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π-Electron Systems

Diarylated Bi(thieno[2,3-*c*]thiophene)s: A Ring-Fusing Strategy for Controlling the Molecular Alignment of Oligoarenes**

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A highly attractive feature of π-conjugated molecules is that their electronic properties in the solid state are often completely different from those in solution. For example, J-aggregates show red-shifted and narrower-bandwidth emissions upon the formation of an appropriate offset π-stacked structure.[1] A π-conjugated skeleton with a characteristic electronic structure as well as optimal intermolecular interactions in the solid state would have superior properties, such as intense luminescence and high charge-carrier mobility, and thus great potential for application in organic electronics.

To this end, we adopted a strategy of incorporating a ring-fused structure at the lateral positions of one-dimensional oligoarenes. Ring fusion at the lateral position of each aromatic building unit reduces the aromaticity and concomitantly increases the quinoid character of the π skeleton. Thus, the ring-fusing strategy is useful for producing an intriguing building unit with a characteristic electronic structure. For example, benzo[*c*]thiophene has been studied extensively as a building unit for narrow-bandgap polymers.[2] Besides this electronic effect, we envisioned that widening the π skeleton by ring fusion would also significantly affect the molecular alignment in the solid state. On the basis of this idea, we designed a thieno[2,3-*c*]thiophene dimer **1** as a core framework, which can be considered as a bithiophene skeleton that has been widen by one thiophene unit (Figure 1).

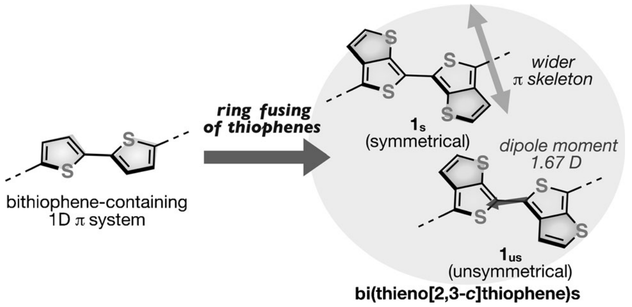

Figure 1. Molecular design of the bi(thieno[2,3-*c*]thiophene)s.

Notably, the HOMO–LUMO energy gap of thieno[2,3-*c*]thiophene is narrower than that of the parent thiophene, yet wider than that of benzo[*c*]thiophene owing to the smaller contribution of the quinoid resonance without an excessive increase in the HOMO energy level.[3–6] This moderate electronic effect is beneficial for the production of a π-conjugated system that is stable to oxidation by air. Various fascinating polymers have been synthesized by the use of thieno[2,3-*c*]thiophene monomers, some of which showed high performance as p-type semiconductors for bulk-heterojunction solar cells.[3–7] Besides this electronic feature, the thiophene-widened bithiophene skeleton of **1** should favor effective intermolecular π stacking in the solid state. In particular, a change in the orientation of the fused thiophene ring from symmetrical $\mathbf{1}_{\mathrm{s}}$ to unsymmetrical $\mathbf{1}_{\mathrm{us}}$ leads to a skeleton with a dipole moment of 1.67 D, despite the absence of polar functional groups. This dipole moment would aid the formation of a different molecular alignment in the condensed phase. To explore the impact of the ring-fusing strategy, we synthesized bi(thieno[2,3-*c*]thiophene)-based π-conjugated compounds. Herein we describe a robust synthetic method for a series of diarylated bi(thieno[2,3-*c*]thiophene)s and their solid-state structures and properties.

As a clue to synthetic access to the bi(thieno[2,3-*c*]thiophene) skeleton, we previously reported that *o*-arylcarbonyl-substituted diphenylacetylenes efficiently undergo a double 5-*exo*-dig cyclization upon photoirradiation to produce 3,3′-diaryl-1,1′-bi(benzo[*c*]furan)s in one step.[8] The products have narrow HOMO–LUMO gaps, but were rather unstable owing to the excessively high HOMO levels. We hypothesized that the replacement of the substrate with a thiocarbonyl-substituted dithienylacetylene **3** would enable the construction of the bi(thieno[2,3-*c*]thiophene) framework through a similar reaction course.[9]

To generate the thiocarbonyl precursor **3** in situ, we treated the bis(3-phenylcarbonyl-2-thienyl)acetylene **2a** with the Lawesson reagent in toluene at reflux. The intramolecular double 5-*exo*-dig cyclization proceeded under these thermal conditions without photoirradiation to produce the bi(thieno-[2,3-*c*])thiophene **4a** in 82 % yield (Scheme 1). Since **2a** did not undergo any reaction in the absence of the Lawesson reagent at the same temperature, an initial step of this

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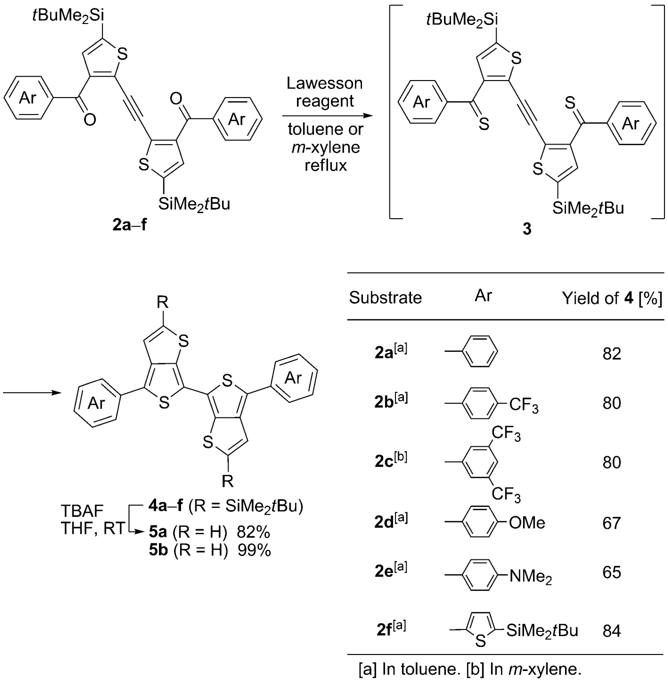

Scheme 1. Double 5-*exo*-dig cyclization of bis(3-carbonyl-2-thienyl)acetylenes **2** and desilylation.

reaction is thought to be the transformation of the carbonyl groups into thiocarbonyl groups. We synthesized a series of derivatives **4b**–**f** with various terminal aryl groups in 65–84 % yield by this versatile one-pot protocol. Compounds **4a** and **4b** were further desilylated with tetrabutylammonium fluoride (TBAF) to give **5a** and **5b** in 82 and 99 % yield, respectively.

We evaluated the electronic structures of the synthesized bi(thieno[2,3-*c*]thiophene)s by cyclic voltammetry (Table 1; see also Figure S23 in the Supporting Information). Phenyl-substituted **4a** showed two-step reversible redox waves with $E_{1/2,\mathrm{ox1}}$ and $E_{1/2,\mathrm{ox2}}$ values of +0.23 and +0.86 V (versus Fc/Fc$^+$; Fc = ferrocene), respectively. Notably, the first oxidation peak potential E_{pa1} of **4a** (+0.30 V) was negatively shifted by 0.37 V as compared to that of a non-thiophene-fused congener, 5,5′-diphenyl-2,2′-bithiophene (E_{pa1} = +0.67 V versus Fc/Fc$^+$),[10] and thus indicated that the incorporation of the fused thiophene rings into the 2,2′-bithiophene framework enhanced its electron-donating character. Furthermore, the terminal aryl groups greatly influenced the electronic structure of the bi(thieno[2,3-*c*]thiophene)-based π-electron systems. Whereas the introduction of electron-withdrawing aryl groups into the bi(thieno[2,3-*c*]thiophene) skeleton resulted in a higher oxidation potential ($E_{1/2,\mathrm{ox1}}$ = +0.42, +0.53 V for **4b** and **4c**, respectively), compounds with electron-donating aryl groups, including *p*-anisyl (compound **4d**), 4-(dimethylamino)phenyl (compound **4e**), and thienyl groups (compound **4f**) exhibited a significantly lower oxidation potential ($E_{1/2,\mathrm{ox1}}$ = +0.08, −0.22, +0.12 V for **4d**, **4e**, and **4f**, respectively). In particular, the $E_{1/2,\mathrm{ox1}}$ value of the Me$_2$N-substituted derivative **4e** was more negative than that of ferrocene, which indicates the high electron-donating ability of the 4-(dimethylamino)phenyl groups. All derivatives were fairly stable in the two-electron oxidation process, regardless of the terminal aryl groups. These results demonstrate the potential utility of bi(thieno[2,3-*c*]thiophene)-containing π-electron systems to function as p-type semiconducting materials.

Table 1: Electrochemical data for the TBDMS-substituted bi(thieno[2,3-*c*])thiophenes **4**.

Compound	Oxidation potential[a] $E_{1/2,\mathrm{ox1}}$ [V][b] (E_{pa1} [V][c])	 $E_{1/2,\mathrm{ox2}}$ [V][d] (E_{pa2} [V][e])
4a	+0.23 (+0.30)	+0.86 (+0.92)
4b	+0.42 (+0.51)	+1.02 (+1.11)
4c	+0.53 (+0.59)	+1.10 (+1.12)
4d	+0.08 (+0.13)	+0.53 (+0.57)
4e	−0.22 (−0.16)	−0.05 (+0.01)
4f	+0.12 (+0.18)	+0.63 (+0.69)

[a] The oxidation potential was determined by cyclic voltammetry under the following conditions: **4** (1 mM), Bu$_4$N$^+$PF$_6^-$ (0.1 M), CH$_2$Cl$_2$; scan rate: 100 mV s^{-1}. [b] First oxidation potential versus Fc/Fc$^+$. [c] First oxidation peak potential versus Fc/Fc$^+$. [d] Second oxidation potential versus Fc/Fc$^+$. [e] Second oxidation peak potential versus Fc/Fc$^+$. TBDMS = *tert*-butyldimethylsilyl.

During the purification of a series of diarylated bi(thieno[2,3-*c*]thiophene)s, we observed that the photophysical properties of the 4-trifluoromethylphenyl-substituted derivative **5b** in the solid state were totally different from those of a dilute solution of **5b** (Figure 2a; see also Table S2 in the Supporting Information). In CH$_2$Cl$_2$, **5b** was yellow and emitted green fluorescence. The absorption (λ_{abs}) and fluorescence maximum wavelengths (λ_{em}) were 473 and 520 nm, respectively (Figure 2b). In stark contrast, crystalline **5b** was red and emitted intense red luminescence. Its excitation (λ_{ex}) and fluorescence maximum wavelengths (λ_{em})[11] were 610 and 667 nm, respectively, and thus red-shifted from those in CH$_2$Cl$_2$ by 4700 cm^{-1} (0.59 eV) and 4200 cm^{-1} (0.53 eV).

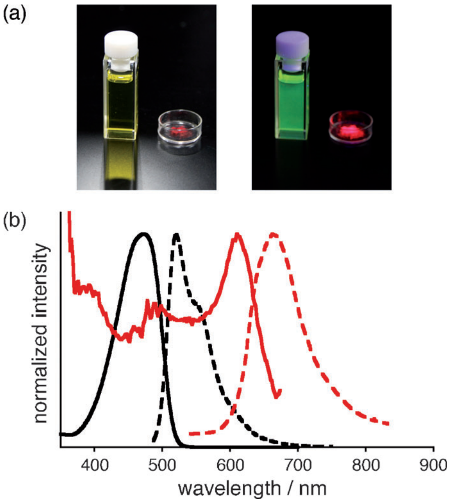

Figure 2. a) Photographs of **5b** dissolved in CH$_2$Cl$_2$ and crystals of **5b** under room light (left) and irradiation with a hand-held UV lamp (365 nm). b) Electronic spectra of **5b**. Black solid line: absorption spectrum in CH$_2$Cl$_2$; black broken line: emission spectrum in CH$_2$Cl$_2$; red solid line: excitation spectrum in the crystal; red broken line: emission spectrum in the crystal.

These significant shifts resulted from the strong intermolecular interactions in the crystalline state. Moreover, the fluorescence quantum yield of **5b** in the crystal ($\Phi_F = 0.13$) was higher than that in solution ($\Phi_F = 0.04$). Although the phenyl-substituted derivative **5a** showed similar red shifts in the absorption and emission maxima, the extent of the shifts was smaller (see Figure S34 and Table S2). The energy difference between the absorption maximum in solution and the excitation maximum in the solid state ($\Delta\nu_{abs}$) was 3600 cm^{-1}, whereas the difference between the emission maxima ($\Delta\nu_{em}$) in solution and in the solid state was 3200 cm^{-1}. The terminal substituents play a crucial role in causing these differences between the solution and the solid state.

Figure 3 shows the crystal structure of **5b** as determined by X-ray crystallography.[12] The CF_3-substituted compound **5b** has a coplanar conformation of the bi(thieno[2,3-*c*]thiophene) skeleton with a dihedral angle of 0°. The two sulfur atoms in each bay area were located in close proximity to one another at distances of 3.293 and 3.330 Å, which are shorter than the sum of the van der Waals radii (3.70 Å). This compound formed a slipped π-stacked array in which an electron-accepting trifluoromethylphenyl moiety was located above the fused thiophene ring of an electron-donating thienothiophene moiety in the adjacent molecule. As a consequence, there was significant intermolecular overlap, which led to a strong intermolecular interaction.

To assess the degree of the intermolecular interaction in the crystal packing, we conducted DFT calculations (B3LYP/6-31G*) on three stacked molecules of **5b**. The stacking arrangement was derived directly from the X-ray crystal structure of **5b**. An intermolecular orbital interaction between the HOMOs of the adjacent molecules gave rise to a significant decrease in the HOMO–LUMO energy gap and an increase in the oscillator strength for the lowest-energy transition as compared to the isolated molecule in gas phase (see Figure S37). This finding indicated stronger exciton coupling in **5b**, which is probably responsible for the pronounced red shift in the absorption and fluorescence spectra and the enhanced Φ_F value in the crystalline state.

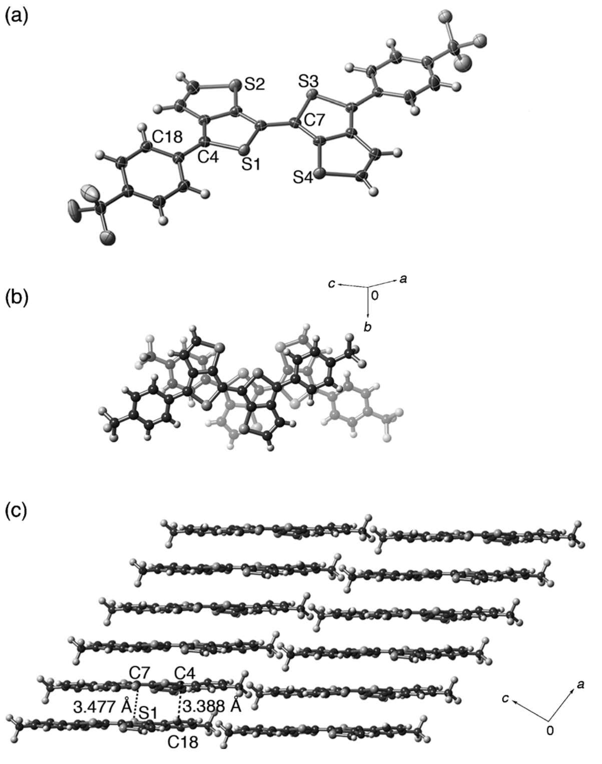

Figure 3. X-ray crystal structure of **5b**: a) thermal-ellipsoid plot (50% probability for thermal ellipsoids); b) overlap of two adjacent molecules; and c) packing structure shown as a ball-and-stick model.

We compared the packing structure of **5b** with the packing structures of analogous compounds either without CF_3 groups or without fused thiophene rings, namely, the phenyl-substituted derivative **5a** and 5,5′-bis(4-trifluoromethylphenyl)-2,2′-bithiophene (**6**), the latter of which exhibits strong n-type semiconducting properties.[13] Both compounds adopted herringbone packing structures with much less intermolecular overlap between the stacked molecules (see Figures S27 and S28). These comparisons indicated that the introduction of terminal CF_3 groups[14] as well as the widening of the π skeleton with the fused thiophene moieties in the bi(thieno[2,3-*c*]thiophene) unit is crucial for the formation of the π-stacked array in **5b**.

To explore the impact of the linkage pattern in the bi(thieno[2,3-*c*]thiophene) skeleton on the solid-state properties, we synthesized an unsymmetrical analogue, the *p*-$CF_3C_6H_4$-substituted 2,6′-bi(thieno[2,3-*c*]thiophene) **7**. A three-step synthesis from 2-bromo-3-iodothiophene produced an unsymmetrical dithienylacetylene precursor, which successfully underwent double 5-*exo* cyclization to afford the target compound **7** in 52% yield (see Scheme S1 in the Supporting Information). Cyclic voltammetry of this compound in CH_2Cl_2 showed a reversible redox wave for one-electron oxidation. The first oxidation potential was +0.44 V (versus Fc/Fc$^+$), which was comparable to that of **4b** and demonstrated that the orientation of the fused thiophene ring does not have a significant effect on the electronic structure. However, this orientation of the fused thiophene ring significantly affects the solid-state packing structure. Thus, unlike the symmetrical 2,2′-bi(thieno[2,3-*c*]thiophene) **5b**, crystallization of the unsymmetrical **7** led to two polymorphs with an apparent color difference (Figure 4a). Recrystallization from a 1,2-dichloroethane/CH_3CN mixed solvent system gave red needlelike crystals (polymorph α, abbreviated as α-**7**), the color of which was similar to that of **5b**. In contrast, sublimation under vacuum afforded violet needlelike crystals (polymorph β, abbreviated as β-**7**). Differential scanning calorimetry (DSC) measurements demonstrated that the polymorph β-**7** was thermally more stable than α-**7** (see Figures S40 and S41).

Whereas the absorption and fluorescence spectra of solutions of **5b** and **7** in CH_2Cl_2 were almost identical to each other (Figure 4b), the diffuse reflectance spectrum of β-**7** in the crystalline state was significantly red-shifted relative to those of **5b** and α-**7** (Figure 4c). The absorption-edge wavelengths determined by the diffuse reflectance method were estimated to be 647, 679, and 723 nm for **5b**, α-**7**, and β-**7**, respectively. The energy shift in the absorption edge from

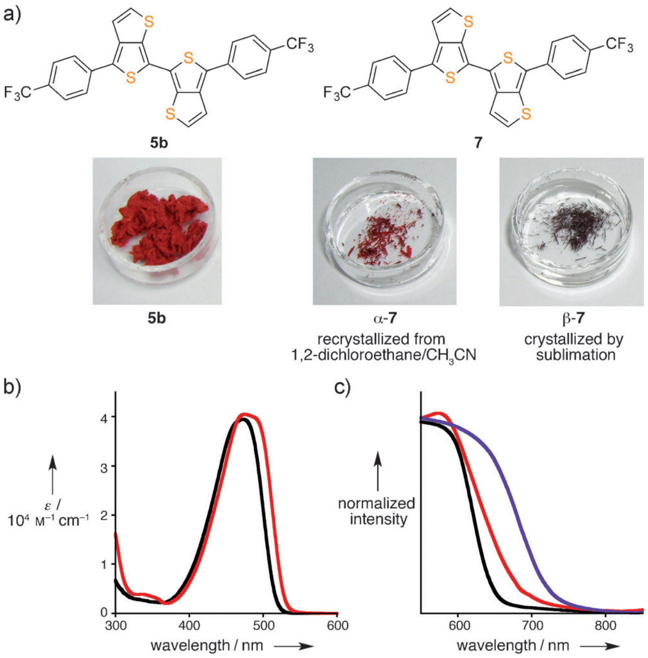

Figure 4. a) Photograph of crystalline **5b**, α-**7**, and β-**7** under room light. b) UV/Vis absorption spectra of **5b** (black) and **7** (red) in CH_2Cl_2. c) Diffuse reflectance spectra of crystalline **5b** (black), α-**7** (red), and β-**7** (violet).

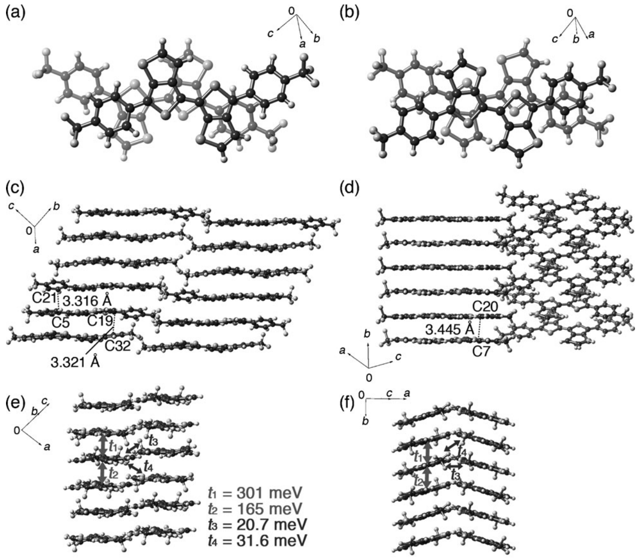

Figure 5. Crystal-packing structures of α-**7** (a,c,e) and β-**7** (b,d,f), and the transfer integrals (t) calculated with the ADF program.

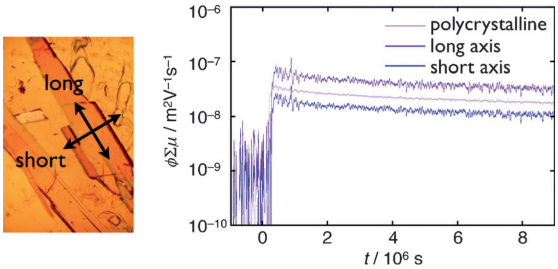

Figure 6. Conductivity transient of α-**7** in its crystal forms upon excitation at 355 nm (2.7×10^{15} photons cm^{-2}) under ambient conditions. Kinetic traces are recorded for the polycrystalline state and for a single crystal along the directions indicated by arrows in the picture.

5b to β-**7** was 1600 cm^{-1} (0.20 eV). These findings clearly demonstrate the significant impact of the linkage pattern of the bi(thieno[2,3-*c*]thiophene) skeleton on the extent of the intermolecular interaction.

Indeed, X-ray crystallographic analysis revealed that the crystal-packing structure in the red crystal α-**7** was almost identical to that of the symmetrical congener **5b**, with the molecules stacked on one another in a slipped fashion along the long axis (Figure 5a). In contrast, the molecules in β-**7** formed π-stacked arrays with a small displacement along the shorter axis of the diarylated bi(thieno[2,3-*c*]thiophene) framework (Figure 5b).[12] These results indicate that the difference in the linkage pattern altered the packing structure and led to the significant difference in the electronic structure and thus the photophysical properties in the solid state. The difference in the molecular alignment is probably due to the slight difference in steric demands and/or the dipole moment ($\mu = 0$ and 0.97 D for **5b** and **7**, respectively, as calculated at the B3LYP/6-31G* level).

Flash-photolysis time-resolved microwave conductivity (FP-TRMC) measurements confirmed that the intrinsic charge-carrier mobility of α-**7** was highly anisotropic (Figure 6).[15] High mobilities were obtained for the direction along the longer axis of the crystal ($\Sigma\mu = 4.0$ cm^2 V^{-1} s^{-1} along the longer axis, 1.3 cm^2 V^{-1} s^{-1} as an isotropic value) under O_2-saturated conditions without effective scavenging of charge carriers, which suggests that the major charge carriers are positive holes. The transfer integrals (t) among the HOMOs in the crystal-packing structures were estimated for both α-**7** and β-**7** by calculations with the ADF program[16,17] and were found to be highly anisotropic with very high values along the π-stacking direction ($t_1 = 301$ meV and $t_2 = 165$ meV for α-**7**, and $t_1 = 247$ meV and $t_2 = 206$ meV for β-**7**, as calculated at the PW91/DZP level); these values are consistent with the experimental results. Importantly, these values are significantly higher than those of pentacene and rubrene,[18] which are representative p-type organic semiconducting materials with excellent hole mobility.

In summary, we have developed an intramolecular double 5-*exo*-dig cyclization of bis[(arylcarbonyl)thienyl]acetylenes as a general and efficient method for the synthesis of diaryl-substituted bi(thieno[2,3-*c*]thiophene)s. The π-electron systems thus produced form a dense π-stacking structure in the solid state. The resulting intriguing solid-state photophysical properties were found to depend on the terminal substituents as well as the linkage pattern. FP-TRMC measurements and ADF calculations confirmed the highly anisotropic and large charge-carrier mobility along the π-stacking array. These findings demonstrate the efficacy of the ring-fusing strategy not only for modifying the electronic structure, but also for altering molecular alignment in the solid state with the production of potent core skeletons for excellent semiconducting materials.

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[12] See the Supporting Information for the crystal data for **5a**, **5b**, α-**7**, and β-**7**. CCDC 948611 (**5a**), 948610 (**5b**), 948608 (α-**7**), and 948609 (β-**7**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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