Thus, conjugated systems with multifused heteroarenes possess reduced λreorgS and a better coplanarity. Along with suitable lateral solubilizing side chains, effective intermolecular electronic coupling and a high μ have also been reported. Recently, non-fused conjugated polymers also showed comparable and even higher μ values than their fused counterparts. Without chemical rigidification, thiophene-based conjugated backbones are easily distorted through inter-annular rotation, as indicated by the low twist glass transition temperatures of poly(3-alkylthiophenes). The low energy barriers for the inter-annular rotation and the low conformational preferences of many non-fused donor–acceptor (D–A) backbones also lead to multiple possible spatial arrangements of the conjugated backbones and affect the polymer packing in the condensed phases. Moreover, the backbone coplanarity and packing order of non-fused conjugated polymers are more sensitive to the bulkiness, chain lengths and attachment densities of the alkyl side chains. To physically rigidify the non-fused backbones, the stability of the coplanar state, that is, the rigidity of the conjugated backbone, should be modulated. The rigidity of the conjugated backbone can be affected by the main chain structure as well as the solubilizing side chains. 5,6-Difluorobenzo-2,1,3-thiadiazole (FBT) based D–A copolymers are conjugated polymers with high performances. However, the ways of modulating the rigidity of FBT polymers and the influence of the backbone rigidity on the packing order and the charge mobility have not been carefully studied. Since, theoretically, the FBT unit is considered to be inefficient at locking the conformations, the backbone properties of non-fused FBT polymers can be critical to the solid-state order and the OFET performances. Herein, a family of 5,6-difluorobenzo-2,1,3-thiadiazole-4,7-diyl (FBT)-bis-(bithiophenylene)vinylene PVTh4FBT copolymers – P1, P2, and P3 (Scheme 1) – was synthesized. All three polymers share the same backbone structure, but P1 and P2 are different in their side chain positions and P3 has a higher side chain density than the other two. The influence of the vinylenne group, along with the position and attached density of the side chains, on the backbone rigidity, solid-state morphology and OFET mobility was investigated. The results show that the backbone...
rigidity of PVTh_{4}FBT can be effectively modulated by adjusting the side chain position and density. More importantly, the solid-state order and crystal orientations of the PVTh_{4}FBT polymers were affected by the backbone properties. The highest backbone rigidity of P1 resulted in the most ordered and well-oriented edge-on lamellae on the substrate, which rendered P1 with the highest μ_{h} among the three polymers.

### Experimental section

#### General measurements and characterization

All chemicals were purchased from Aldrich or Acros and were used as-received unless otherwise specified. The synthesis and characterization of the FBT monomers, DTV monomers and polymers were summarized in the ESI.† FBT-1 was synthesized according to the literature.\textsuperscript{14} \textsuperscript{1}H and \textsuperscript{13}C NMR spectra were recorded using a Varian 300 MHz instrument spectrometer. Molecular weights and polydispersity indices (PDI) of the polymers were determined by high temperature (120 °C) gel permeation chromatography (GPC) using a Viscotek module-350 system with polystyrene as the standard and 1,2,4-trichlorobenzene (TCB) as the eluent. Differential scanning calorimetry (DSC) was performed on a TA Q200 Instrument and thermogravimetric analysis (TGA) was performed on a Perkin Elmer Pyris under a nitrogen atmosphere at a heating rate of 10 °C min\textsuperscript{-1}. Absorption spectra were collected on an HP8453 UV-vis spectrophotometer. The electrochemical cyclic voltammetry (CV) was conducted on a CH Instruments Model 611D. A carbon glass coated with a thin polymer film was used as the working electrode and an Ag/Ag\textsuperscript{+} electrode was used as the reference electrode, while 0.1 M tetrabutylammonium hexafluorophosphate (Bu\textsubscript{4}NPF\textsubscript{6}) in acetonitrile was used as the electrolyte. CV curves were calibrated using ferrocene as the standard whose oxidation potential was set at −4.8 eV with respect to zero vacuum level. The E\textsubscript{HOMO} were derived from the equation $E_{\text{HOMO}} = -(E_{\text{onset}}^{\text{onset}} - E_{\text{onset}}^{(\text{ferrocene})} + 4.8) \text{ eV}$. A Veeco Diinnova atomic force microscope (AFM) in the tapping mode was used to characterize the surface morphology of the polymer thin films. The grazing incidence X-ray diffraction (GIXD) patterns of PVTh_{4}FBT polymers were recorded at the BL01C2 beamline of the National Synchrotron Radiation Research Center (NSRRC) in Taiwan. The ring energy of NSRRC was operated at 1.5 GeV with a typical current of 300 mA. The wavelength of the incident X-rays was 1.0332 Å (12.0 keV), delivered from the superconducting wavelength-shifting magnet, and an Si(111) double-crystal monochromator. The samples were placed horizontally on a sample stage. With an incident angle of 0.2°, GIXD was conducted and the pattern was collected with a detector system that included a CMOS flat panel X-ray detector, C9728DK. The scattering wave vector, defined as $q = 4\pi\sin\theta/\lambda$ (with $\theta$ being the scattering angle), was calibrated using silver behenate, sodalite, and silicon powders, respectively. The thin films used in the AFM and GIXD measurements were prepared according to the processes used in the OFET fabrication.

#### Computational details

Quantum-chemical calculations were performed with the Gaussian09 suite employing the B3LYP density functional in combination with the 6-311G(d,p) basis set. Geometry optimizations were performed with tight SCF and convergence criteria and an ultrafine integration grid applying the GEDIIS optimization algorithm. The energy minimized conformations of each polymer segment was confirmed by frequency analysis. The torsion potential energy surface was produced by scan of single-point energy calculations at the B3LYP/6-311G(d,p) level, and the dihedral angle $\theta$ was stepped in 10° increments from the optimized geometry.

#### OFET fabrication

An n-type heavily doped Si wafer with an SiO\textsubscript{2} layer of 300 nm and a capacitance per unit area of 11 nF cm\textsuperscript{-2} was used as the gate electrode and the dielectric layer. Thin films (40–60 nm in thickness) of polymers were deposited on the octadecyltri-chlorosilane (ODTS)-treated SiO\textsubscript{2}/Si substrates by spin-coating ODCB solutions (2.5 mg mL\textsuperscript{-1} and 5 mg mL\textsuperscript{-1}) or TCB solutions (2.5 mg mL\textsuperscript{-1}) of the polymers. Then, the thin films were annealed at 200 °C under a nitrogen atmosphere for 30 min. The gold source and drain electrodes (30 nm in thickness) were deposited by vacuum evaporation on the organic layer through a shadow mask, affording a bottom-gate, top-contact device configuration. Electrical measurements of OFET devices were carried out at room temperature under nitrogen using a 4156C (Agilent Technologies). The field-effect mobility was calculated in the saturation regime using the equation $\mu_{DS} = (\mu W C_{i}/2L)(V_{G} - V_{T})^{2}$, where $\mu_{DS}$ is the drain–source current, $\mu$ is the field-effect mobility, $W$ is the channel width (1 mm), $L$ is the channel length (0.1 mm), $C_{i}$ is the capacitance per unit area of the gate dielectric layer, and $V_{G}$ is the gate voltage.
Results and discussion

Synthesis and thermal analysis

The synthetic routes to the PVTh₄FBT polymers are depicted in Scheme 1. Pd-catalyzed Stille-coupling copolymerization of 5,6-difluoro-4,7-bis(5-trimethylstannyl)thiophen-2-yl)benzo[c]-[1,2,5]thiadiazole (FBT-1) and (E)-1,2-bis(5-bromo-3-(2-octyl dodecyl)thiophen-2-yl)ethene (DTV-1) afforded the formation of P1 in 73% yield; copolymerization of 4,7-bis(5-bromo-4-(2-octyl dodecyl)thiophen-2-yl)-5,6-difluoro-benzo[c][1,2,5]thiadiazole (FBT-2) and (E)-1,2-bis(5-trimethylstannyl)thiophen-2-yl)ethene (DTV-2) resulted in the formation of P2 in 63% yield; and copolymerization of 4,7-bis(5-bromo-4-dodecylthiophen-2-yl)-5,6-difluorobenzol[c][1,2,5]thiadiazole (FBT-3) and (E)-1,2-bis(3-dodecyl-5-(trimethylstannyl)thiophen-2-yl)ethene (DTV-3) resulted in the formation of P3 in 39% yield. The molecular weights and polydispersity (PDI) of the polymers are $M_n = 32.3$ kDa (PDI = 2.8) for P1, $M_n = 38.2$ kDa (PDI = 2.1) for P2, $M_n = 11.2$ kDa (PDI = 1.5) for P3. The PVTh₄FBT polymers exhibited good thermal stability with 1% weight loss temperatures ($T_{\text{ds}}$) over 360 °C as measured by thermogravimetric analysis (Fig. S1†). The polymers were heated up to 300 °C to avoid thermal degradation in the differential scanning calorimetry (DSC) analysis (Fig. S2†). The melting temperatures ($T_m$) and the crystallization temperature of P2 were observed at 262 °C and 232 °C, respectively, but no phase transition was found for P1 and P3 below 300 °C. Since the grazing-incidence X-ray diffraction (GIXD) measurements discussed below confirmed that P1–P3 all form ordered solid-state phases, the $T_m$s of the ordered phases of P1 and P3 should be above the upper temperature limit of the DSC measurements (300 °C), and thus, the melting processes of the two polymers were not detected. The lower $T_m$ of P2 indicated that the bulky 2-octyl-dodecyl (OD) substituent at the 4′ position (see Fig. S3† for the number code) of the (E)-1,2-bis(2,2′-bithiophen-5-yl)ethene structural unit decreases the thermal stability of the crystalline state. Since the three polymers share the same backbone, the DSC results gave the first indication that the alkyl chain position affects the backbone rigidity and phase stability of the PVTh₄FBT polymers.

Optical and electrochemical properties

The optical behaviors of the polymers were investigated by ultraviolet-visible (UV-Vis) spectroscopy in dilute o-dichlorobenzene (ODCB) solutions and as thin films on glass. The characteristics of the UV-Vis spectrum of the PVTh₄FBT polymers are summarized in Table 1. As shown in Fig. 1, the absorption bands with $\lambda_{\text{max}}$s of about 450 nm can be attributed to a localized $\pi-\pi^*$ transition. The $\lambda_{\text{max}}$ of the photo-induced intramolecular charge transfer (ICT) absorptions of P1 is 655 nm. Compared to the $\lambda_{\text{max}}$ of PTh₄FBT (the polymer analogue without the vinylene structural unit) in our previous study, they the absorption of P1 bathochromic shifts by 80 nm. Thus, the vinylene unit effectively increases the conjugation length of the polymer. Compared to the ICT band of P1, the hypsochromic shifts of the P2 and P3 absorptions (Table 1) suggest decreases in the effective conjugation lengths.

| Table 1 | Optical and electrochemical properties of the PVTh₄FBT polymers |
|--------|-----------------|----------------|----------------|----------------|
| Polymer | Solution (nm)   | Film (nm)      | $E_{\text{g,opt}}$ (eV) | $E_{\text{HOMO}}$ (eV) | $E_{\text{LUMO}}$ (eV) |
| P1     | 652, 704        | 652, 710       | 1.54               | −5.23           | −3.43           |
| P2     | 620, 704        | 640, 706       | 1.57               | −5.31           | −3.02           |
| P3     | 600, 706        | 655, 706       | 1.54               | −5.27           | −3.23           |

Fig. 1 Normalized UV-vis absorption spectra of (a) P1, (b) P2 and (c) P3 in an ODCB solution at room temperature (black square), at 120 °C (red circle), and in the thin-film state (green triangle).
The three polymers share the same conjugated backbone, the disruption of the effective conjugation was attributed to the decreased backbone coplanarity caused by the OD side chains near the inter-thienyl bond (in the case of P2), and the increased side chain density (in the case of P3). Pre-aggregations of the copolymers in the ODCB solutions are evident at room temperature, since the 710 nm absorption shoulder observed in the thin films can also be found in the solutions. The weakest absorption shoulder of P3 in solution indicates that the high side chain density may prevent effectively inter-chain interactions in the solution. Deduced from cyclic voltammetry measurements (Fig. S4†), the $E_{\text{HOMO}}$ and $E_{\text{LUMO}}$ of the polymers are also summarized in Table 1.

The backbone rigidities of the polymers were further evaluated by thermochromic experiments. At a solution temperature of 120 °C, the three polymers responded differently to the thermal disturbance. The increased solution temperature resulted in only a 2 nm hypsochromic shift to the ICT band of P1, but 37 nm and 15 nm hypsochromic shifts to those of P2 and P3. Therefore, the effective conjugation and backbone coplanarity of P1 are much more difficult to be thermally disturbed than the other two. The increased solution temperature also disaggregated the PVTh$_4$FBT polymers in the solution, as indicated by the decreased intensity of the 710 nm absorption bands. The photophysical behaviors of the PVTh$_4$FBT polymers thus reveal the strong influence of the side chain position and side chain density on the backbone properties of the polymers.

**Theoretical calculations**

Using Gaussian 09, density functional theory (DFT) calculations were performed on the simplified repeat units of the polymers at the B3LYP/6-311G(d,p) level. The molecular segment of the PVTh$_4$FBT polymer shown in Fig. 2a was selected for the calculations to emphasize the influence of the alkyl side chains on the interannular dihedral angles ($\theta_1$–$\theta_3$) and the coplanarity of the backbone. To evaluate the effect of the vinylene group, comparison of the PVTh$_4$FBT and PTh$_4$FBT backbones was made under conditions where alkyl side chains were excluded. As shown in Fig. 3, the smaller $\theta_2$ and $\theta_3$ angles of PVTh$_4$FBT indicate its better backbone coplanarity than that of PTh$_4$FBT. The improved coplanarity was attributed to the fact that the vinylene unit reduces the interannular steric hindrance.

The optimized conformations of the molecular segments of P1, P2 and P3 are shown in Fig. 2b–2d. The dihedral angles ($\theta_1$–$\theta_3$) in the optimized geometries of the three polymers are summarized in Table 2. The alkyl side chains degraded the backbone coplanarity as indicated by the increased interannular dihedral angles. The degree of interannular torsion depends on the alkyl side chain placement. As can be seen in the cases of P1 and P3, the alkyl groups closer to the vinylene unit (4-position, see the number codes for the substituents in Fig. S3†) are less effective in distorting the backbone, while those closer to the inter-thienyl single bond (3′-position) evidently increased $\theta_2$ from 12° to over 32°.

The backbone rigidity was further investigated by potential energy profiles of the molecular segments plotted in Fig. 4. In this figure, $\theta_2 = 0^\circ$ corresponds to a fully planar conformation.
The potential energy minima calculated for P1, P2, and P3 are located at $\theta_2 = 12^\circ$, $32^\circ$, and $34^\circ$, respectively, suggesting a gradual decrease in the backbone coplanarity. Upon rotation around the inter-thienyl bond, the potential energy increases, and attains a maximum $E^*$ of 3.8 kcal mol$^{-1}$ for P1 and 1.62–1.75 kcal mol$^{-1}$ for P2 and P3 at $\theta_2 = 90^\circ$. The increase of potential energy upon bond rotation indicates that torsion of the backbone is energetically unfavorable. The highest $E^*$ of P1 thus represents its highest backbone rigidity. The calculations agree with the results of the UV-Vis absorption experiments, where P1 demonstrates the highest effective conjugation length and yet the lowest sensitivity to thermal agitation in the solution.

**Grazing-incidence X-ray diffraction analysis**

To analyze the solid-state order and chain orientation in the thin film, grazing-incidence X-ray diffraction (GIXD) measurements were performed on the thin films of the three polymers. The $d$-spacing and correlation length ($L_{hkl}$) deduced from the GIXD data are summarized in Table 3. In the GIXD patterns of the polymers shown in Fig. 5, the scattering from lamellar stacking ($(h00)$ peaks) was observed along the $q_z$ axis and the scattering from $\pi$–$\pi$ stacking was observed along the $q_{xy}$ axis. Thus, the edge-on lamellar orientation is preferable for the three polymers. However, the polymers did show different degrees of packing order and the orientational uniformity. High order peaks up to (400) were observed for the lamellar packing of P1 and P2, while only up to (300) were found for the P3 thin film. Moreover, as shown in Fig. 6, the broadness of the (100) peaks in the azimuthal scan increases from P1 to P2 to P3. Thus, the edge-on lamellar crystals of P1 are more orderly oriented in the thin film than the other two. The lowest structural order of P3 suggests that the increased side-chain density may deter the side-chain interdigitation and the registry between layers. Consequently, the lamellar packing of P3 is not only less ordered but also less oriented on the substrate. In contrast, as indicated by the thermochromic and calculation results, P1 possesses a more planar and rigid backbone than the other two. The highly ordered and well-oriented edge-on lamellae of P1 are thus related to its coplanar conformation in solution. The relationship is in line with Chen’s study about Isoindigo-based polymers.

**Table 3** Summary of the polymer packing parameters in the thin films determined from the GIXD patterns

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Lamellar spacing (Å)</th>
<th>$L_{100}$ (nm)</th>
<th>$\pi$–$\pi$ spacing (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>19.2</td>
<td>39</td>
<td>3.62</td>
</tr>
<tr>
<td>P2</td>
<td>19.7</td>
<td>28</td>
<td>3.62</td>
</tr>
<tr>
<td>P3</td>
<td>21.5</td>
<td>24</td>
<td>3.62</td>
</tr>
</tbody>
</table>

**Fig. 6** The azimuthal-angle scans for the (100) peaks in the GIXD patterns of the PVTh4FBT polymers. The inset shows the full width at half maximum (FWHM) of each azimuthal scan.

**Fig. 7** Transfer (right) and output (left) characteristics of the OFET devices of (a) P1, (b) P2 and (c) P3.

**OFET performances**

The charge transport properties of the PVTh4FBT polymers were studied in OFET devices with a bottom-gate, top-contact configuration. The PVTh4FBT polymers exhibited p-channel OFET characteristics, as shown in Fig. 7. The electrical characteristics of the devices including $\mu_{th}$, threshold voltage ($V_{th}$), and on/off ratio ($I_{on}/I_{off}$) are summarized in Table 4. The $\mu_{th}$ values of P1, P2, and P3 were found to be 0.12, 0.08, and 0.05 cm$^2$ V$^{-1}$ s$^{-1}$, respectively. The $I_{on}/I_{off}$ values were calculated to be 100, 1000, and 10000 for P1, P2, and P3, respectively. The $V_{th}$ values were found to be 5, 5, and 5 V for P1, P2, and P3, respectively. The results indicate that P1 exhibits the best charge transport properties among the three polymers.
edge-on lamellar packing among the three polymers. The highest \( \mu_h \) of 0.26 cm\(^2\) V\(^{-1}\) s\(^{-1}\) was delivered by P1, because its better solid-state order and suitable crystal orientation is conducive to the charge transfer in the OFET devices. Thus, the study revealed the critical role of the vinylene unit and the alkyl side chains in modulating the rigidity, packing order and OFET performances of FBT based polymers.

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### Notes and references


### Table 4

<table>
<thead>
<tr>
<th>Polymer</th>
<th>( \mu_{h, avg} ) (cm(^2) V(^{-1}) s(^{-1}))</th>
<th>( V_{th} ) (V)</th>
<th>( I_{on}/I_{off} )</th>
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<tr>
<td>P1</td>
<td>0.22 (0.26)</td>
<td>−2.6</td>
<td>10(^7)</td>
</tr>
<tr>
<td>P2</td>
<td>0.027 (0.037)</td>
<td>−9.6</td>
<td>10(^5)</td>
</tr>
<tr>
<td>P3</td>
<td>0.086 (0.12)</td>
<td>−9.8</td>
<td>10(^5)-10(^6)</td>
</tr>
</tbody>
</table>

\( \mu_{h, avg} \) and \( V_{th} \) values are averaged over five devices.

### Table 5

<table>
<thead>
<tr>
<th>Solvent</th>
<th>( \mu_{h, avg} ) (cm(^2) V(^{-1}) s(^{-1}))</th>
<th>( V_{th} ) (V)</th>
<th>( I_{on}/I_{off} )</th>
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<tr>
<td>ODCB</td>
<td>0.089 (0.13)</td>
<td>−14.7</td>
<td>10(^4)-10(^5)</td>
</tr>
<tr>
<td>TCB</td>
<td>0.12 (0.17)</td>
<td>−16.7</td>
<td>10(^3)-10(^5)</td>
</tr>
</tbody>
</table>

\( \mu_{h, avg} \) and \( V_{th} \) values are averaged over five devices.

Conclusions

In this study, the vinylene group was introduced into a FBT based D–A polymer to physically planarize the conjugated backbone. The influence of alkyl chain position and density on the coplanarity and rigidity of the non-fused FBT based polymers was systematically compared in three PVTh\(_4\)FBT polymers. The thermochromic behaviors and DFT calculations indicated that the alkyl side chains close to the inter-thienyl bond and the high attached density increase the inter-thienyl dihedral angle, and decrease the energy barrier of the inter-annual bond rotation. Consequently, the backbones of P2 and P3 are less coplanar and less rigid than P1. The backbone coplanarity in solution further affects the packing order and crystal orientation of the polymers in the thin film. GIXD results showed that P1 formed the most ordered and oriented and the \( I_{on}/I_{off} \) ratio extracted from the figures are summarized in Table 4. P1 delivered the highest \( \mu_h \) (0.26 cm\(^2\) V\(^{-1}\) s\(^{-1}\)) among the three polymers, which can be attributed to its most ordered and oriented solid-state structure. Unexpectedly, despite P2 having better solid-state order than P3, it delivered the lowest averaged \( \mu_h \) of 0.027 cm\(^2\) V\(^{-1}\) s\(^{-1}\). AFM revealed the surface topographies of the three polymer thin films (Fig. S5†). In Fig. S5b,† more grain boundaries were observed in P2. Because the presence of grain boundaries in the active layer is detrimental to charge mobility,\(^{34–37}\) improving the thin-film morphology of P2 was attempted. As shown in Fig. S6,† by reducing the concentration of P2 solutions from 5.0 to 2.5 mg mL\(^{-1}\), the film roughness (\( R_{RMS} \)) and the density of the grain boundary of the P2 thin film can be significantly decreased. Consequently, the characteristics of the P2 OFET devices (Fig. 7S†) were improved and the \( \mu_h \) was increased to 0.089–0.12 cm\(^2\) V\(^{-1}\) s\(^{-1}\) (Table 5) due to the improved morphology.