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Backbone Rigidity and Its Influences on the Morphology and Charge Mobility of FBT Based Conjugated Polymers

Kuan-Yi Wu, Chun-Chieh Chiu, Wei-Tsung Chuang, Chien-Lung Wang and Chain-Shu Hsu

A series of three PVThFBT polymers containing different alkyl side chain placements were synthesized. The thermochromic behaviors and the DFT calculations indicated that the backbone coplanarity and rigidity of the PVThFBT polymers can be effectively modulated through 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 cm²V⁻¹s⁻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 applications as low-cost components in large-area flexible electronics. Significant progresses in molecular design, and device physics have led to polymer-based OFETs with charge mobility (μ) over 1.0 cm²V⁻¹s⁻¹. Based on the Macrus theory, low reorganization energies (λreorg) and high degrees of intermolecular electronic coupling are conducive for conjugated molecules to reach high μ. Via fusing the neighboring aromatic units, chemical rigidification inhibits the inter-annular rotation. Thus, conjugated systems with multifused heteroarenes possess reduced λreorg, and better coplanarity. Along with suitable lateral solubilizing side chains, effective intermolecular electronic coupling and high μ have been reported. Recently, non-fused conjugated polymers also delivered comparable and even higher μ 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-alkylthiophene). 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, in other words, 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. However, the ways of modulating the rigidity of the FBT polymers, and the influences of the backbone rigidity to the packing order and the charge mobility have not been carefully studied. Since theoretically, the FBT unit is considered as inefficient at locking the conformations, the backbone properties of the 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 (FBT) based D-A copolymers, are conjugated polymers with high performances. However, the backbone properties of the non-fused FBT polymers can be critical to the solid-state order and the OFET performances. The backbone properties of the non-fused FBT polymers can be critical to the solid-state order and the OFET performances. The backbone properties of the non-fused FBT polymers can be critical to the solid-state order and the OFET performances. The backbone properties of the non-fused FBT polymers can be critical to the solid-state order and the OFET performances. The backbone properties of the non-fused FBT polymers can be critical to the solid-state order and the OFET performances. The backbone properties of the non-fused FBT polymers can be critical to the solid-state order and the OFET performances. The backbone properties of the non-fused FBT polymers can be critical to the solid-state order and the OFET performances. The backbone properties of the non-fused FBT polymers can be critical to the solid-state order and the OFET performances. The backbone properties of the non-fused FBT polymers can be critical to the solid-state order and the OFET performances. The backbone properties of the non-fused FBT polymers can be critical to the solid-state order and the OFET performances. The backbone properties of the non-fused FBT polymers can be critical to the solid-state order and the OFET performances. The backbone properties of the non-fused FBT polymers can be critical to the solid-state order and the OFET performances. The backbone properties of the non-fused FBT polymers can be critical to the solid-state order and the OFET performances. The backbone properties of the non-fused FBT polymers can be critical to the solid-state order and the OFET performances. The backbone properties of the non-fused FBT polymers can be critical to the solid-state order and the OFET performances. The backbone properties of the non-fused FBT polymers can be critical to the solid-state order and the OFET performances. The backbone properties of the non-fused FBT polymers can be critical to the solid-state order and the OFET performances. The backbone properties of the non-fused FBT polymers can be critical to the solid-state order and the OFET performances. The backbone properties of the non-fused FBT polymers can be critical to the solid-state order and the OFET performances.

A series of three PVThFBT polymers containing different alkyl side chain placements were synthesized. The thermochromic behaviors and the DFT calculations indicated that the backbone coplanarity and rigidity of the PVThFBT polymers can be effectively modulated through 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 cm²V⁻¹s⁻¹) among the three analogues because its thin-film morphology is in favor of charge transport.
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resulted in the most ordered and well-oriented edge-on lamellae on the substrate, which rendered P1 the highest \( \mu_b \) of among the three polymers.

**Experimental Session**

**General Measurement and Characterization:** All chemicals were purchased from Aldrich or Acros and used as received unless otherwise specified. Synthesis and characterizations of the FBT monomers, DTV monomers and polymers were summarized in the supporting information. FBT-1 was synthesized according to the literature.\(^1\) \(^1\)H and \(^13\)C NMR spectra were measured 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 standard and 1,2,4-trichlorobenzene (TCB) as eluent. Differential scanning calorimetry (DSC) was measured on a TA Q200 Instrument and thermogravimetric analysis (TGA) was recorded on a Perkin Elmer Pyris under nitrogen atmosphere at a heating rate of 10 °C min\(^{-1}\). Absorption spectra were collected on a HP8453 UV-vis spectrophotometer. The electrochemical cyclic voltammetry (CV) was conducted on a CH Instruments Model 611D. A carbon glass electrode coated with a thin polymer film was used as the working electrode and Ag/Ag\(^{+}\) electrode as the reference electrode, while 0.1 M tetrabutylammonium-hexafluorophosphate (Bu\(^4\)NPF\(_6\)) in acetonitrile was the electrolyte. CV curves were calibrated using ferrocene as the standard, whose oxidation potential is set at -4.8 eV with respect to zero vacuum level. The \( E_{HOMO} \) were derived from the equation \( E_{HOMO} = -(E_{ox}^{onset} - E_{(ferrocene)^{onset}} + 4.8) \) eV. The \( E_{LUMO} \) were derived from the equation \( E_{LUMO} = -(E_{red}^{onset} - E_{(ferrocene)^{onset}} + 4.8) \) eV. A Veeco Diimmova atomic force microscope (AFM) in the tapping mode was used to characterize surface morphology of the polymer thin films. The Grazing Incidence X-ray diffraction (GIXD) patterns of PVTh\(_b\)FBT polymers were recorded at the BL01C2 beamline of the National Synchrotron Radiation Research Center (NSRRRC) in Taiwan. The ring energy of NSRRRC 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 a Si(111) double-crystal monochromator. The samples were placed horizontally on a sample stage. With an incident angle \( 0.2° \), GIXD was conducted and the pattern was collected with the detector system included a CMOS flat panel X-ray detector C9728DK. The scattering wave vector, defined as \( q = 4\pi \sin \theta / \lambda \) (with 20 the scattering angle), was calibrated using silver benenate, 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 by applying the GEDIIS optimization algorithm. The minimum nature of each stationary point was confirmed by a frequency analysis. The torsion potential energy surface was produced by the scan of single-point energy calculations at the B3LYP/6-311G(d,p) level, and the dihedral angle \( \theta_2 \) was stepped in 10° increments from the optimized geometry.

**OFET Fabrication:** An n-type heavily doped Si wafer with a SiO\(_2\) layer of 300 nm and a capacitance per unit area of 11 nF cm\(^{-2}\) was used as the gate electrode and dielectric layer. Thin films (40–60 nm in thickness) of polymers were deposited on the octadecltrichlorosilane (ODTS)-treated SiO\(_2\)/Si substrates by spin-coating the ODCB solutions (2.5 mg mL\(^{-1}\) and 5 mg mL\(^{-1}\)) or the TCB solutions (2.5 mg mL\(^{-1}\)) of the polymers. Then, the thin films were annealed at 200 °C in nitrogen atmosphere for 30 min. 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 in nitrogen using a 4156C, Agilent Technologies. The field-effect mobility was calculated in the saturation regime by using the equation \( \mu_{DS} = (\mu C/WL)(V_G - V_T)^2 \), 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), \( C \) is the capacitance per unit area of the gate dielectric layer, and \( V_G \) is the gate voltage.

**Result and Discussion**

**Synthesis and Thermal Analysis**

The synthetic routes of the PVTh\(_b\)FBT polymers are depicted in the 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-octyldodecyl)thiophen-2-yl)-5,6-difluorobenzo[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-difluorobenzox[c][1,2,5]thiadiazole (FBT-3) and (E)-1,2-bis(3-dodecyl-5-(trimethylstannyl)thiophen-2-yl)ethene (DTV-3) afforded 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 PVTh\(_b\)FBT polymers exhibited good thermal stability with 1% weight loss temperatures \( (T_w) \) over 360 °C measured by thermogravimetric analysis (Figure S1). The polymers were heated up to 300 °C to avoid thermal degradation in the differential scanning calorimetry (DSC) analysis (Figure 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 \( T_w \) 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-octyldodecyl (OD) substituent at the 4’ position (see Figure S3 for number code) of the (E)-1,2-bis(2,2’-bithiophen-5-
yl)ethene structural unit, decreasing 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 the phase stability of the PVTh₄FBT polymers.

Scheme 1. Synthetic procedures of PVTh₄FBT polymers. Reagents and conditions: (i) tris(dibenzylideneacetone)dipalladium(0), tri(o-tolyl)phosphine, chlorobenzene, 120°C, 48 hrs.

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 UV-Vis spectrum of the PVTh₄FBT polymers are summarized in Table 1. As shown in Figure 1, the absorption bands with λ_max around 450 nm can be attributed to localized π-π* transition. The λ_max of the photo-induced intramolecular charge transfer (ICT) absorptions of P1 is at 655 nm. Compared to λ_max of PTh₄FBT (the polymer analogue without the vinylene structural unit) in our previous study, the absorption of P1 bathochromic shifts for 80 nm. Thus, the vinylene unit effectively increases the conjugation length of the polymer. Compared the ICT band of P1, the hypsochromic shifts of the P2 and P3 absorptions (Table 1) suggest the decreases in the effective conjugation lengths. Since 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-aggregation 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 the effectively inter-chain interactions in the solution. Deduced from cyclic voltammetry measurements (Figure S4), the E_HOMO and E_LUMO of the polymers were also summarized in Table 1.
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The backbone rigidities of the polymers were further evaluated through 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-FBT polymers in the solution, as indicated by the decreased intensity of the 710 nm absorption bands. The photophysical behaviors of the PVTh-FBT polymers thus reveals the strong influences of the side chain position and side chain density to the backbone properties of the polymers.

Theoretical Calculation

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-FBT polymer shown in Figure 2a was selected for the calculations to emphasize the influences of the alkyl side chains to the interannular dihedral angles (θ₁ - θ₃) and the coplanarity of the backbone. To first evaluate the influence of the vinylenic group, comparison of the PVTh-FBT and PTh-FBT backbones were made under the condition where the alkyl side chains were excluded. As shown in Figure 3, the smaller θ₂ and θ₃ angles of PVTh-FBT indicate its better backbone coplanarity than that of PTh-FBT. The improved coplanarity was attributed that the vinylenic unit reduces the interannular steric hindrance.

The optimized conformations of the molecular segments of P1, P2 and P3 are shown in Figure 2b-2d. The dihedral angles (θ₁ - θ₃) in the optimized geometries of the three polymers were summarized in Table 2. The alkyl side chains degraded the backbones coplanarity as indicated by the increased interannular dihedral angles. The degree of interannular torsion depends on the alkyl side chain placements. As can be seen in the cases of P1 and P3, the alkyl groups closer to the vinylenic unit (4-position, see the number codes for the substituents in Figure S3) is less effective in distorting the backbone, while those closer to the inter-thienyl single bond (3'-position) evidently increased θ₂ from 12° to over 32°.

![Figure 2](image1.png)

Figure 2. (a) Illustration of the molecular segment of the PVTh-FBT backbone and the interannular dihedral angles - θ₁, θ₂, and θ₃. Side views of the optimized geometries of (b) P1, (c) P2 and (d) P3 at the B3LYP/6-311G(d,p) level of theory.

![Figure 3](image2.png)

Figure 3. The optimized geometries of (a) the PVTh-FBT backbone and (b) the PTh-FBT backbone at the B3LYP/6-311G(d,p) level of theory.
peaks) were observed along the 
highly ordered and well-oriented edge-on lamellae of 
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 ($L_{100}$) deduced from the GIXD data are summarized in Table 3. In the GIXD patterns of the polymers shown in Figure 5, the scattering from lamellar stacking ((h00) peaks) were observed along the $q_z$ axis, and the scattering from π-π stacking were 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 Figure 6, the broadness of the (100) peaks in the azimuthal scan increases from P1 to P2, and to P3. Thus, the edge-on lamellar crystals of P1 is 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 the 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 is thus related to its coplanar conformation in solution. The relationship is in line with Chen’s study about the Isoindigo-based polymers.

![Figure 4](image_url) Potential energy profiles of the PVTh$_4$FBT segments at the B3LYP/6-311G(d,p) level of theory.

![Figure 5](image_url) GIXD patterns of (a) P1, (b) P2, and (c) P3.

![Figure 6](image_url) The azimuthal-angle scan for the (100) peaks in the GIXD patterns of the PVTh$_4$FBT polymers. The inset shows the full width at half maximum (FWHM) of each azimuthal scan.

**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>π-π 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>

**OFET Performances**

The charge transport properties of the PVTh$_4$FBT polymers were studied in OFET devices with a bottom-gate, top-contact configuration. The PVTh$_4$FBT polymers exhibited the p-channel OFET characteristics, as shown in Figure 7. The electric characters of the devices including $\mu_{dc}$ threshold voltage ($V_{th}$) and $I_{on}/I_{off}$ ratio extracted from the figures were summarized in Table 4. P1 delivered the highest $\mu_{dc}$ (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 has better solid-state order than P3, it delivered the lowest averaged $\mu_{dc}$ of 0.027 cm$^2$V$^{-1}$s$^{-1}$. AFM revealed the surface topographies of the three polymer thin films (Figure S5). In Figure S5b, more grain boundaries were observed in P2. Because the presence of grain boundaries in the active layer is detrimental to charge mobility, improving the thin-film morphology of P2 was attempted. As shown in Figure S6, through reducing the concentration of P2 solutions from 5.0 to 2.5 mg mL$^{-1}$, film roughness ($R_{BAM}$) and the density of grain boundary of the P2 thin film can be significantly decreased. Consequently, the characteristics of the P2 OFET devices (Figure 7S) was improved and the $\mu_{dc}$ was increased to 0.089-0.12 cm$^2$V$^{-1}$s$^{-1}$ (Table 5) due to the improved morphology.
behaviors and DFT calculations indicated that the alkyl side chains concentration (2.5 mg mL\(^{-1}\)) close to the interOthienyl bond and the high attached density increase the inter-thienyl dihedral angle, and decrease the energy barrier of the interannual 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 the P1 formed the most ordered and oriented edge-on lamellar packing among the three polymers. 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 on modulating the rigidity, packing order and OFET performances of the FBT based polymers.

**Acknowledgements**

This work is supported by the National Science Council and “ATP” of the National Chiao Tung University and Ministry of Education, Taiwan. The authors thank Prof. Keng S. Liang at Institute of Physics, Academia Sinica, Taiwan; Dr. Hwo-Shuenn Sheu at beamline BL01C; Dr. U-Ser Jeng at beamline BL23A of the National Synchrotron Radiation Research Center (NSRRC) in Taiwan for assistance with the XRD measurements.

**Notes and references**


**Table 4. OFET characteristics of the PVThFBT polymers prepared from ODCB solution at a concentration of 5 mg mL\(^{-1}\).**

<table>
<thead>
<tr>
<th>Polymer</th>
<th>(\mu_h)(_{\text{avg}}) ((\mu_h) highest) (cm(^2)V(^{-1})s(^{-1}))</th>
<th>(V_{th}) (V)</th>
<th>(I_{on}/I_{off})</th>
</tr>
</thead>
<tbody>
<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(^3)-10(^6)</td>
</tr>
</tbody>
</table>

\(^a\) Averaged value of over five devices.

**Table 5. OFET characteristics of P2 prepared from reduced solution concentration (2.5 mg mL\(^{-1}\)).**

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

\(^a\) Averaged value of over five devices.

**Conclusions**

In this study, vinylene group was introduced into a FBT based D-A polymer to physically planarize the conjugated backbone. The influences of alkyl chain position and density to the coplanarity and rigidity of the non-fused FBT based polymers were systematically compared in three PVThFBT polymers. The thermochemical behaviors and DFT calculations indicated that the alkyl side chains close to the inter-thienyl bond and the high attached density increase the interannual 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 the P1 formed the most ordered and oriented edge-on lamellar packing among the three polymers. 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 vinylen unit and the alkyl side chains on modulating the rigidity, packing order and OFET performances of the FBT based polymers.

Electronic Supplementary Information (ESI) available: The synthesis details, TGA measurement, DSC thermograms, cyclic voltammograms, AFM image, transistor data and calculated input profile of PTthVFEBT polymers can be found in the Supporting Information. See DOI: 10.1039/b000000x/