Synthesis of the *anti* and *syn* Isomers of Thieno[*f,f′*]bis[1]benzothiophene. Comparison of the Optical and Electrochemical Properties of the *anti* and *syn* Isomers[1]

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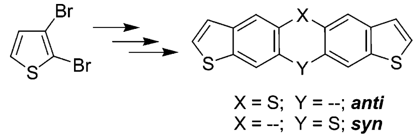
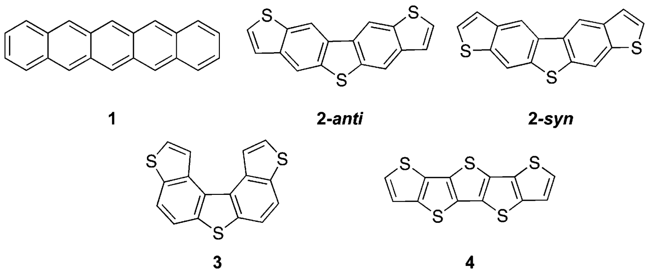


We report isomer-pure synthesis of thieno[2,3-*f*:5,4-*f′*]bis[1]benzothiophene and thieno[3,2-*f*:4,5-*f′*]bis[1]benzothiophene, the *anti* and *syn* isomers of a pentacyclic compound consisting of alternating thiophene and benzene rings. The optical and electrochemical properties of both are reported. In the *anti* isomer, the ribbonlike embedding of three thiophene units leads to a near-planar molecule with favorable $\pi-\pi$ stacking behavior in the solid state as shown by X-ray crystal structure analysis.

Pentacene (**1**, Scheme 1), a member of the acene series of linear polycyclic aromatic hydrocarbons, is a fundamental component of organic field-effect transistors (OFET).[2] Attempts to rectify its shortcomings such as poor solubility, limited stability in solution,[3] and unfavorable stacking in the solid state are ongoing.[4]

When fused into ladder-type aromatic compounds, a sulfur atom affords unique properties. Carruthers[5] demonstrated that, unlike anthracene, naphtho[2,3-*b*]thiophene undergoes no cycloaddition with benzyne. Wynberg and co-workers[6] showed that benzo[1,2-*b*:5,4-*b′*]dithiophene is unreactive with dienophiles even under drastic conditions. Similar stability trends were shown recently in more extended fused compounds. Anthra[*b*:*b′*]dithiophenes have improved stability toward oxidation and solubility compared to pentacene.[7] This overall decrease in reactivity vanishes as the acene unit in the center of the molecule is elongated. Thiaheterohelicenes are also composed of alternating thiophene and benzene rings fused on the [*a*,*c*]-bond of the benzene. These compounds can easily be prepared via a photochemical "stilbene-phenanthrene" cyclization.[8] Starting with the pentacyclic representative thieno[3,2-*e*:4,5-*e′*]bis[1]benzothiophene (**3**), the compounds lose planarity as they twist out of plane to accommodate the crowdedness. This twist results in the formation of enantiomeric helical structures.[9] Thienoacenes are composed only of fused thiophenes. Therein, the pentacyclic representative, bis(thieno[2′,3′:4,5]thieno[3,2-*b*:2′,3′-*d*])thiophene (**4**), exhibits less stability compared to pentacene,[10] indicating the importance of the benzene units for stability.

SCHEME 1. Ladder-Type Aromatics



Synthetic strategies for heteronuclear, benzo-fused, ladder-type materials include cyclization, annulation to the heterocyclic ring, vacuum pyrolysis, and ring closure at the heteroatom.[11] Viable approaches for large-scale synthesis for such compounds are scarce.[12] Recent syntheses include double condensation of thiophenedicarboxaldehyde with 1,4-cyclohexanedione under basic conditions, followed by the reduction of the generated dione. An inseparable mixture of anthradithiophene isomers was obtained.[7] Dibenzo[*b*,*b′*]thieno[2,3-*f*:5,4-*f′*]bis[1]benzothiophene was synthesized via the intramolecular acid-

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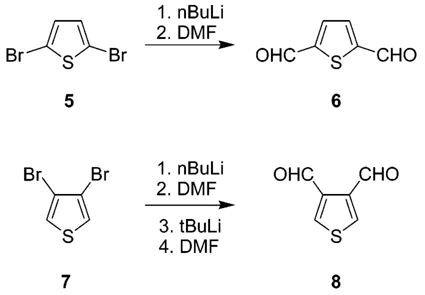
SCHEME 2. Synthesis of Dialdehydes 6 and 8



induced coupling reaction of aromatic methyl sulfoxides.[13] Similarly, this approach yielded a mixture of three isomers.

We have now developed a new approach for the synthesis of pentacyclic ladder-type aromatic compounds of alternating thiophene and benzene units in which the thiophenes are fused at the [*a*,*d*]-bonds of the benzene units. In contrast to their carbon analogues, thiophene-terminated heteroacenes are expected to be more stable in air and more soluble, pack well in the solid state, and be easily modified at the terminal thiophene units. Our strategy in preparing pure **2** employed a tandem intramolecular cyclodehydration (i.e., hetero-Bradsher reaction[14]) as the key step. This approach essentially eliminates the possibility of isomer formation for either compound.

Following isomer-pure synthesis, we report a first comparison of the optical and electronic properties of thieno[3,2-*f*:4,5-*f* ′]bis[1]benzothiophene (**2-*syn***)[15] and thieno[2,3-*f*:5,4-*f* ′]bis[1]benzothiophene (**2-*anti***). The packing behavior of **2-*anti*** is reported as well.

Compound **2-*syn*** was synthesized from 2,5-thiophenedicarboxaldehyde (**6**), which was prepared from 2,5-dibromothiophene (**5**, Scheme 2).[16] The key starting material for the synthesis of **2-*anti*** was 3,4-thiophenedicarboxaldehyde[17] (**8**). Previous synthetic reports of **8** were unsatisfactory in that they either yielded a complex mixture of isomers[18] or were based on starting materials that were not readily available.[17] Successful preparation of **8** from **7** was achieved in a one-pot procedure by stepwise replacement of the halogens (Scheme 2). The first bromine−lithium exchange was carried out using ^{n}BuLi. This salt was quenched with a stoichiometric amount of DMF, and without further hydrolysis, the second bromine−lithium exchange was carried out using the stronger base ^{t}BuLi. The kinetically formed organolithium salt was quenched with DMF quickly to avoid rearrangements. Sublimation and recrystallization resulted in **8** in 34% yield.

Synthesis of **2-*syn*** was carried out according to Scheme 3. To a solution of 3-bromo-2-lithiothiophene (**10**) was added a solution of thiophene-2,5-dicarboxaldehyde (**6**). A mild and effective reducing agent NaCNBH$_3$/ZnI$_2$[19] yielded pure **12** in 80%. Because of the instability of **11**, traditional reducing agents such as LiAlH$_4$/AlCl$_3$,[20] NaBH$_4$/TFA,[21] and even TMSCl/NaI[22] did not produce the desired product **12** in satisfactory yields. Careful monitoring of the lithiation conditions (time and temperature) allowed near quantitative formation of dialdehyde **13**. Effective cyclization of dialdehyde **13** occurred when refluxed in benzene in the presence of Amberlyst-15 using a Dean−Stark trap. The product **2-*syn*** was isolated in 46% by sublimation and recrystallization from ethanol.

The synthesis of **2-*anti*** was accomplished in a similar four-step procedure starting from 2,3-dibromothiophene (**9**, Scheme 3). Reaction of **10** with dialdehyde **8** is followed by the reduction using NaCNBH$_3$/ZnI$_2$ to yield **14** in 43%. Double bromine−lithium exchange at the β-positions of the terminal thiophene units of **14** is followed by formylation using DMF to yield dialdehyde **15** in 54% yield. The acid-catalyzed cyclodehydration furnished **2-*anti*** as a pale yellow, crystalline solid in 24% yield. The overall yield of **2-*anti*** was 6%, and the overall yield of **2-*syn*** was 34%. As expected, both compounds exhibit reasonable solubility in dichloromethane of 1−2 mg/mL (room temperature).

The UV−vis absorption spectra of **2-*anti*** and **2-*syn*** (Figure S15) showed that the longest wavelength absorption band of the *anti* isomer (375 nm) is 12 nm red-shifted relative to the maximum absorption of the *syn* isomer (363 nm). The longest wavelength absorption band of the parent dibenzo[*b*,*d*]thiophene (DBT) is at 327 nm.[23] The fluorescence emission of **2-*syn*** exhibits a 12 nm blue-shift from that of **2-*anti*** (Table 1). Both isomers show an equally small Stokes shift, indicating that they are of equal rigidity. Emission quantum yields vary significantly by isomer and are listed in Table 1.[24] The emission quantum yields of both isomers of **2** are compared to DBT ($\Phi_F = 0.025$, $\Phi_P = 0.47$).[25] The fluorescence quantum yield of **2-*anti*** is 0.14, a 6-fold increase relative to that of the parent. In comparison, the fluorescence quantum yield of **2-*syn*** (0.01) is comparable to that of the parent compound. The phosphorescence emission quantum yield of **2-*syn*** is 0.56 in a frozen matrix as expected as a result of the intramolecular heavy atom effect. In contrast, the phosphorescence is effectively shut off in the *anti* isomer where the quantum yield is only 0.04. This observation suggests that the electronic excited state structures and nonradiative decay channels vary considerably with constitution of the isomers of **2**.

Crystal packing is of pivotal concern for efficient charge-transport in devices such as OFETs.[26] Single-crystal X-ray analysis revealed that **2-*anti***[27] crystallized

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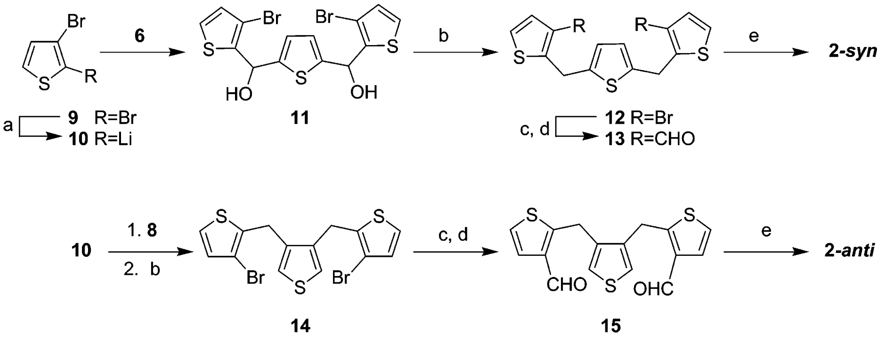
SCHEME 3. Preparation of 2-*syn* and 2-*anti*[a]



[a] Regents and conditions: (a) ^{n}BuLi, THF/Et$_2$O (1:5), −78 °C; (b) NaCNBH$_3$/ZnI$_2$, DCE; (c) ^{n}BuLi, Et$_2$O, −78 °C; (d) DMF; (e) Δ, Amberlyst-15, benzene.

TABLE 1. Spectroscopic Properties and Thermal Stability of 2-*anti* and 2-*syn*

	$\lambda_{\max}{}^{a}$	$\lambda_{\max}^{\mathrm{fl}\ b}$	$\phi_{\mathrm{fl}}{}^{c}$	$\lambda_{\max}^{\mathrm{ph}\ d}$	$\phi_{\mathrm{ph}}{}^{e}$	T_{on} (air)^{f}	T_{on} (N$_2$)^{f}
2-*anti*	375 nm	384 nm 401 nm	0.14	523 nm	0.04	344.23	375.04
2-*syn*	363 nm	372 nm 390 nm	0.01	471 nm	0.56	341.57	400.91

[a] Longest wavelength absorption band in dichloromethane. [b] Wavelength of maximum of fluorescence emission. [c] Fluorescence quantum yield. Standard: anthracene (EtOH) $\phi_{\mathrm{fl}} = 0.27$; 9-bromoanthracene (EtOH) $\phi_{\mathrm{fl}} = 0.02$.[28] [d] Wavelength of maximum of phosphorescence emission. [e] Phosphorescence quantum yield. Standard: biphenyl (EPA, 77 K) $\phi_{\mathrm{ph}} = 0.24$.[29] [f] Onset decomposition temperature as observed by TGA.

in the orthorhombic space group $Pmn2_1$ with two molecules in the unit cell. The central atom S2 resides on the crystallographic mirror plane that relates the two halves of the molecule. Molecules of **2-*anti*** are nearly planar with the highest deviation of atoms from the best plane through the entire molecule of ±0.174(2) Å.

The crystals of **2-*anti*** exhibit a herringbone-packing pattern with favorable molecular overlap along the *c*-axis of the unit cell. The alternating π-stacked columns are tilted at an angle of 50.24° (viewed down *a*-axis, Figure 1). In comparison, this tilt-angle is 51.9° in pentacene.[30] Tight packing in the solid state increases the material's stability toward oxygen in that it decreases the amount of oxygen diffusing into the bulk material.[31] The effective volume occupation is expressed as the Kitaigorodskii packing index (KPI).[32] Compound **2-*anti*** has a packing coefficient of 0.75 compared to **3**[33] with 0.72, whereas pentacene shows with a KPI of 0.76, the highest percent of filled space.

The stability of **2-*anti*** and **2-*syn*** was tested under air and nitrogen atmospheres by thermogravimetric analysis (TGA). Under a nitrogen atmosphere, the onset temperature for decomposition is the highest for **2-*syn***, reaching 400 °C, about 70 °C higher compared to pentacene.[34] Both isomers of **2** exhibit comparable stability under air and start to decompose around 340 °C (Table 1). This constitutes an increase of 20 °C compared to the reported decomposition temperature of 319 °C of pentacene.[34]

Compound **2-*anti*** exhibits a quasi-reversible oxidation at 1.15 V, whereas **2-*syn*** exhibits a reversible oxidation at a half wave potential of 1.12 V vs Ag/AgNO$_3$, respectively. Formation of an intensely colored film from **2-*anti*** on the electrode surface and the gradual appearance of lower potential waves upon repeated cyclization indicates electropolymerization of the generated radical cations. A reversible redox behavior is desired for OFET materials to avoid trapping of charge carriers at the injection site. Our future work therefore includes a suitable substitution and end-capping of the terminal thiophene groups to prevent oxidative coupling of the generated radical cations.[35]

We have developed a viable synthetic procedure for the synthesis of 3,4-thiophenedicarboxaldehyde from the readily available 3,4-dibromothiophene. We have successfully synthesized two new representatives of pentacyclic, [*a*,*d*]-fused ladder-type, sulfur-containing materials. Our synthetic approach yields isomer-pure **2-*anti*** and **2-*syn***. The absorption and emission properties were compared to DBT. The phosphorescence of **2-*anti*** is substantially decreased compared to the isomer and the parent compound. Isomer **2-*anti*** packs in a herringbone-fashion with good molecular overlap. The redox behavior indicates that substitution of the terminal thiophenes will be favorable to obtain reversibility and to block electropolymerization.

Experimental Section

General experimental details can be found in Supporting Information.

3,4-Thiophenedicarboxaldehyde (8). 3,4-Dibromothiophene (**7**, 8.75 g, 4.0 mL, 36.17 mmol) was dissolved in 100 mL of

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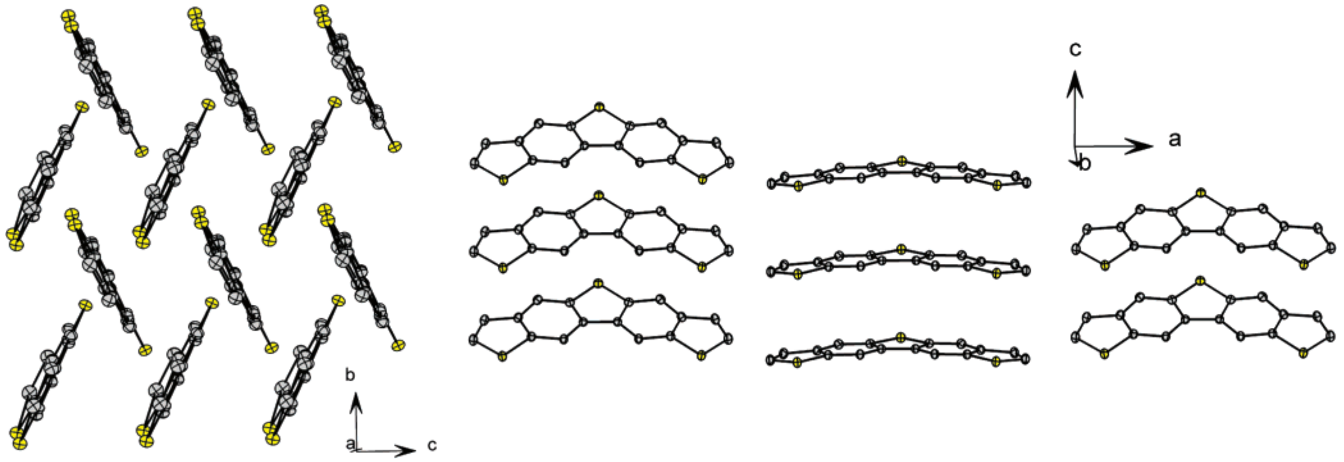

FIGURE 1. Crystal packing of **2-*anti*** as viewed along the *a*- (left) and *b*-axis (right). All hydrogens are omitted.

diethyl ether and the solution purged with Ar. After cooling to −78 °C, a solution of ^{n}BuLi (15.91 mL, 39.78 mmol) was added dropwise over a period of 5 min. Then, DMF (3.07 mL, 2.91 g, 39.78 mmol) was added and the reaction was stirred for 1 h. ^{t}BuLi (57.88 mL, 86.83 mmol) was chilled to − 78 °C and then rapidly added. After 5 min, DMF (6.70 mL, 6.34 g, 86.83 mmol) was added and the reaction was stirred overnight. The reaction mixture was then poured onto 2 N HCl at − 20 °C and warmed to room temperature. After separating the organic layer, the aqueous layer was extracted with copious amounts of diethyl ether. The combined organic layers were washed with brine and water and subsequently dried over $MgSO_4$. After evaporation of the solvent, the orange-brown solid was sublimed at 110 °C under vacuum (ca. 28 in. Hg). The yellowish-white solid was dissolved in hot cyclohexane and the supernatant was decanted. This process was repeated until only a dark-brown residue remained in the flask. The cyclohexane fractions were combined, reheated, and left for crystallization in a freezer (−20 °C). This process yielded 1.72 g (34%) of a yellowish-white solid, mp 76−77 °C (lit.[17] 78−80 °C). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.23 (2H, s), 10.31 (2H, s). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 137.6, 140.3, 185.8.

3,4-Bis(3-bromo-2-thienylmethyl)thiophene (14). 2,3-Dibromothiophene (**9**, 10.00 g, 41.33 mmol) was dissolved in diethyl ether/THF (5:1, 200 mL). At −78 °C, ^{n}BuLi (20.0 mL, 47.1 mmol) was added dropwise and the solution was stirred for 5 min. A chilled solution of **8** (3.0 g, 21.4 mmol) in THF (160 mL) was subsequently added and the reaction was allowed to warm to room temperature. After addition of water, the aqueous layer was extracted with diethyl ether and the combined organic layers washed with water and dried over $MgSO_4$. Evaporation of the solvent yielded a yellow liquid, which was dissolved in 1,2-dichloroethane. Zinc iodide (20.50 g, 64.21 mmol) and sodium cyanoborohydride (20.18 g, 321.06 mmol) were added and the reaction was stirred overnight. The reaction mixture was subsequently filtered through Celite, washed with aqueous saturated NH_4Cl, dried over $MgSO_4$, and evaporated. Column chromatography using hexanes yielded 3.99 g (43%) of a yellow oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 4.02 (4H, s), 6.93 (2H, d, J = 5.1 Hz), 6.99 (2H, s), 7.14 (2H, d, J = 5.1 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 28.8, 109.3, 123.6, 124.1, 130.0, 137.6, 137.9. Anal. Calcd for $C_{14}H_{10}Br_2S_3$: C, 38.72; H, 2.32. Found: C, 38.69; H, 2.53.

2,2′-[3,4-Thiophenediylbis(methylene)]bis[3-thiophenecarboxaldehyde] (15). ^{n}BuLi (8.27 mL, 19.86 mmol) was chilled to −78 °C in diethyl ether. Compound **14** (3.92 g, 9.03 mmol) in diethyl ether was added dropwise. Ten minutes after the addition, DMF (1.53 mL, 1.45 g, 19.84 mmol) was added and the reaction was stirred for 2 h. The mixture was poured into a separatory funnel containing ice-cold saturated NH_4Cl. After separation of the organic layer, the aqueous layer was extracted with diethyl ether (2 × 100 mL) and the combined organic layers (400 mL) washed with water and dried over $MgSO_4$. Recrystallization of **15** from diethyl ether yielded a white solid, 1.62 g (54%), mp 89−90 °C. An analytical sample was prepared using column chromatography (4:1 hexanes/ethyl acetate as eluent), mp 93−94 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 4.45 (4H, s), 7.04 (2H, s), 7.12 (2H, d, J = 5.4 Hz), 7.39 (2H, d, J = 5.4 Hz), 10.05 (2H, s). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 27.8, 123.9, 124.4, 128.2, 136.7, 138.0, 154.3, 184.7. Anal. Calcd for $C_{16}H_{12}O_2S_3$: C, 57.80; H, 3.64. Found: C, 57.60; H, 3.79.

Thieno[2,3-*f*:5,4-*f*′]bis[1]benzothiophene (2-*anti*). Compound **15** (1.63 g, 4.90 mmol) was dissolved in dry benzene and Amberlyst-15 (0.5 g) was added. The reaction was refluxed for 36 h while water was removed by means of a Dean−Stark trap. After cooling, dichloromethane was added to dissolve the precipitate and the mixture was filtered through a cotton plug. The filtrate was washed with saturated NH_4Cl (aqueous) and then dried over $MgSO_4$. Evaporation of the solvent furnished a brown solid. Purification by column chromatography on silica gel using hexanes as eluent yielded a pale white solid. Recrystallization from $CHCl_3$ yielded 0.35 g (24%) of pale-white crystals, mp 237−238 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.39 (2H, d, J = 5.4 Hz), 7.54 (2H, d, J = 5.4 Hz), 8.24 (2H, s), 8.68 (2H, s). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 115.0, 117.0, 123.1, 127.8, 132.7, 136.9, 137.1, 139.8. Anal. Calcd for $C_{16}H_8S_3$: C, 64.83; H, 2.72. Found: C, 64.54; H, 2.95.

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Supporting Information Available: General experimental procedure; synthetic procedures for **6**, **11**−**13**, and **2-*syn***; NMR spectra of compounds **6**, **8**, **11**−**15**, **2-*anti***, **2-*syn***; cyclic voltammogram of **2-*syn*** and **2-*anti***; X-ray crystallographic data and cif file of **2-*anti***. This material is available free of charge via the Internet at http://pubs.acs.org.

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