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Semiconducting Properties and Geometry-Directed Self-Assembly of Heptacyclic Anthradithiophene Diimide-Based Polymers

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Supporting Information

ABSTRACT: Backbone geometry and side-chain self-assembly are key factors that govern the aggregation of conjugated semiconducting polymers and affect charge transport. Tuning of charge transport properties hinges on being able to strike a balance between electronic structures, self-assembly, and robustness to disorder. This work describes a top-down design strategy focusing on the geometry of polymer aggregates. A heptacyclic acceptor anthradithiophene diimide was designed to build self-assembled polymers. The corresponding polymers possess a pseudolinear rodlike



backbone geometry with interdigitated alkyl chains. Using a fluorinated comonomer suppresses the rotational disorder and preserves the backbone symmetry at a relatively long length scale, leading to improved planarity and facilitating intrachain charge transport. These polymers exhibit ambipolar transistor performance with the maximum hole mobility of 4.21 cm² V⁻¹ s⁻¹. The experimental microstructures are in good agreement with the simulated unit cells, indicating an extended dimensionality of charge transport pathways. These promising results may help to complement the design rationales of semiconducting polymers.

INTRODUCTION

Central to the area of semiconducting polymers has been the exploration of structure-function maps. To optimize candidate materials for flexible electronics, material scientists have developed diverse π -conjugated chromophores.¹⁻¹⁰ The promise of high-mobility flexible field-effect transistors (FETs) and high-efficiency organic solar cells based on lowband-gap semiconductors has driven the rapid advance in donor-acceptor (D-A)-type semiconducting oligomers and polymers over the past few years.¹¹⁻¹⁵ Although many structural parameters affecting charge transport properties have been intensively evaluated (such as coplanarity, conformational preference, molecular symmetry, and structural isomerism), $^{16-23}$ those relevant to mesoscale (submicrometer) ordering remain elusive. In this context, a conventional materials design involves a bottom-up strategy by which diverse building blocks are compiled to achieve functionoriented local structural features. It focuses on the molecule's electronic structure, an important feature that realizes the tunability of frontier orbital energetics but ignores the mesoscale assembly. Such overlooked assembly behavior at various length scales is important to reveal the molecular origin of semiconducting properties but has yet to be manipulated. Moreover, the increasing molecular complexity poses a daunting challenge to expand the chemical space of these materials.

To close the understanding gap, we aimed at adapting a design approach toward controllable self-assembled aggregates in a predictable manner. Rather than simple installation of chemical functionalities to the poly(arylene-vinylene) conjugation pathway, we first formulated the overview of polymer geometry using a top-down design strategy and then added suitable groups to fill in the frameworks. Using computational tools, the supramolecular organization can be quantitatively, or at least semiquantitatively, predicted by an ideal packing model, which reflects, in an extreme form, the general structure-property relationship. As shown in Figure 1, a densely packed aggregate of a semiconducting polymer often manifests itself in interdigitation.²⁴ Molecular mechanics (MM)/molecular dynamics (MD) simulations can realize this atomistic understanding. Most of the state-of-the-art highmobility materials pack in fully interdigitated motifs, whereas those with moderate to low performances usually possess partly interdigitated or noninterdigitated assembly. Herein, we report the design and synthesis of a new heptacyclic molecule to build conjugated semiconductors with fully interdigitated distribution of the side chains and discuss the importance of molecular geometry in designing high-mobility materials.

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Figure 1. Design strategies toward high-performance polymer semiconductors: (a) different interdigitated packing motifs for aggregates, (b) representation of changes in self-assembly via three different modifications of molecular geometries, and (c) determinants of packing motifs.

RESULTS AND DISCUSSION

Design, Synthesis, and Structural Characterization. A quick survey of recent state-of-the-art semiconducting polymers bearing lactam or imide reveals that linear backbone aids the π -stacking, whereas a wavelike backbone geometry is sensitive to site disorders or conformational traps.^{25,26} In principle, most high-mobility semiconducting polymers possess collinear (or, in other terms, pseudostraight) conjugated units. On the premise that a linear backbone is indispensable, the backbone geometry and the substitution position of side chains correlate the incoherent molecular attributes with the mesoscale self-assembly. If the side chain is selected, the number of carbon atoms across the conjugation pathway is likely the determinant of the self-assembled structure. We note that commercially available 2-decyltetradecyl or 2-octyldodecyl alkyl chains favor a backbone with approximately 14 $(P(NDI2OD-T2)^{27})$ to 22 $(PDVT-10^{28})$ atoms across the conjugation pathway of a co-repeating unit (n_{atom}) (Figure 1c). In these cases, branched alkyl chains form interdigitated aggregates that exhibit preferable molecular order than noninterdigitated polymers. Take the example of polymers bearing the 2-decyltetradecyl side chain. Figure 1a shows the schematic view of four typical types of polymer geometry, where the alignment of 2-decyltetradecyl chains was extracted from snapshots of MM/MD-simulated state-of-the-art polymers (for detailed data, see the Supporting Information).^{24,29,30} Structural modification of the molecular geometry leads to a significant change in packing mode. For $n_{\text{atom}} < 12$, overcrowded side chains with a possible formation of a distorted globule disable the interdigitation. For $n_{\text{atom}} > 24$, the presence of cavities can be predicted when the side chain is interdigitated, generating a thermodynamically disfavored structure; consequently, the branched chains deviate from the a-axis direction and pack into a partially interdigitated "open-armed" pattern that can fill in the cavities to afford a denser structure. This MM-simulated packing mode results in limited solubility as well as a lamellar *d*-spacing of shorter than

20 Å, as described in many reports.^{31,32} Similar situations are found for different substitution positions or tilting angles between the side chain and the backbone. A modification of the alkylated monomer's geometry exerts a significant effect on packing. Owing to the cavity or steric crowding, a large *c*- or *a*axis projection of the connection between the substitution positions of the side chains in a unit cell also leads to the openarmed packing. As illustrated in the schematic picture, the branched chain lying adjacent to the backbone interacts only with one chain, thus providing a less stable structure than the fully interdigitated assembly. This open-armed geometry is likely sensitive to thermal fluctuations of the lattice that cause displacement of the main chain, accompanying an uncertain transfer integral. The absence of fully staggered conformations of alkyl chains further indicates the instability of the lattice. Orientational disorders, stacking faults, and dislocations may occur,³³ thereby leading to a deleterious effect on charge hopping.

Our design commenced with the choice of the 2decyltetradecyl side chain to construct a highly interdigitated polymer aggregate (type A or B) because it is operationally simple and commercially available. Other structural considerations include (1) a conjugated backbone with n_{atom} of ca. 20; (2) suitable protruding sites for side-chain attachment so that the steric interactions between the side chain and backbone can be minimized to enhance π -stacking; (3) a pseudolinear backbone motif that has robustness to conformational rotation and propensity for aggregation; and (4) a minimized conformational ambiguity that enables long-range ordering. We chose maleimides as the substituent sites and an angular-shaped anthradithiophene as the core structure, namely, anthradithiophene diimide (ADTDI). This new planar heptacyclic electron acceptor can form an interdigitated assembly when coupled with conventional donors such as bithiophene. Moreover, the steric hindrance between exocyclic carbonyl groups in the maleimides and spatially adjacent atoms Scheme 1. Synthetic Route to PADTDI-Based Polymers



is minimized. These features represent the manifestation of our design strategy.

The synthetic route to ADTDI involves two cyclization reactions (Scheme 1).^{34–36} 2-Oxo-2-(thiophen-3-yl)acetic acid was sequentially treated with thionyl chloride and ammonia water to afford 2-oxo-2-(thiophen-3-yl)acetamide (1). This compound was mixed with dimethyl 2,2'-(2,5-dibromo-1,4phenylene)diacetate (2) and sodium tert-butoxide. The resulting imide (3) was alkylated in the presence of alkyl iodide and potassium carbonate to obtain diastereoisomeric mixtures (4) (Figure S2). These diastereoisomers were converted to the same product in the next cyclization step. The key intramolecular cyclization proceeded under mild conditions in the presence of KOAc as the base and $Pd(PPh_3)_4$ as the catalyst. The next bromination step encountered a synthetic difficulty due to the electron-withdrawing nature of the ADTDI greatly retarding the reaction. We used a strong acid system, trifluoroacetic acid, to increase the reactivity. The reaction mixture was stirred for a day to give dibromo ADTDI in a yield of ca. 25%.

Bithiophene (BT) and 3,3'-difluoro-2,2'-bithiophene (FBT) were selected to copolymerize with ADTDI. Both monomers have topological linkages similar to that of ADTDI, preserving the backbone linearity to maximize long-range ordering, persistence length of the chain, and robustness to positional lattice disorder.³⁷ For FBT, the F atom tends to approach the adjacent S atom in the σ_S^* direction, forming a nonbonded S… F interaction that can further improve the backbone rigidity.

Such fluorination strategy serves as a common approach to reduce the dihedral angle distribution of the polymer chain and to allow the delocalization of extended π -orbitals (Figure S4).³⁸ The resulting polymers, PADTDI-BT and PADTDI-FBT, have moderate number-averaged molecular weights of 21.2 and 25.6 kg mol⁻¹, respectively. This is due to the moderate coupling reactivity in the presence of imide functional groups.³⁹ Thermogravimetric analyses show that the 5% weight loss temperatures are 388 and 399 °C for PADTDI-BT and PADTDI-FBT, respectively, indicative of good thermal stabilities. Differential scanning calorimetry traces of the two polymers exhibited no phase transitions in the range of 25–300 °C (Figure S7).

Optical and Electrochemical Properties. Experimental UV–vis absorption spectra of ADTDI-based monomers and polymers were recorded in chloroform solution and in thin films (Figure 2 and Table 1). We also performed time-dependent density functional theory (TD-DFT) calculations at the B3LYP/6-31G(d) level in chloroform solution to illustrate the electronic transitions of ADTDI. The spectrum of monomers in chloroform solution reveals well-matched multiple absorption bands. The low-energy absorption bands in the 440–510 nm range are attributed to the transitions from the ground state to the first and second excited states. The highest occupied molecular orbital–lowest unoccupied molecular orbital (HOMO–LUMO) excitation (98.2%) is the major contributor of the first excited state. The excitation energy is 2.7450 eV with an oscillator strength of 0.0451. The second



Figure 2. UV–vis absorption spectra of ADTDI-based monomers and polymers: (a) ADTDI in dilute chloroform solution (concentration: ca. 3×10^{-5} mol L⁻¹); TD-DFT-calculated absorption spectrum of (b) ADTDI, (c) PADTDI-BT, and (d) PADTDI-FBT. The spectrum was calculated at the B3LYP/6-31G(d) level in chloroform.

Table 1. Optical and Electrochemical Properties

	λ_{\max} (nm)					
polymer	soln	film	$\stackrel{E_{ m g}^{ m opt}}{ m (eV)}$	E _{LUMO} (eV)	E _{HOMO} (eV)	$\stackrel{E_{\mathrm{g}}^{\mathrm{cv}}}{(\mathrm{eV})}$
PADTDI-BT	506	507	2.05	-3.47	-5.41	1.94
PADTDI-FBT	508	507	2.06	-3.54	-5.89	2.35

excited state is composed mainly of two transitions, HOMO -1 to LUMO (94.2%) and HOMO to LUMO + 2 (3.8%), with an oscillator strength of 0.2050. By comparing the molecular orbital distributions, both low-energy absorption bands indicate push-pull interactions between the internal anthradithiophene (electron-donating) and peripheral imide (electron-accepting) units. Because rigid π -conjugated frameworks and donor-acceptor structures can typically lead to fluorescence, we also measured the emission spectrum of ADTDI. The solution of ADTDI displays green-yellow fluorescence with a moderate Stokes shift of 27 nm, indicative of the relatively rigid backbone (Figure S8). Figure 2c,d illustrates the UV-vis absorption spectra of polymers in dilute chloroform solution and in thin films. All spectra exhibit broad absorption bands. The absorption maxima are 506 and 508 nm in solution for PADTDI-BT and PADTDI-FBT, respectively. For thin films, vibronic fine structures are shown in the absorption spectra, revealing slightly different aggregate tendencies. The optical gaps are estimated to be 2.05 eV for PADTDI-BT and 2.06 eV for PADTDI-FBT. This result implies the minute effect of the backbone fluorination on optical gaps. After thermal annealing, increased relative strengths of 0-0 to 0-1 vibronic peaks, together with approximately 5 nm bathochromic shifts of absorption maxima, correspond to enhanced aggregation for both polymers (Figure **S9**).

We measured the electrochemical characteristics (Figure S10) by cyclic voltammetry (CV) measurements using ferrocene⁺/ferrocene as internal calibration, a Ag/AgCl (Ag in 0.01 mol L^{-1} KCl) electrode as the reference electrode, a platinum wire as the counter electrode, and a glassy carbon stick electrode coated with a dip-coated polymer film as the working electrode. A solution of 0.1 M tetrabutylammonium

hexafluorophosphate in anhydrous acetonitrile was used as the electrolyte. The HOMO and LUMO energy levels of PADTDI-BT are estimated to be -5.41 and -3.47 eV from the onset potentials of 1.01 and -0.93 V, respectively, with a band gap of 1.94 eV, using the equation $E = -(E_{onset} E_{1/2}$ (Fc⁺/Fc) + 4.80 eV). In comparison, fluorinated PADTDI-FBT exhibits deep-lying HOMO (-5.89 eV, onset potential: 1.49 V) and LUMO (-3.54 eV, onset potential: -0.86 V)energy levels because of the stabilization effect of fluorine atoms. The HOMO energy levels are corroborated by ultraviolet photoelectron spectroscopy measurements. Using the equation IP = $h\nu - (E_{\text{cutoff}} - E_{\text{H,onset}})$, the ionization potentials are 5.49 and 5.86 eV for PADTDI-BT and PADTDI-FBT, respectively. These energy levels indicate possible ambipolar semiconducting properties. Fluorination also leads to backbone planarization that suppresses the rotational disorder, as demonstrated by calculated geometries of trimers (Figure S4) and resonance Raman spectroscopy (Figures S11).

Simulated and Experimental Microstructures. We performed MM simulations with periodic boundary conditions to simulate the infinite system. As previously reported,⁴⁰ the chirality of side chains is not a determinant factor to the calculation of *d*-spacing; therefore, we used (R,S)-alkylated ADTDI to perform the calculation, in which the two alkyl chains are centrosymmetrically distributed so as to simplify the modeling. The simulation of PADTDI-based polymers involves the following steps. First, a simplified model of a PADTDI-BT aggregate containing four dimers was built (Figure S6). This model confirms that ADTDI-based polymers favor side-chain interdigitation to afford a dense packing with an interlayer distance of less than 30 Å and a π -stacking distance of approximately 3.5 Å. A single co-repeating unit was extracted from the model and used as the input for MM calculations. We built many starting cell structures by slightly varying the lattice parameters and the orientation of the alkyl chains. We performed 100 ps-quenched dynamics on each structure at 300 and 600 K to afford the most stable structures. The simulated structure shows that alkyl chains self-assemble into ordered lamellar packing; the branched decyl chains lie parallel to the *a*-axis of the unit cell, whereas the dodecyl chains bend to adopt a supramolecular organization with adjacent chains. Such a structure extends the backbone order to the spatially adjacent chains and improves the dimensionality of charge transport. Introducing fluorine atoms into the backbone has a minute effect on the lattice parameters, providing similar interdigitated packing modes. The simulated crystal of PADTDI-FBT exhibits weak CH…F interactions with adjacent alkyl chains (2.77-2.78 Å), as well as enhanced backbone planarity, leading to the variance of d-spacing. The calculated d_{100} distances are 26.6 and 26.8 Å for PADTDI-BT and PADTDI-FBT, respectively.

To evaluate the geometric design strategy, we obtained the microstructural information using two-dimensional grazing incidence X-ray diffraction (GIXRD) measurements (Figures 3 and S11, Table S2). The GIXRD patterns exhibit typical arc (h00) peaks up to the fourth order along the out-of-plane direction. The (h00) peaks of the as-spun and annealed PADTDI-BT thin-film diffraction patterns correspond to interlayer *d*-spacings of 26.3 and 26.5 Å, respectively, in good agreement with the simulated values. The (001) diffraction peaks are also observed in the patterns, demonstrating a moderate ordering along the *c*-axis that extends the



Figure 3. Simulated unit cells and experimental grazing incidence Xray diffraction (GIXRD) patterns of PADTDI-BT and PADTDI-FBT.

dimensionality of charge transport pathways. The corresponding $d_{(001)}$ distance is approximately 17.5 Å. This value is smaller than the calculated distance of a co-repeating D-A unit (ca. 19.7 Å), indicating the tilt along the *c*-axis of the polymer semicrystal. In the in-plane direction, the (010) peak at q_{xy} = ca. 1.80 Å⁻¹ corresponds to a cohesive π -stacking of 3.49 Å. According to the Scherrer equation, the average grain size D_{hkl} = $2\pi K/\Delta q_{hkb}$ where K is the Scherrer constant (0.89) and Δq_{hkl} is the full width at half-maximum of the diffraction peak with regard to the scattering vector q.⁴¹ The average grain sizes of the as-spun PADTDI-BT thin film were 248 and 40.4 Å for d-d and $\pi - \pi$ stacking, respectively, corresponding to average numbers of Bragg planes of 9 and 11 with respect to the (100) and (010) Bragg reflections. After annealing, such average grain sizes increased to 272 and 46.7 Å, respectively. The d-d (26.6 Å) and $\pi - \pi$ (3.49 Å) distances of PADTDI-FBT films are almost identical to those of PADTDI-BT films. The average grain sizes of each Bragg reflections are slightly smaller than those of the nonfluorinated analogues. Such microstructural information validates the well-packed feature of these polymers.

Field-Effect Transistors and Device Optimization. The semiconducting characteristics of PADTDI-BT- and PADTDI-FBT-based devices were measured using the top-gate/bottomcontact (TGBC) FET configuration (channel length/width = $50/4500 \ \mu m$). We used poly(ethylene terephthalate) (PET) substrates and hybrid bilayer poly-(perfluorobutenylvinylether)/poly(vinyl alcohol) (Cytop/ PVA) dielectrics (40 nm thick Cytop, 300 nm thick PVA, C_i = 15.6 nF cm⁻²).⁴² The mobilities were extracted from the saturation regimes using the following equation $I_{DS} = (W/2L)$ $C_{\rm i}\mu(V_{\rm GS}-V_{\rm th})^2$, where $I_{\rm DS}$ is source–drain saturation current, W/L is the channel width/length, C_i is the capacitance per unit area of the insulator, μ is the mobility, V_{GS} is the gate voltage, and $V_{\rm th}$ is the threshold voltage. Figure 4 shows the transfer and output characteristics of the PADTDI-BT- and PADTDI-FBT-based devices with approximately ideal I-V curves, and the corresponding FET parameters are listed in Table 2. Both



Figure 4. Typical transfer and output characteristics of the TGBC FETs based on (a) PADTDI-BT and (b) PADTDI-FBT thin films.

polymers exhibit ambipolar charge transport behaviors with predominant p-channel characteristics. Annealing treatment at a mild temperature of 100 °C afforded the highest carrier mobilities (Figure S13). The electron mobilities of the two polymers are in the range of 10^{-3} - 10^{-2} cm² V⁻¹ s⁻¹. By contrast, PADTDI-BT-based devices exhibit the maximum hole mobility of 1.47 cm² V⁻¹ s⁻¹ with an on/off current ratio of 10^3 and a threshold voltage of -12 V. By contrast, PADTDI-FBT-based devices show higher mobilities of up to 4.21 cm² V⁻¹ s⁻¹ with an on/off current ratio of 10³ and a threshold voltage of -18 V. The average mobilities of at least five devices for PADTDI-BT- and PADTDI-FBT-based thinfilm transistors are 1.19 and 3.84 cm² V⁻¹ s⁻¹, respectively (Figure S14). The high charge-carrier mobility is among the highest mobility values reported for new-core polymer-based FET devices in recent years (Table S1). To evaluate the reliability of the devices, we measured the mobilities at the linear regimes using the equation $I_{\rm DS} = (W/L)C_{\rm i}\mu(V_{\rm GS} - V_{\rm th})$ $V_{\rm DS}$. The maximum linear hole mobilities for PADTDI-BTand PADTDI-FBT-based devices are 0.99 and 3.53 cm² V⁻¹ s^{-1} with the average values of 0.80 and 3.10 cm² V⁻¹ s⁻¹, respectively. Moreover, the relatively small gate-voltage dependence of mobility, sweep-rate dependence, and hysteresis were observed during the test (Figures S15-S18). This result may pave the way for the potential in organic electronics. Evidently, such high mobilities highlight that the underlying geometry-directed assembly facilitates the charge transport.

The effect of annealing treatment was characterized by atomic force microscopy (AFM), GIXRD, and carbon K-edge near-edge X-ray absorption fine structure (NEXAFS) spectroscopy. First, we studied the surface morphological changes using tapping-mode AFM. The topological AFM images of the PADTDI-BT and PADTDI-FBT thin films are shown in Figure 5, exhibiting interconnected textures in both thin films. PADTDI-BT films exhibit granular morphologies, whereas fibrillar-like features are observed in PADTDI-FBT thin films. Compared with the as-spun thin film, annealing tends to afford a homogeneous film that fills in the energetic traps and

Table 2	2. FET	Characteristics	of	ADTDI-	Based	Copol	ymers ^a
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	p-channel			n-channel				
polymer	$\mu_{\rm h} \; ({\rm cm}^2 \; {\rm V}^{-1} \; {\rm s}^{-1})^b$	$I_{\rm on}/{I_{\rm off}}^c$	$V_{\rm th}~({ m V})$	$\mu_{\rm e} \; ({\rm cm}^2 \; {\rm V}^{-1} \; {\rm s}^{-1})^b$	$I_{\rm on}/{I_{\rm off}}^c$	$V_{\rm th}~({ m V})$		
PADTDI-BT	$1.19 \pm 0.28 \ (0.80 \pm 0.19)$	$10^2 - 10^3 (10^4 - 10^5)$	-11 ± 2	$0.010 \pm 0.004 \ (0.009 \pm 0.003)$	$10^{0} - 10^{1} (10^{3} - 10^{4})$	15 ± 5		
PADTDI-FBT	$3.84 \pm 0.37 \ (3.10 \pm 0.43)$	$10^3 - 10^4 (10^3 - 10^4)$	-16 ± 2	$0.005 \pm 0.001 \ (0.002 \pm 0.001)$	$10^0 - 10^1 (10^3 - 10^4)$	19 ± 6		
^a TGBC devices with $L = 50 \ \mu m$ and $W = 4500 \ \mu m$ fabricated on PET substrates. ^b Mobilities were extracted from the saturation and linear (in								

parentheses) regime. The average mobilities were obtained from at least five devices. 'Estimated from the saturation and linear (in parentheses) regime.



Figure 5. AFM height images of as-spun and annealed polymer thin films of (a, b) PADTDI-BT and (c, d) PADTDI-FBT on a PET substrate. From left to right: as-spun and annealed films at 100 $^{\circ}$ C.

morphological defects, leading to fewer grain boundaries and facilitating charge transport.

The orientation preferences of the polymer chains were qualified by Herman's orientation parameter (*S*) (Figure S19). All of the thin films exhibit weak edge-on packings. The calculated $S_{(200)}$ values of as-spun and annealed PADTDI-BT thin films are in the range of 0.24–0.25, demonstrating minute orientation changes toward edge-on packing during the annealing treatment. In contrast, decreased edge-on fractions with the decreased *S* values are evident in the fluorinated polymer films. These fluorinated polymer-based thin films showed a slight tendency toward isotropic alignment after thermal treatment as the *S* value changes from 0.314 for the asspun thin film to 0.290 for the film after annealing at 100 °C.

To further reveal the variation of crystallinity during the annealing treatment, we performed paracrystalline disorder analysis. The paracrystalline disorder due to numerous degrees of conformational freedom results in the broadening of diffraction peaks because of the variance of interplanar spacing.⁴³⁻⁴⁶ For paracrystals, $\Delta b = l/d[l/N + (\pi gh)^2]$, where Δb is the integral breadth $(b = 2 \sin \theta / \lambda = q/2\pi)$, N is the average number of Bragg planes, h is the order of the diffraction peak, and g is the paracrystalline distortion parameter. The g value can be readily obtained from the slope of the $\Delta b - h^2$ plot (Figure S21). An ideal crystal is described by g = 0, whereas g values of semicrystalline conjugated polymers are in the range of 1-10%. Given the significant overlap between the (400) diffraction and the alkyl chain stacking peaks, only the first three peaks were used to calculate the g value. The g value for as-spun PADTDI-BT is 5.71% and decreases to 5.05 and 4.81% after thermal treatment at 60 and 100 °C, respectively. In the case of PADTDI-FBT,

the corresponding values are 6.35, 5.95, and 5.76%. These results demonstrate that the enhanced crystallinity of grains is beneficial to the charge transport.

We performed carbon K-edge near-edge X-ray absorption fine structure (NEXAFS) spectroscopy in total electron yield (TEY) mode to further study the surface microstructures before and after annealing (Figure 6).^{47–49} TEY detection is



Figure 6. Angle-resolved NEXAFS spectra of polymer thin films in total electron yield mode: (a) as-spun PADTDI-BT, (b) annealed PADTDI-BT, (c) as-spun PADTDI-FBT, (d) annealed PADTDI-FBT, and (e) schematic picture of the geometry of NEXAFS spectroscopy. The inset values are the dichroic ratio (*R*) of the 1s $\rightarrow \pi^*$ intensity and the average tilt angle ($\langle \alpha \rangle$) of a polymer backbone.

surface sensitive with the information depth of a few nanometers for a polymer sample.⁵⁰ This measurement reflects the molecular orientation at the dielectric/polymer interface where charge transport occurs for a top-gate transistor. The lower energy features at approximately 284.8 eV correspond to the transition of an electron-withdrawing aromatic core, and those in the 285–287 eV range are associated with the 1s $\rightarrow \pi^*$ transition of bithiophene and substituted unsaturated carbon atoms. These spectra also exhibit significant C 1s $\rightarrow \sigma^*$ features due to the presence of alkyl side chains. The resonance intensity is dependent on the relative molecular orientation to the electric field vector of the synchrotron beam. For the C 1s

 $\rightarrow \pi^*$ transition, the transition dipole moment is oriented perpendicular to the aromatic backbone. The variation in resonance intensity as a function of incidence angle can be used to determine the backbone orientation. The dichroic ratio (R), defined as the difference of the intensities at 90 and 0° incidence divided by their sum, and the corresponding average tilt angle $(\langle \alpha \rangle)$ are two typical parameters to describe the orientation. We fitted the π^* intensities of each curve (details are given in the Supporting Information); the results show that the R values are 0.58, 0.70, 0.70, and 0.53 for as-spun PADTDI-BT, annealed PADTDI-BT, as-spun PADTDI-FBT, and annealed PADTDI-FBT thin films, respectively. These positive values indicate large average tilt angles of the transition dipole with respect to the substrate normal. Consequently, polymer strains at the top surface pack in a highly edge-on manner. Thermal treatment leads to different propensities for backbone alignment; after annealing, PADTDI-BT prefers an enhanced edge-on packing, whereas PADTDI-FBT gives a reduced fraction of edge-on crystallites. This phenomenon is likely due to fluorination altering the surface energy of the polymer. Such tendencies are consistent with GIXRD analyses described above.

CONCLUSIONS

The design of new semiconducting polymers is still difficult to rationalize because many parameters are involved. Recent design strategies have focused mainly on electronic structures, molecular planarity, torsional barriers, conformational locks, robustness to structural disorder, and side-chain engineering. Besides tuning of electronic structures, other factors are all related to geometric control at various length scales. In this contribution, we develop a new heptacyclic acceptor, anthradithiophene diimide, and discuss in detail the correlations between backbone geometry and semiconducting properties. The high mobility of up to 4.21 cm² V⁻¹ s⁻¹ is likely ascribed to the geometry-directed self-assembled nature of the polymer. The ideal packing modes show sufficient evidence that geometric factors, including the side-chain length, backbone linearity, positions of substituents, and tilting angle between the side chain and the backbone, contribute to the formation of self-assembly at short range. Interdigitation of side chains is supramolecularly preferable for high-mobility semiconducting polymers. These insights may help to probe into the underlying of the self-assembled structure beyond the molecular formula and the design of high-mobility materials with bulk dimensionalities of charge percolation pathways. A modification of the D-A polymers is not a simple permutation and combination. Geometric control is equally important to electronic structures. A good candidate should be both electronically preferable and geometrically optimized. Ruling out the unfavorable candidates in the first stage accelerates the study in this field that holds promise for the future evolvement of polymeric semiconductors.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.chemma-ter.8b05353.

Experimental details; theoretical calculations; thermogravimetric analysis traces and differential scanning calorimetry traces; additional absorption and fluorescent Article

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Notes

The authors declare no competing financial interest.

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