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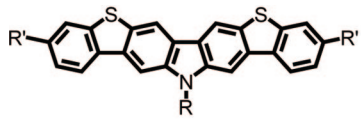
Conjugated Ladder-Type Heteroacenes Bearing Pyrrole and Thiophene Ring Units: Facile Synthesis and Characterization

Peng Gao, Xinliang Feng, Xiaoyin Yang, Volker Enkelmann, Martin Baumgarten, and Klaus Müllen*

Max Planck Institute for Polymer Research, Ackermannweg 10, D-55128, Mainz, Germany

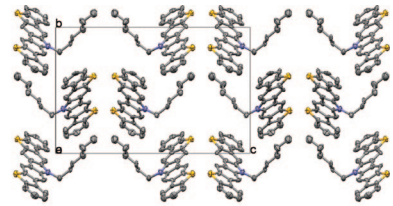
muellen@mpip-mainz.mpg.de

Received August 27, 2008



DBTCZs

R = CH_3, C_4H_9, C_6H_{13}, C_8H_{17}
R' = H, C_4H_9



R = C_6H_{13}; R' = H

Ladder-type heteroacenes containing pyrrole and thiophene rings, dibenzo[*b*,*b*′]thieno[2,3-*f*:5,4-*f*′]-carbazoles (DBTCZ, **1**), and diindolo[3,2-*b*:2′,3′-*h*]benzo[1,2-*b*:4,5-*b*′]bis[1]benzothiophene (DIBBBT, **2**), were facilely synthesized through proper precursors (**7**, **11**, and **18**) respectively. The key step is a triflic acid induced intramolecular electrophilic coupling reaction of corresponding aromatic methyl sulfoxides with activated aromatic building blocks, which enables regioselective ring closure. Both precursors (**7** and **11**) toward DBTCZ gave the symmetrical product but with solubilizing alkyl chains in two different fashions. DIBBBT was also synthesized as the extended ladder-type heteroacene with defined structure. These obtained heteroacenes are fully characterized (mass spectrometry, NMR, elemental analysis), and their X-ray analysis and optical and electrochemical properties are reported.

Introduction

Fused acenes such as pentacene are attractive materials for organic electronics. Both pentacene single crystals and thin polycrystalline pentacene films exhibit charge mobilities above 1 $cm^2/V \cdot s$ in organic field effect transistors (OFETs).[1,2] However, pentacene suffers from insolubility and sensitivity to visible light due to their high-lying HOMO levels and narrow band gaps, which limit its practical applications under ambient conditions.[3] During the past years, a large number of new heteroacenes as pentacene analogues have been developed and tested as active semiconducting channels in OFETs, showing dramatically improved stability and high performance close to that of pentacene.[4] This success could be attributed to their coplanar structure and pronounced molecular assembly through the intermolecular π-interactions and additive sulfur−sulfur (S−S) interactions which are essential to achieve high charge mobility.[5] Therefore, one of the approaches toward high-performance semiconducting materials is the development of new ladder-type heteroacenes.

Compared with the tremendous amount of work focusing on the synthesis of pentacene analogues, only a few examples of further extended ladder-type molecules containing fused heterocycles (e.g., thiophene or/and pyrrole) have been reported,[6−8]

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10.1021/jo801898g CCC: $40.75 © 2008 American Chemical Society
Published on Web 11/11/2008

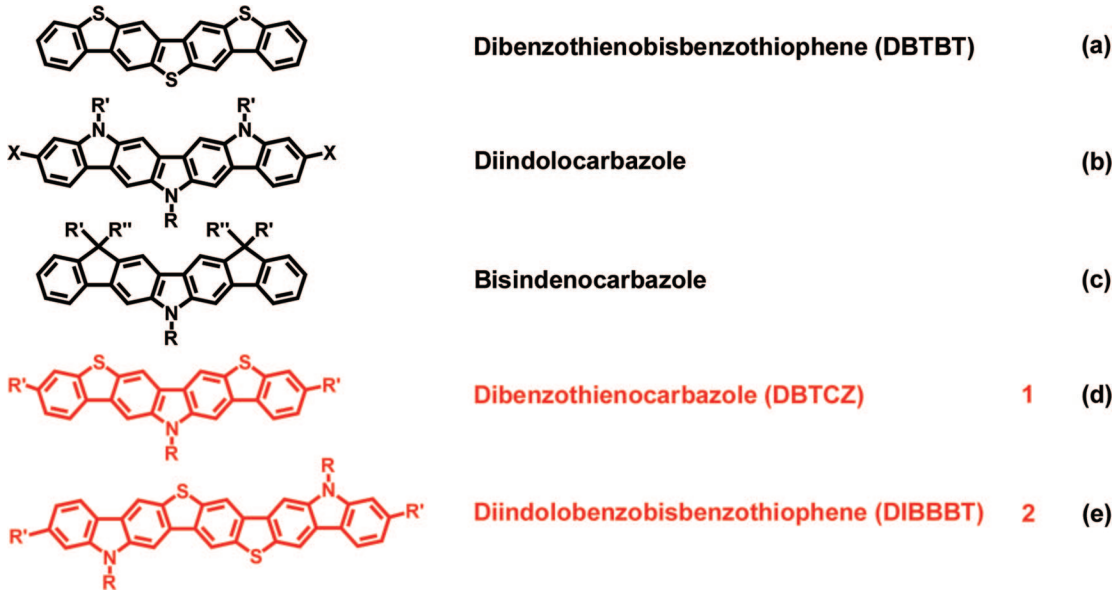
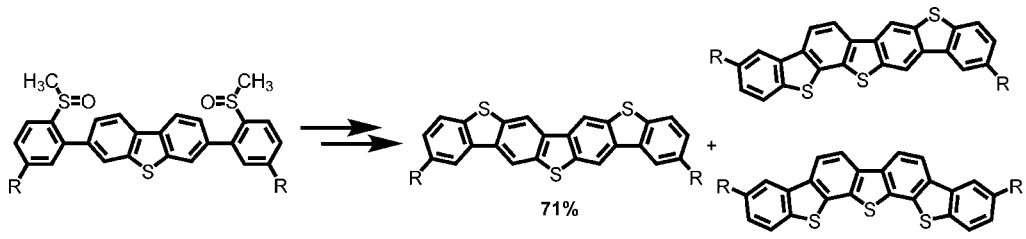


FIGURE 1. Ladder-type π-conjugated heteroacenes with thiophene or pyrrole ring units.

SCHEME 1. Synthesis of DBTBT via Double Intramolecularly Electrophilic Coupling Reaction



presumably due to the difficulty in the establishment of efficient and practical synthetic protocols. For example, the sulfur atom bridged *p*-quaterphenyl dibenzothienobisbenzothiophene (DBTBT, Figure 1a) was synthesized as an inseparable mixture of three different regioisomers due to the poor selectivity of acid-induced electrophilic coupling reaction (Scheme 1).[6] During the same time, Bouchard et al. have tried several methods to get symmetrical ladder oligo(*p*-aniline) (diindolocarbazole) as a fully nitrogen atom bridged *p*-quaterphenyl (Figure 1b), and finally they found that the intramolecular Ullmann reaction instead of an unregioselective Cadogan ring closure was the most effective pathway.[7] In contrast, Sonntag et al. successfully synthesized bisindenocarbzole via the Friedel−Crafts-type alkylation ring closure which occurred exclusively at the 3 and 6 position of the carbazole (Figure 1c).[8]

On the basis of the known examples described above, we tried to further broaden the family of π-extended oligoacences, especially with the combination of electron-rich thiophene and pyrrole ring units in one molecular skeleton. Herein we report a regioselective synthetic approach toward a new series of dibenzo[*b*,*b*′]thieno[2,3-*f*:5,4-*f*′]-carbazole (DBTCZ **1**, Figure 1d) and its ring-extended derivative diindolo[3,2-*b*:2′,3′-*h*]benzo[1,2-*b*:4,5-*b*′]bis[1]benzothiophene (DIBBBT **2**, Figure 1e). Their crystal structure and physicochemical properties are also described.

Results and Discussion

Synthesis of Dibenzo[*b*,*b*′]thieno[2,3-*f*:5,4-*f*′]-carbazole (DBTCZ). The carbazole skeleton is a modest nucleophile that can be readily derivatized with a variety of electrophiles, and the most reactive positions for electrophilic substitution are the 3 and 6 positions ("para" to the nitrogen atom). On the other hand, triflic acid activated aromatic methyl sulfoxides are well-known for use as an electrophile,[9] and the intramolecular electrophilic coupling reaction could introduce the thiophene ring units easily. The problem of regioisomers met in synthesizing DBTBT raised the question: how to construct a useful precursor molecule for DBTCZ **1**?[6] Here both precursors **7** and **11** seemed possible (Scheme 2). Through precursor **7**, one could get compound **1** with alkyl chains lying in one side of molecular central rings, whereas precursor **11** allows the facile introduction of two alkyl substituents in the *long-axis* of the molecular skeleton. The total synthetic route toward **1** via these two different precursors is therefore described in Scheme 3.

Obviously, the shortest synthetic route toward **1** is via the synthesis of precursor **7**. Starting from 2,7-dibromocarbazole, compounds **5a**−**d** were made by introducing different alkyl side chains.[10] Subsequently, compounds **5** were treated with *n*-BuLi in hexane at −78 °C and quenched with 2-isopropoxy-4,4,5,5-

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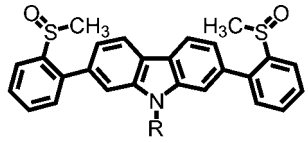
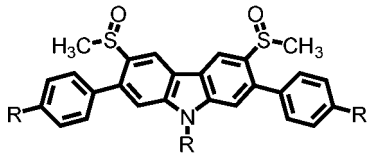
SCHEME 2. Two Possible Precursor Structures 7 and 11 for the Synthesis of DBTCZ 1



7



11

tetramethyl-1,3,2-dioxaborolane to yield *N*-alkyl-2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane-2-yl)carbazole (**6a**−**d**).[11] Suzuki coupling of **6a**−**d** with 1-bromo-2-(methylsulfinyl)benzene (**3**) gave precursors **7a**−**d** in good yields. The final ring-closure reaction was crucial to determine the isomeric purity. Instead of following exactly the procedure described in the synthesis of DBTBT, precursors **7a**−**d** were treated with trifluoromethanesulfonic acid in the presence of phosphorus pentoxide at 0 °C and reacted for 72 h in the dark. Then the as-formed clear mixture was poured into ice/water to give a yellowish powder as precipitate, followed by filtration, drying, and reflux in pyridine for 12 h. After normal workup, only one spot was observed on thin layer chromatography (TLC) plates, which was supposed to be the inseparable isomers or desired pure product of DBTCZ. After column chromatography, the yellow powder of DBTCZ was achieved in good yield (85−95%). The further determination of isomeric purity by ^{1}H NMR spectroscopy (Figure 2a) and the single-crystal structure (Figure 3) indicated that the desired ladder-type acene DBTCZ **1** was the sole product. We ascribe this high regioselectivity to two reasons: first, the 3 and 6 positions on carbazole are the most reactive positions for electrophilic substitution, and second, the reactions were all conducted near 0 °C since the regioselectivity of the thermodynamically controlled reaction is strongly influenced by reaction temperature and steric hindrance.[12a,b]

Apart from the success in synthesizing **1a**−**d** from precursors **7a**−**d**, we followed the second route via precursor **11** toward **1e**, which opened the opportunity to introduce two additional alkyl chains in the molecular long-axis direction. A Suzuki coupling reaction between **5a** and **4** was carried out in a two-phase system of toluene and aqueous potassium carbonate, with $Pd(PPh_3)_4$ as catalyst, and gave **8** in good yield. Afterward, with 2 equiv of *N*-bromosuccinimide in acetic acid, it was possible to regioselectively introduce two bromine groups at the 3 and 6 positions on the carbazole unit of compound **8**. Compound **9** was obtained after a simple column chromatography and further reacted with 2 equiv of *n*-BuLi to form the corresponding 3,6-dilithiated species which was then quenched by dimethyl disulfide to afford compound **10** in 70% isolated yield. Oxidation of **10** with hydrogen peroxide in acetic acid gave precursor **11** in 72% yield. Finally, by following the same procedure as for precursor **7**, compound **1e** was received as yellow flakes in 96% yield. Compounds **1a**−**e** were fully characterized by ^{1}H NMR, ^{13}C NMR spectroscopy, elemental analysis, and mass spectrometry (FD).

Synthesis of Ring-Extended Diindolo[3,2-*b*:2′,3′-*h*]benzo[1,2-*b*:4,5-*b*′]bis[1]benzothiophene. By following the similar strategy as described above, we synthesized another precursor **18**, which allowed the final triflic acid induced ring closure toward further extended but soluble oligoacene **2** (Scheme 4). The easily available 2-bromo-7-chlorocarbazole[13] was alkylated with an ethyl group on the nitrogen atom to give **15**, which was then reacted with 1 equiv of *n*-BuLi at −78 °C. The monolithiated species was then quenched with hexyl iodide to generate the 2-chloro-7-hexyl-9-ethylcarbazole (**16**). Monoboronic ester **17** from **16** was made in high yield by using a mixture of $Pd_2(dba)_3$ and 2-dicyclohexylphosphino-2′,4′,6′-triisopropylbiphenyl as catalyst system.[14] A double Suzuki cross-coupling reaction between **17** and **14** using $Pd(PPh_3)_4$ as catalyst afforded precursor **18** in 72% yield. Subsequent treatment of **18** with trifluoromethanesulfonic acid at 0 °C for 72 h induced double intramolecular ring closure. Later on, the intermediate was refluxed in pyridine to afford target **2** in 95% yield as a yellow solid. The ^{1}H NMR spectrum of **2** confirmed the pure product formation and indicated the high regioselectivity of the electrophilic ring closure reaction (Figure 2c).

Structure Proof of the Heteroacenes by ^{1}H NMR Spectroscopy. As depicted in Figure 2, the ^{1}H NMR spectra provide evidence for the regioselectivity of the ring-closure reaction since all the typical singlets can be assigned to the corresponding aromatic protons in the molecules. No isomers could be discerned from the spectra. The signals of aromatic protons 2, 3, and 5 of **1c** (Figure 2a) shift to high field in the case of **1e** (aromatic protons 2, 3, and 4, Figure 2b), owing to the electron-donating effects of the substituted alkyl chain. In Figure 2c, all the aromatic proton signals were in good agreement with the highly symmetrical structure of compound **2**. The chemical shifts of the aromatic resonances for all the compounds are independent of the concentration and temperature, indicating that there is minimum or no aggregation in solution.

X-ray Diffraction Study on the Single Crystals and the Thin Film of 1c. Crystals of **1c** suitable for single-crystal X-ray diffraction (XRD) studies were grown from cold chloroform. The skeleton of **1c** is found to be planar and further confirms the regioisomeric purity of the compound (Figure 3). Two molecules form a pair with antiparallel structure, possibly due to the steric effect of the substitution on N (Figure 3a). The antiparallel pairs further stack in a tilted cofacial manner, resulting in two-dimensional (2D) π-stacking lamella with adjacent molecules partially overlapping each other (Figure 3b). The angle α between two molecules in one antiparallel pair is 60°. The marked interplanar separation of 3.33 Å between the adjacent molecules in one column indicates the presence of π-interactions along the intermolecular stacking axis (Figure 3a). For **1a**, **1b**, **1d**, **1e**, and **2**, however, no suitably sized crystals for single-crystal X-ray analysis could be obtained from different solvents.

X-ray diffraction in reflection mode of the drop-cast thin film from **1c** was also carried out, with the result being illustrated in Figure 4. The large number of higher order scattering intensities in the diffractogram in Figure 4 point toward high crystallinity of the drop-cast thin film. The appearance of only

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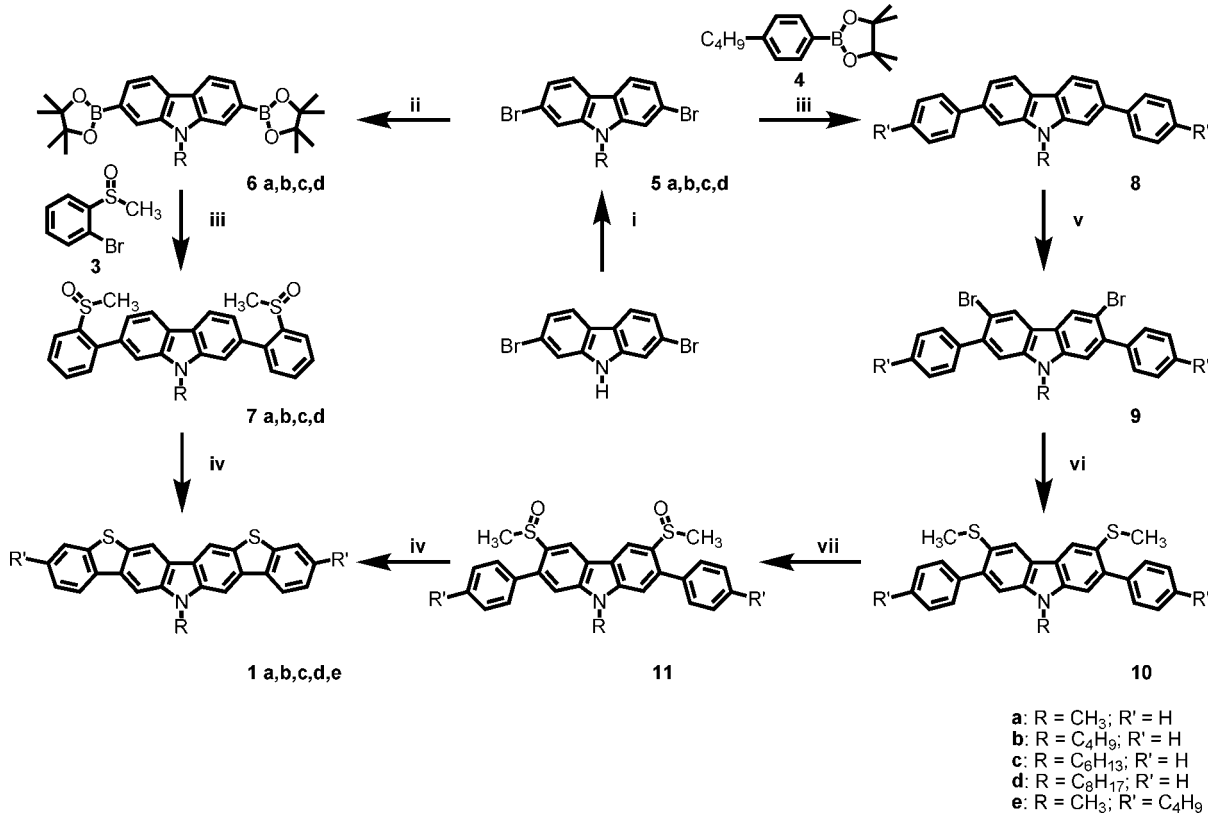
SCHEME 3. Synthesis of DBTCZ 1 through Triflic Acid Induced Ring-Closure Reaction[a]



[a] Reagents and conditions: (i) NaH, alkyl bromide, dry DMF, rt; (ii) THF, *n*-BuLi, −78 °C, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane; (iii) toluene, 2 M K_2CO_3, **3**, $Pd(PPh_3)_4$, 90 °C, 65%; (iv) a. CF_3SO_3H, rt, b. pyridine, reflux, 95%; (v) NBS, AcOH, $CHCl_3$, 86%; (vi) THF, *n*-BuLi, −78 °C, CH_3SSCH_3, 70%; (vii) AcOH, H_2O_2, 0 °C, 72%.

*h*00 reflections indicates an extraordinarily uniform arrangement of the molecules toward the surface over a macroscopic area. From the position of the 100 reflection, a *d*-spacing of 18.1 Å was calculated, which is in good agreement with the molecular length determined from the single-crystal data (17.2 Å). This suggests that the molecules in the thin film are oriented with their long molecular axes perpendicular to the substrate surface, a phenomenon reported also for oligothiophenes as well as anthradithiophenes.[15]

UV−Vis Absorption, Photoluminescence Spectra (PL), and Electrochemical Properties of Ladder-Type π-Conjugated Heteroacenes. UV absorption and photoluminescence spectra (PL) of oligomers **1c** and **2** are shown in Figure 5. In the UV spectra, the strong absorptions at 338, 345, and 363 nm for **1c** as well as 366 and 387 nm for **2** are attributed to the β band of $\pi-\pi^*$ transitions of the benzothienocarbazole backbones. On the other hand, the longer wavelength and weaker absorption observed at 400−450 nm for both compounds originates from the α and/or p band of the $\pi-\pi^*$ transition.[16] The HOMO−LUMO energy gap of **1c** of 2.81 eV can be evaluated from the absorption edge (λ = 442 nm), which is larger than that of pentacene (1.77 eV)[4a] and diindolocarbazole (2.59 eV)[7b] and smaller than that of bisindenocarbazole (3.2 eV).[8] On the basis of the absorption edge (λ = 438 nm), the band gap of **2** is calculated to be 2.83 eV. In the PL spectra, both compounds exhibit weak blue fluorescence with the emission maximum at 439 nm. The small Stokes shift of 8 or 15 nm is similar to that of bisindenocarbazoles due to the rigid planar structure.[17] The UV−vis absorption and photoluminescence spectra of other derivatives of **1** do not show obvious differences compared to **1c**.

To investigate the redox potentials of the new ladder-type molecules, cyclic voltammetry (CV) measurements were performed in dry CH_2Cl_2 (with 0.1 M tetrabutylammonium hexafluorophosphate) by using Au as the working electrode and Ag/Ag^+ as the reference electrode. The cyclic voltammogram of **1c** revealed a quasi-reversible oxidation potential at E^{ox}_{onset} = 0.98 V (vs Ag/Ag^+) (Figure S1a in the Supporting Information). According to $E_{HOMO} = -(E^{ox}_{onset} + 4.34)$ eV, a HOMO level of −5.2 eV for **1c** is estimated, which is lower than that of pentacene (−5.14 eV)[4a] and higher than that of bisindenocarbazole (−5.3 eV).[8] This value is consistent with the HOMO level calculated by using density functional theory (DFT) (−5.1 eV) (see the Supporting Information). Compounds **1a**, **1b**, **1d**, and **1e** are also characterized by CV, indicating oxidation behavior similar to that of **1c**. However, due to the reduction, part of the compound is out of the range of our experimental setup, and we cannot observe the reduction in the CV data. Therefore, there is no way to calculate the LUMO level by this method. Taking into account an optical band gap of 2.81 eV derived from the absorption onset of the UV−vis spectrum, the LUMO value of **1c** is empirically calculated to be −2.4 eV, which may be an error compared with the real value of the electron affinity since the optical band gap also includes the

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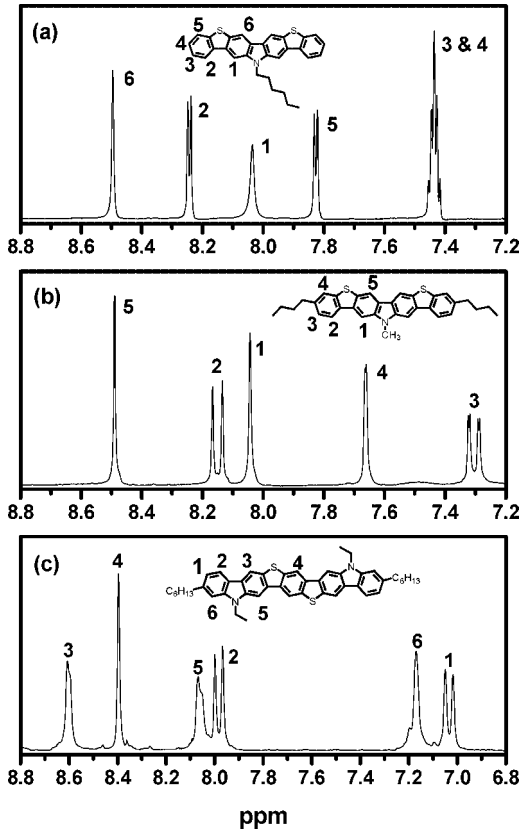


FIGURE 2. Extended aromatic region of ^{1}H NMR spectra of compounds (a) **1c** (700 MHz, 420 K, 1,1,2,2-tetrachloroethane-d_2), (b) **1e** (250 MHz, 300 K, dichloromethane-d_2), and (c) **2** (250 MHz, 300 K, dichloromethane-d_2).

exciton binding energy. The redox behavior of compound **2** indicates an E^{ox}_{onset} of ~0.98 eV as well as a reduction wave at the potential of 0.92 V (Figure S1b in the Supporting Information). Therefore, a HOMO level similar to that of compound **1** could be calculated for compound **2**.

Conclusion

In conclusion, we have described a facile approach to the synthesis of two new ladder-type π-conjugated heteroacenes (DBTCZ and DIBBBT) with the inclusion of both thiophene and pyrrole ring units from proper precursors, respectively. Triflic acid induced electrophilic coupling reactions showed surprisingly high regioselectivity on the 3,6 position of carbazole and gave the pure products with overall yields of about 48%. The second precursor toward DBTCZ also gave the desired symmetrical product but with solublizing alkyl chain in different fashion. Single-crystal studies demonstrated that **1c** adopts a shifted cofacial stacking, and the thin film XRD of **1c** showed a preferred specific orientation relative to the substrate surface. DIBBBT is by far the longest ladder-type heteroacene with well-defined structure. The spectroscopic and electrochemical characterizations of **1** and **2** indicate their much lower HOMO energy levels and larger band gaps compared with those of pentacene, in spite of their much more extended π system. Further studies on the applications of these materials to semiconducting materials are in progress in our laboratory.

Experimental Section

Synthesis of 2,7-Bis[2-(methylsulfinyl)phenyl]-*N*-hexylcarbazole (7c). A mixture of **6c** (1.5 g, 2.98 mmol), 2-bromo(methylsulfinyl)benzene (**3**) (1.44 g, 6.56 mmol) was dissolved in 25 mL of toluene. Then a 2 M K_2CO_3 solution (8 mL) was added. The reaction mixture was degassed by three freeze/pump/thaw cycles before 80 mg (6.92×10^{-5} mol) of $Pd(PPh_3)_4$ was added under argon. The mixture was stirred for 24 h at 90 °C. The mixture was then allowed to cool to room temperature, and the reaction mixture was extracted three times with CH_2Cl_2 and dried with $MgSO_4$. The product was purified by silica chromatography with 2:1 THF/hexane as the eluent, affording the pure product as colorless powder (1.1 g, 70% yield): ^{1}H NMR (250 MHz, CD_2Cl_2) δ (ppm) 0.75 (t, 2H), 1.19 (m, 8H), 1.80 (m, 2H), 2.22 (s, 6H), 4.27 (t, 2H), 7.18 (dd, 2H), 7.40 (d, 2H, J = 7.5 Hz), 7.42 (s, 2H), 7.50 (m, 4H), 8.04 (dd, 2H, J = 7.5 Hz), 8.12 (d, 2H, J = 7.5 Hz); ^{13}C NMR (62.5 MHz, CD_2Cl_2) δ (ppm) 14.1, 21.0, 25.0, 27.5, 29.4, 32.0, 41.9, 110.1, 120.8, 121.2, 122.6, 123.7, 128.9, 130.9, 131.0, 136.3, 140.6, 141.4, 145.2; mp 95−98 °C; FD-MS m/z = 527.20 (M^+, 100.0%). Anal. Calcd for $C_{32}H_{33}NO_2S_2$: C, 72.83; H, 6.30. Found: C, 72.82; H, 6.33.

Synthesis of Dibenzo[*b*,*b*′]thieno[2,3-*f*:5,4-*f*′]-*N*-hexylcarbazole (DBTCZ) (1c). A 10 mL round-bottomed flask was filled with 2,7-bis[2-(methylsulfinyl)phenyl]-*N*-hexylcarbazole (**7c**) (200 mg, 0.38 mmol), phosphorus pentoxide (28 mg, 0.2 mmol), and trifluoromethanesulfonic acid (6 mL). The mixture was stirred for 72 h at room temperature to give a dark brown solution, which was then poured into ice−water (100 mL). The yellow precipitate was collected by suction filtration and dried under vacuum. The structure of this compound, which was insoluble in apolar organic solvents, was assumed to be the sulfonium salt. Demethylation of the solid was achieved by refluxing in pyridine (30 mL) for 12 h. When the suspension was cooled to room temperature, a large volume of CH_2Cl_2 was added to extract the product. Dibenzo[*b*,*b*′]thieno[2,3-*f*:5,4-*f*′]-*N*-hexylcarbazole (**1c**) was thus obtained as a yellow powder after silica chromatography with CH_2Cl_2/hexane = 1/9 as an eluent (165 mg, 94% yield): ^{1}H NMR (250 MHz, CD_2Cl_2) δ (ppm) 0.80 (t, 3H), 1.31 (m, 6H), 1.94 (m, 2H), 4.43 (t, 2H), 7.41 (m, 2H), 7.81 (d, 2H, J = 7.5 Hz), 8.06 (s, 2H), 8.22 (d, 2H, J = 7.5 Hz), 8.49 (s, 2H); ^{13}C NMR (62.5 MHz, CD_2Cl_2) δ (ppm) 14.2, 23.0, 27.4, 28.9, 32.1, 101.0, 121.9, 123.3, 123.5, 124.6, 127.1, 130.7, 135.0, 136.1, 140.6, 140.9; mp 215−217 °C; FD-MS m/z = 463.14 (M^+, 100%). Anal. Calcd for $C_{30}H_{25}NS_2$: C, 77.71; H, 5.43. Found: C, 77.75; H, 5.36.

Synthesis of 2,7-Bis(4-*n*-butyphenyl)-*N*-methylcarbazole (8). 2,7-Dibromo-*N*-methylcarbazole **5a** (1.5 g, 4.42 mmol) and 2.53 g (9.73 mmol) of **4** were dissolved in 25 mL of toluene. A 2 M K_2CO_3 solution (6 mL) and 0.1 g of trimethylbenzylammonium chloride were added. The reaction mixture was degassed by three freeze/thaw cycles before 100 mg (8.6×10^{-6} mol) of $Pd(PPh_3)_4$ was added under argon. The mixture was stirred for 24 h at 90 °C. The reaction mixture was extracted three times with CH_2Cl_2 and dried with $MgSO_4$. The product was purified by silica chromatography with hexane as an eluent. Compound **8** (1.67 g, 85%, related to **5a**) was obtained as a white solid: ^{1}H NMR (250 MHz, CD_2Cl_2) δ (ppm) 1.03 (t, 6H), 1.44 (m, 4H), 1.74 (m, 4H), 2.74 (s, 6H), 3.96 (s, 3H), 7.36 (d, 4H, J = 8.1 Hz), 7.53 (dd, 2H, J = 8.1 Hz), 7.67 (s, 2H), 7.72 (dd, J = 8.1 Hz), 8.16 (d, 2H, J = 8.1 Hz); ^{13}C NMR (62.5 MHz, CD_2Cl_2) δ (ppm) 14.2, 22.8, 29.5, 34.2, 35.7, 107.2, 118.9, 120.8, 121.9, 127.6, 129.3, 139.4, 139.7, 142.5, 142.6; mp 192−193 °C; FD-MS m/z = 445.64 (M^+, 100.0%). Anal. Calcd for $C_{33}H_{35}N$: C, 88.94; H, 7.92. Found: C, 88.93; H, 7.91.

Synthesis of 3,6-Dibromo-2,7-bis(4-*n*-butyphenyl)-*N*-methylcarbazole (9). A 100 mL flask was charged with 1 g (2.24 mmol) of **8** and a 1:1 mixture of CH_3Cl and acetic acid and cooled in an ice−water bath. Then, 818.7 mg (4.6 mmol) of *N*-bromosuccinimide (NBS) was added in several portions, and the mixture was stirred overnight at room temperature in the dark. The mixture was quenched with 15 mL of distilled water and extracted three times with CH_2Cl_2. The combined organic fractions were dried over magnesium sulfate, and the solvent was removed under reduce pressure. The crude material was purified by silica chromatography

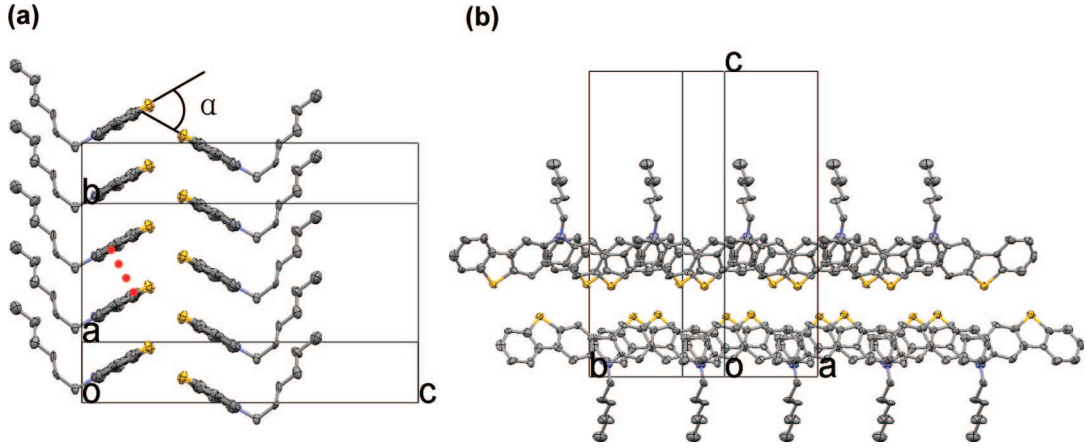
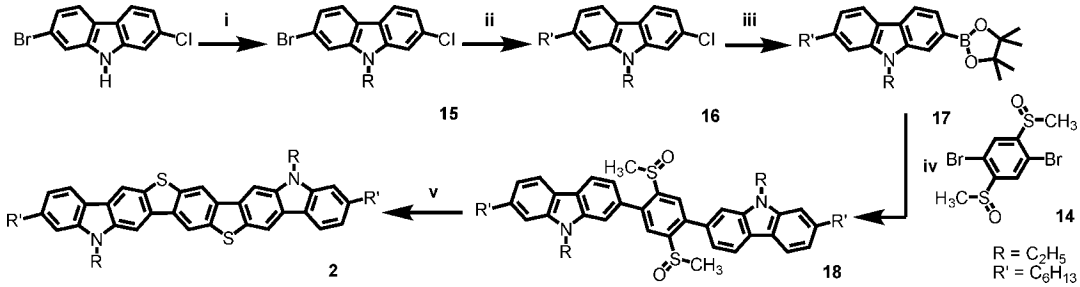


FIGURE 3. Packing of **1c** in solid state: (a) side view of the antiparallel column pair with the red dash line indicating the interplanar distance and (b) top view of the shifted $\pi-\pi$ stacking (hydrogen atoms were omitted for clarity).

SCHEME 4. Synthesis of DIBBBT (2) through Triflic Acid Induced Ring-Closure Reaction[a]



[a] Reagents and conditions: (i) NaH, ethyl bromide, dry DMF, rt; (ii) THF, *n*-BuLi, −78 °C, hexyl iodide, 65%; (iii) $Pd_2(dba)_3$, 2-dicyclohexylphosphino-2′,4′,6′-triisopropylbiphenyl, bis(pinacolato)diboron, KOAc, 110 °C, 90%; (iv) toluene, 2 M K_2CO_3, **14**, $Pd(PPh_3)_4$, 90 °C, 72%; (v) a. CF_3SO_3H, rt, b. pyridine, reflux. 95%.

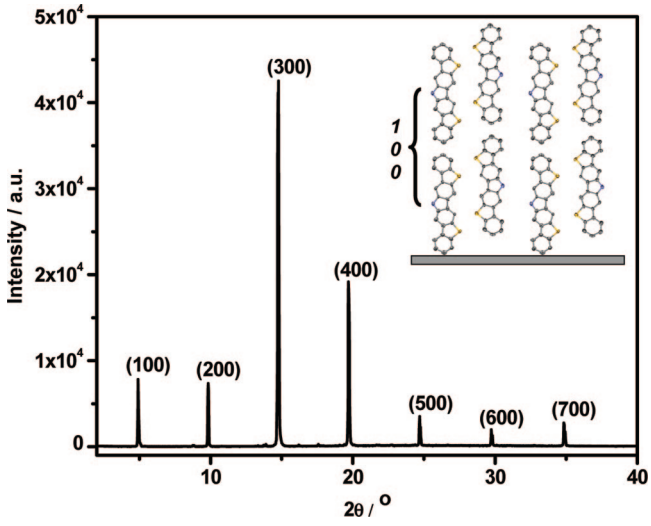


FIGURE 4. X-ray diffractogram of the drop-cast thin film of **1c** (40 mg/mL 1,2-dichlorobenzene solution) on an untreated SiO_2 substrate. The reflections are assigned by the Miller's indices. Inset: schematic illustration of the edge-on arrangement of **1c** on the substrate; side chains are omitted.

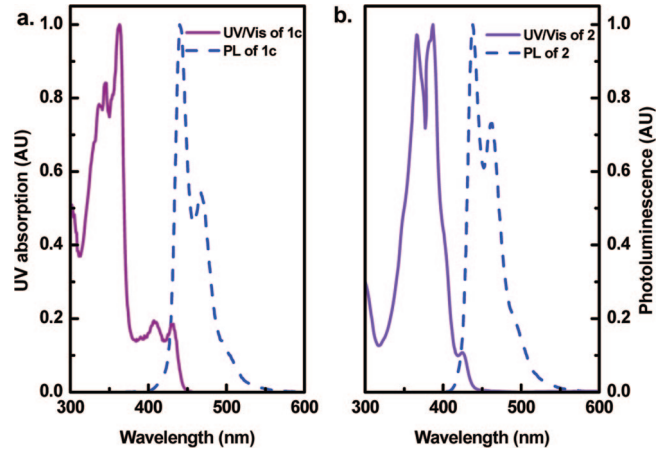


FIGURE 5. Normalized UV−vis absorption and PL spectra of compound **1c** (a) and **2** (b) (10^{-6} M).

with hexane as an eluent to offer 1.16 g of the product as a white solid (86% yield): ^{1}H NMR (250 MHz, CD_2Cl_2) δ (ppm) 0.89 (t, 6H), 1.29 (m, 4H), 1.61 (m, 4H), 2.61 (t, 4H), 3.69 (s, 3H), 7.20 (d, 4H, J = 8.1 Hz), 7.29 (s, 2H), 7.33 (d, 2H, J = 8.1 Hz), 8.23 (s, 2H); ^{13}C NMR (62.5 MHz, CD_2Cl_2) δ (ppm) 14.2, 22.9, 29.7, 34.1, 35.8, 111.8, 113.1, 122.4, 124.8, 128.3, 130.0, 139.7, 140.7, 141.3, 142.9; mp 203−205 °C; FD-MS m/z = 603.43 (M+, 100.0%). Anal. Calcd for $C_{33}H_{33}Br_2N$: C, 65.68; H, 5.51. Found: C, 65.67; H, 5.52.

Synthesis of 3,6-Dimethylsulfide-2,7-bis(4-*n*-butyphenyl)-*N*-methylcarbazole (10). 3,6-Dibromo-2,7-bis(4-*n*-butyphenyl)-*N*-methylcarbazole (**9**) (600 mg, 0.994 mmol) was dissolved in dry THF (40 mL) and cooled to −78 °C. *n*-Butyllithium (1.6 M in hexane, 1.37 mL, 2.19 mmol) was added dropwise at this temperature. After the addition was complete, the mixture was stirred for an additional hour. Dimethyl disulfide (206 mg, 2.19 mmol) was added dropwise. The cooling bath was removed, and the solution was stirred at room temperature overnight. The crude material was purified by silica chromatography with hexane/CH_2Cl_2 = 10:1 as the eluent, and **10** was obtained as a light yellow solid (374 mg, 70% yield): ^{1}H NMR

(250 MHz, CD_2Cl_2) δ (ppm) 0.89 (t, 6H), 1.33 (t, 4H), 1.58 (t, 4H), 2.35 (s, 6H), 2.62 (t, 4H), 3.71 (s, 3H), 7.19 (d, 4H, $J = 8.1$ Hz), 7.22 (s, 2H), 7.35 (d, 2H, $J = 8.1$ Hz), 8.00 (s, 2H); ^{13}C NMR (62.5 MHz, CD_2Cl_2) δ (ppm) 14.1, 18.2, 22.9, 29.6, 34.1, 35.8, 111.0, 120.1, 122.1, 127.2, 128.3, 129.9, 139.3, 140.4, 140.9, 142.6; mp 208−213 °C; FD-MS $m/z = 537.82$ (M+, 100.0%). Anal. Calcd for $C_{35}H_{39}NS_2$: C, 78.16; H, 7.31. Found: C, 78.158; H, 7.32.

Synthesis of 3,6-Dimethylsulfoxide-2,7-bis(4-*n*-butyphenyl)-*N*-methylcarbazole (11). 3,6-Dimethylsulfide-2,7-bis(4-*n*-butyphenyl)-*N*-methylcarbazole (**10**) (300 mg, 0.558 mmol) was dissolved in a 1:1 mixture of glacial acetic acid and chloroform and cooled with an ice bath until the solvent was about to freeze. Hydrogen peroxide (35%, 109 mg, 1.13 mmol) was added slowly. The cooling bath was removed, and the mixture was stirred at room temperature for 12 h. Acetic acid was removed by vacuum evaporation, and CH_2Cl_2 was added to the residue. The organic fraction was washed with saturated $NaHCO_3$ solution and dried over $MgSO_4$. The product was purified by silica chromatography with THF/hexane (3:1) as the eluent, affording the pure product as a diastereomeric mixture of white solid (228 mg, 72% yield): ^{1}H NMR (250 MHz, CD_2Cl_2; signals of diastereomer A are marked with ′, those of diastereomer B with ″) δ (ppm) 0.88 (t, 6H), 1.30 (m, 4H), 1.58 (m, 4H), 2.32 (s′, 3H), 2.34 (s″, 3H), 2.61 (t, 4H), 3.81 (s, 3H), 7.22 (d, 4H, $J =$ 8.1 Hz), 7.31 (s, 2H), 7.33 (d, 4H, $J = 8.1$ Hz), 8.83 (s′, 1H), 8.84 (s″, 1H); ^{13}C NMR (62.5 MHz, CD_2Cl_2) δ (ppm) 14.15, 22.81, 30.08, 34.01, 35.72, 42.89(′), 42.98(″), 111.10(′), 111.14(″), 117.23(′), 117.28(″), 122.51(′), 122.56(″), 129.05(′), 129.08(″), 129.87(′), 129.89(″), 136.13(′), 136.16(″), 136.41, 138.49(′), 138.58(″), 143.27(′), 143.30(″), 143.66(′), 143.67(″); mp 230−235 °C; FD-MS $m/z =$ 569.82 (M^+, 100.0%). Anal. Calcd for $C_{35}H_{39}NO_2S_2$: C, 73.77; H, 6.90. Found: C, 76.78; H, 6.91.

Synthesis of 6,6′-Dibutyl dibenzo[*b*,*b*′]thieno[2,3-*f*:5,4-*f*′]-*N*-methylcarbazole (1e). Following the same method as **1c**, 6,6′-dibutyl dibenzo[*b*,*b*′]thieno[2,3-*f*:5,4-*f*′]-*N*-methylcarbazole was obtained as yellow powder after silica chromatography with CH_2Cl_2/hexane = 1/9 as an eluent (90 mg, 96% yield): ^{1}H NMR (250 MHz, CD_2Cl_2) δ (ppm) 0.95 (t, 6H), 1.42 (m, 4H), 1.69 (m, 4H), 2.77 (t, 4H), 3.98 (s, 3H), 7.30 (dd, 2H, $J = 8.1$ Hz), 7.66 (s, 2H), 8.04 (s, 2H), 8.14 (d, 2H), 8.49 (s, 2H); ^{13}C NMR (62.5 MHz, CD_2Cl_2) δ (ppm) 14.1, 22.8, 39.9, 34.2, 36.2, 100.4, 114.2, 121.5, 122.7, 123.1, 125.6, 130.6, 133.9, 135.0, 140.8, 141.5, 142.6; mp 256−263 °C; FD-MS $m/z =$ 505.74 (M^+, 100%). Anal. Calcd for $C_{33}H_{31}NS_2$: C, 78.37; H, 6.18. Found: C, 78.36; H, 6.17.

Synthesis of 2-Chloro-7-hexyl-*N*-ethylcarbazole (16). 2-Chloro-7-bromo-9-ethylcarbazole (**15**) (1.5 g, 4.86 mmol) was dissolved in dry THF (40 mL) and cooled to −78 °C. *n*-Butyllithium solution (1.6 M in hexane, 3.34 mL, 5.35 mmol) was added dropwise at this temperature. After the addition was complete, the mixture was stirred for an additional hour. Hexyl iodide (0.71 g, 5.35 mmol) was added dropwise. The cooling bath was removed, and the solution was stirred at room temperature overnight. The crude material was purified by silica chromatography with hexane as the eluent, and **16** was obtained as a off-white solid (1.06 g, 70% yield): ^{1}H NMR (300 MHz, CD_2Cl_2) δ (ppm) 0.81 (t, 3H), 1.24 (m, 6H), 1.31 (t, 3H), 1.62 (m, 2H), 1.98 (2.71), 4.20 (m, 2H), 6.68 (dd, 1H, $J = 8.1$ Hz), 7.02 (dd, 1H, $J = 8.1$ Hz), 7.14 (s, 1H), 7.29 (dd, 1H, $J = 8.1$ Hz), 7.83 (dd, 2H, $J = 8.1$ Hz); ^{13}C NMR (75.5 MHz, CD_2Cl_2) δ (ppm) 13.9, 14.3, 23.1, 29.5, 32.1, 32.5, 37.1, 38.0, 108.7, 108.9, 119.3, 120.3, 120.6, 120.7, 121.2, 122.0, 131.0, 141.0, 141.1, 142.1; mp 156−163 °C; FD-MS $m/z =$ 313.86 (M^+, 100%). Anal. Calcd for $C_{20}H_{24}ClN$: C, 76.53; H, 7.71. Found: C, 78.52; H, 7.72.

Synthesis of 2-Hexyl-*N*-ethyl-7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-carbazole (17). An oven-dried Schlenk tube was charged with Pd_2dba_3 (27.6 mg, 0.03 mmol), 2-dicyclohexylphosphino-2′,4′,6′-triisopropylbiphenyl (57.6 mg, 0.12 mmol), bis(pinacolato)diboron (2.28 g, 9 mmol), **16** (942 mg, 3 mmol), and KOAc (883.2 mg, 9 mmol). The Schlenk tube was capped with a rubber septum and then evacuated and backfilled with argon (this sequence was carried out three times). 1,4-Dioxane (10 mL) was added via a syringe, through a septum. The reaction mixture was heated to 110 °C and reacted overnight. At this point, the reaction mixture was allowed to cool to room temperature. The reaction solution was then filtered through a thin pad of Celite (eluting with ethyl acetate), and the eluent was concentrated under reduced pressure. The crude material so obtained was purified via flash chromatography on silica gel with hexane/EtOAc = 10:1 as the eluent to give **17** as light yellow oil: ^{1}H NMR (250 MHz, CD_2Cl_2) δ (ppm) 0.84 (t, 3H), 1.34 (m, 12H), 1.37 (m, 6H), 1.63 (t, 3H), 1.68 (t, 2H), 2.77 (t, 2H), 4.34 (m, 2H), 7.02 (dd, 1H, $J = 8.1$ Hz), 7.20 (s, 1H), 7.56 (d, 1H, $J = 8.1$ Hz), 7.82 (s, 1H), 7.94 (d, 1H, $J = 8.1$ Hz), 8.00 (d, 1H, $J = 8.1$ Hz); ^{13}C NMR (62.5 MHz, CD_2Cl_2) δ (ppm) 12.3, 12.4, 21.1, 23.3, 27.7, 28.3, 30.3, 30.6, 35.3, 35.9, 82.2, 106.7, 113.3, 117.7, 118.3, 118.9, 119.0, 123.3, 123.9, 138.1, 139.4, 140.5; FD-MS $m/z =$ 405.38 (M^+, 100.0%).

Synthesis of 7,7′-(2,5-Bis(methylsulfinyl)-1,4-phenylene)bis(2-hexyl-*N*-ethylcarbazole) (18). Compound **6** (486 mg, 1.2 mmol) and 1,4-dibromo-2,5-bis(methylsulfinyl)benzene (**7**) (100 mg, 0.28 mmol) were dissolved in 10 mL of toluene. A 2 M K_2CO_3 solution (3 mL) was added. The reaction mixture was degassed by three freeze/pump/thaw cycles before 15 mg (1.3×10^{-5} mol) of $Pd(PPh_3)_4$ was added under argon. The mixture was stirred for 24 h at 90 °C. The mixture was then allowed to cool to room temperature and extracted three times with CH_2Cl_2 and dried with $MgSO_4$. The product was purified by silica chromatography with THF/hexane (3:1) as the eluent, affording the pure product as colorless powder (152 mg, 72% yield): ^{1}H NMR (250 MHz, CD_2Cl_2) δ (ppm) 0.83 (t, 6H), 1.29 (m, 18H), 1.59 (m, 4H), 2.27 (s, 6H), 2.76 (t, 4H), 4.33 (m, 4H), 7.05 (d, 2H, $J = 7.5$ Hz), 7.22 (s, 2H), 7.26 (d, 2H, $J = 7.5$ Hz), 7.48 (s, 2H), 7.96 (s, 2H), 8.09 (d, 2H, $J = 7.5$ Hz), 8.12 (s, 2H); ^{13}C NMR (62.5 MHz, CD_2Cl_2) δ (ppm) 14.3, 23.1, 29.5, 32.2, 32.5, 37.1, 38.0, 41.8, 108.8, 109.5, 120.1, 120.6, 120.7, 120.9, 123.7, 126.1, 134.1, 140.5, 140.8, 141.5, 142.5, 147.9; mp 198−201 °C; FD-MS $m/z =$ 757.20 (M^+, 100.0%). Anal. Calcd for $C_{48}H_{56}N_2O_2S_2$: C, 76.15; H, 7.46. Found: C, 76.25; H, 7.40.

Synthesis of Diindolo[3,2-*b*:2′,3′-*h*]benzo[1,2-*b*:4,5-*b*′]bis[1]benzothiophene (2). A 10 mL round-bottomed flask was filled with 7,7′-(2,5-bis(methylsulfinyl)-1,4-phenylene)bis(2-hexyl-*N*-ethylcarbazole) (**2a**) (120 mg, 0.16 mmol), phosphorus pentoxide (1.2 mg, 0.008 mmol), and trifluoromethanesulfonic acid (3 mL). The mixture was stirred for 72 h at room temperature to give a dark brown solution, which was then poured into ice−water (100 mL). The yellow precipitate was collected by suction filtration and dried under vacuum. After refluxing the yellow powder in pyridine (30 mL) for 12 h, the suspension was cooled to room temperature and a large volume of CH_2Cl_2 was added to extract the product. Diindolo[3,2-*b*:2′,3′-*h*]benzo[1,2-*b*:4,5-*b*′]bis[1]benzothiophene (**2**) was thus obtained as a yellow powder by silica chromatography with hexane as the eluent (104 mg, 95%): ^{1}H NMR (250 MHz, CD_2Cl_2) δ (ppm) 0.83 (t, 6H), 1.29 (m, 18H), 1.59 (m, 4H), 2.76 (t, 4H), 4.33 (m, 4H), 7.03 (d, 2H, $J = 7.5$ Hz), 7.17 (s, 2H), 7.97 (d, 2H, $J = 7.5$ Hz), 8.07 (s, 2H), 8.40 (s, 2H), 8.61 (s, 2H); FD-MS $m/z =$ 693.02 (M^+, 100%).

Acknowledgment. We thank Dirk Beckmann, Nok Tsao, and Dr. Wojciech Pisula for helpful discussions. Financial support from Max Planck Society through the program ENERCHEM, European Commission Project NAIMO (NMP4-CT-2004-500355), and the German Science Foundation (Korean-German IRTG) is gratefully acknowledged.

Supporting Information Available: Detailed experimental procedures for **3**, **4**, **12**, **13**, and **14**, spectroscopic data, and summerized ^{1}H and ^{13}C spectra data for all new compounds, as well as crystallographic data of **1c** presented in CIF. This material is available free of charge via the Internet at http://pubs.acs.org.

JO801898G