Note

Synthesis of 1,6- 2,7- 3,8- and 4,9- Isomers of Didodecyl[1]benzothieno[3,2-b][1]benzothiophenes

Christian Ruzié, Jolanta Karpinska, Alan R. Kennedy, and Yves Henri Geerts

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Synthesis of 1,6- 2,7- 3,8- and 4,9- Isomers of Didodecyl[1]benzothieno[3,2-b][1]benzothiophenes

Christian Ruzié[†], Jolanta Karpinska[†], Alan R. Kennedy[‡] and Yves H. Geerts*[†]

[†] Laboratoire de Chimie des Polymères

CP 206/01, Faculté des Sciences

Université Libre de Bruxelles (ULB)

Boulevard du Triomphe

1050 Brussels, Belgium

Email: ygeerts@ulb.ac.be

[‡] Department of Pure and Applied Chemistry

University of Strathclyde

295 Cathedral Street

Glasgow G1 1XL, Scotland

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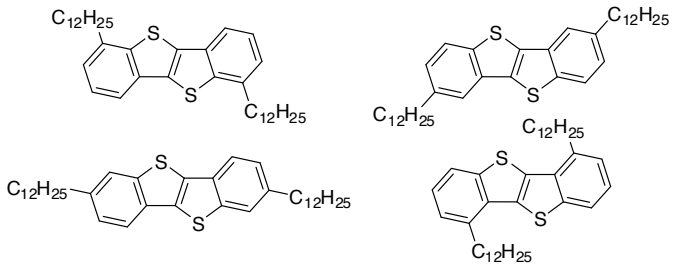


Abstract

The synthesis of 1,6- 2,7- 3,8- and 4,9- isomers of dibromo and didodecyl[1]benzothieno[3,2-b][1]benzothiophenes, via the stilbene pathway, is described. Starting from the synthesis of bromo-2-(methylthio)benzaldehydes, a series of functionalization, McMurry coupling, and finalising cyclization reactions were explored. The stereochemistry of the cyclization mechanism was investigated. Using this methodology didodecyl[1]benzothieno[3,2-b][1]benzothiophenes were formed in overall yields of 5 to 32 %.

The most recently studied conjugated π-systems for charge transport are the diacene-fused thienothiophenes[1,2,3], among which [1]benzothieno[3,2-*b*][1]benzothiophene (BTBT) derivatives are probably the best known for several reasons. They were the first systems to be synthesized,[4] are readily soluble in organic solvents[5], easily crystallize[6], and are available in large quantities via a one-step reaction from o-chlorobenzaldehyde[7]. Most of derivatives described in the literature are substituted at the 2 and 7 positions, whereas functionalization at the other positions is less documented[8,9] despite the fact that the length and position of alkyl side chains play a crucial role on the resulting structures. It is clear that the 3D structure determines to a large extent the semiconducting properties[5,10] of materials used in organic field-effect transistors. Methodologies developed to access 2,7-dialkylBTBT include Friedel–Craft acylation of BTBT followed by Wolff–Kishner reduction,[5,8] Sonogashira coupling on 2,7-diiodoBTBT followed by reduction on Pd/C,[5] Kumada coupling on 2,7-dibromoBTBT,[11] and acidic cyclization of 2-[2-(methylsulfinyl)phenyl]-benzo[b]thiophene[12]. The direct functionalization of the BTBT core either by lithiation or acylation has been extensively described by Svoboda *et al* but only generates 1,6- or 4,9-BTBT in poor yield.[8] We have thus opted for a general synthetic scheme in which functionalization is carried out prior to cyclization. The use of a synthetic pathway via a stilbene intermediate, which was inspired by the work of Takimiya et al.[13,14], allowed us to synthesize 1,6-didodecyl BTBT **1**, 2,7-didodecyl BTBT **2**, 3,8-didodecyl BTBT **3**, and 4,9-didodecyl BTBT **4** (Figure 1), and to propose a revised cyclization mechanism.

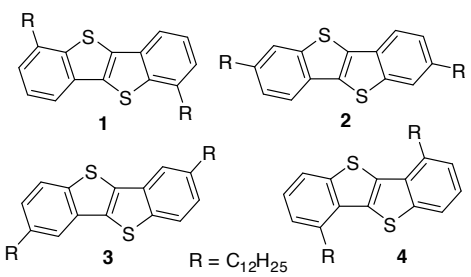
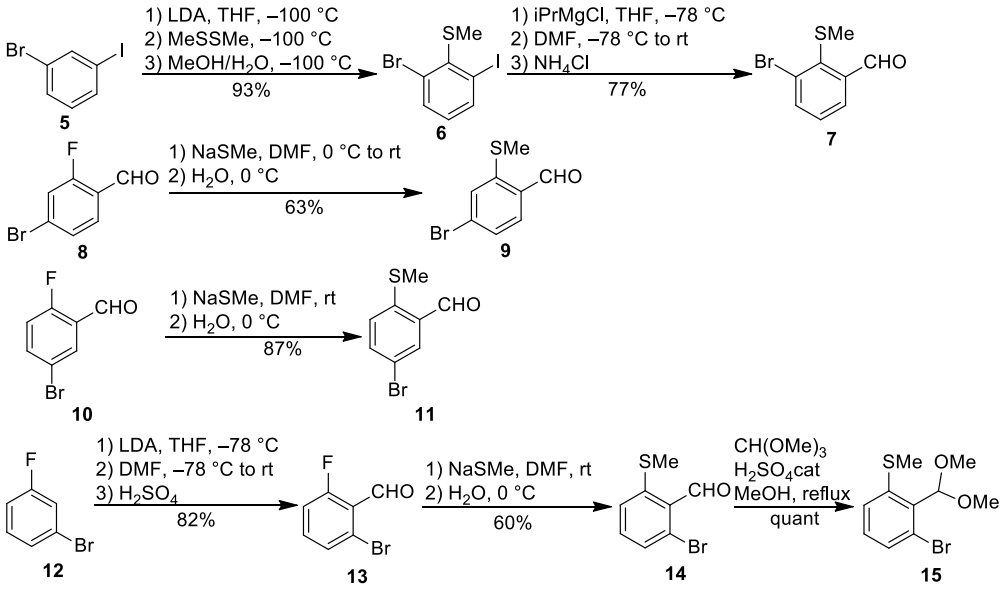


FIGURE 1. Didodecyl[1]benzothieno[3,2-b][1]benzothiophenes

Compounds **1-4** have been synthesized via a McMurry coupling on a 2-methylthiobenzaldehyde derivative followed by a cyclization with iodine.[2,14-16] This synthetic approach required the preparation of dodecyl-2-methylthiobenzaldehydes by distinct synthetic pathways detailed below and that rely on the synthesis of 3-bromo-2-(methylthio)benzaldehyde (**7**).

Starting from commercially available 1-bromo-3-iodobenzene (**5**), the selective thiomethylation at the 2-position, via a lithiation with lithium diisopropylamide[17], followed by a reaction with dimethyl disulfide, gave 1-bromo-3-iodo-2-methylthiobenzene (**6**) in 93 % yield. Subsequent magnesiation of **6** at –78 °C in THF by iodine–magnesium exchange with iPrMgCl[18], followed by trapping with dimethylformamide and hydrolysis with NH_4Cl afforded **7** in 77 % yield. The second pathway entailed the synthesis of 4-bromo-2-(methylthio)benzaldehyde (**9**), a known compound that was previously prepared by a different route starting from 4-bromo-2-fluorobenzoic acid, resulted in a 61 % yield.[19] Starting from commercially available 4-bromo-2-fluorobenzaldehyde (**8**), a S_NAr reaction with freshly prepared sodium thiomethoxyde[20] in DMF[21] at 0 °C generated 4-bromo-2-(methylthio)benzaldehyde (**9**) in 63 % yield. The third pathway is similar to the second one and describes the synthesis of 5-bromo-2-(methylthio)benzaldehyde (**11**) in 87 % yield.[22,23] The fourth pathway deals with the synthesis of 6-bromo-2-(methylthio)benzaldehyde (**14**). Starting from the commercially available 1-bromo-3-fluorobenzaldehyde (**12**), selective formylation[17] at the 2-position via a lithiation with lithium diisopropylamide, followed by a reaction with DMF gave 2-bromo-6-fluorobenzaldehyde (**13**) in 82 % yield. A S_NAr reaction with freshly prepared sodium thiomethoxyde in DMF led to 6-bromo-2-(methylthio)benzaldehyde (**14**) in 60 % yield.

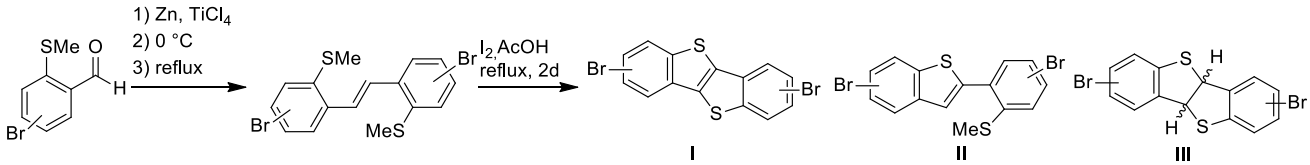
Treatment of the aldehyde moiety with trimethylorthoformate in methanol with a catalytic amount of sulphuric acid gave the dimethyl acetal derivative **15** in quantitative yield.[24] This compound was needed later, see Scheme 2. In summary, the four bromo-substituted 2-(methylthio)benzaldehydes **7**, **9**, **11**, and **14** were synthesized in an overall yield ranging from 49 to 87 %.

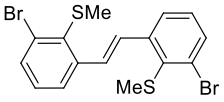
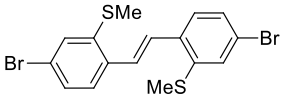
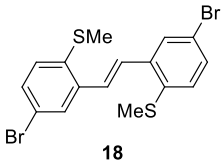
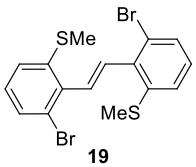


SCHEME 1. Synthesis of dodecyl-2-methylthiobenzaldehydes

McMurry coupling of the four bromo substituted 2-methylthiobenzaldehyde was carried out under similar conditions used by Takimiya *et al.* for dinaphto-[15,25], alkylated dinaphto-[14,26] and dianthra-[2] thieno[3,2-b]thiophene. The conditions are quite standard for McMurry coupling, *i.e.*$TiCl_4$/Zn in THF at reflux. Thus, reaction of **7**, **9**, **11**, or **14**, in these conditions, gave **16**, **17**, **18**, or **19** respectively (Table 1). Yields vary between 61 and 87 % and are similar to those reported for dinaphtothieno[3,2-b]thiophene[14,15,25,26] (26 to 97 %).

TABLE 1. Synthesis of bromostibenes and dibromobenzothienobenzothiophenes



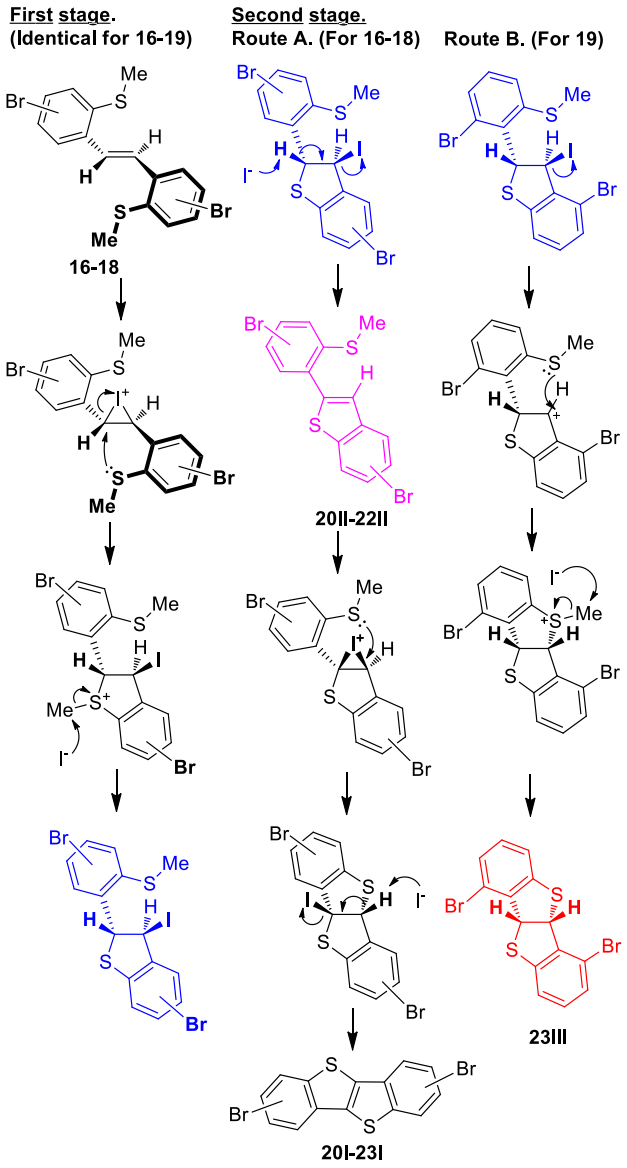
Entry	Aldehyde	Stilbene	[%][a]	BTBT	**I** [%][a]	**II** [%][a]	**III** [%][a]
A	**7**	 **16**	61	**20**	27	37	ND[b]
B	**9**	 **17**	70	**21**	5	53	ND[b]
C	**11**	 **18**	84	**22**	4	40	ND[b]
D	**14**	 **19**	87	**23**	20	ND[b]	28

[a] Isolated yield. [b] Not detected

Finally, **16**, **17**, **18,** and **19** was treated with excess iodine in AcOH[16] for 2 days to perform the ring closing reaction, forming the dibromo benzothienothiophenes **20, 21, 22,** and **23** in 27, 5, 4, and 20 % yield respectively. It is worth noting that in case of stilbenes **16**, **17,** and **18** the reaction afforded the partially cyclized benzothiophenes **II** as a side product. Treatment of benzothiophenes **II** with excess iodine formed a mixture of benzothienothiophenes and benzothiophenes **II**. In the case of the synthon **19**, the reaction gave 4,9-dibromo-4*b*,9*b*-

dihydrobenzothieno[3,2-*b*]benzothiophene (**23III**) with the desired compound **23I**, but surprisingly not the partially cyclized benzothiophenes **23II**. Use of pyridinium perbromide instead of iodine gave similar results. Obviously, the presence of the bulky bromine atoms in the ortho-position of the double bonds is responsible for this unusual reactivity. It is also worth noting also that compounds **20I** to **23I** exhibit a moderate solubility in organic solvents.

To explain the presence of compounds **20II**, **21II**, **22II**, and **23III**, we propose a plausible reaction pathway of the cyclization reactions (Scheme 2), that differs from that suggested by Takimiya *et al.*[13] These authors hypothesized that the last step of the cyclization mechanism involved a "dehydration – oxidation" reaction. This hypothesis appears to be incorrect as **23III** does not convert to **23I**. (*vide infra*).



SCHEME 2. Plausible reaction pathway for iodine-promoted cyclization of bromostilbene **16-18**

In the initial step of the reaction iodine reacts with the alkene bond giving a three-membered cyclic halonium cation. Intramolecular nucleophilic substitution by the sulfur atom of the thiomethyl group follows giving a sulfonium intermediate, with an easily cleavable methyl group. This leads to the formation of a 2,3-dihydro-3-iodobenzothiophene intermediate by attack of iodide anion. At this stage, two routes are conceivable. The first route (Route A) starts with an intramolecular dehydrohalogenation affording partially cyclized benzothiophenes **20II-22II**,

addition of iodine to the alkene to form three-membered cyclic halonium cation, followed by intramolecular nucleophilic substitution by the sulfur atom of the thiomethyl group, and then dehydrohalogenation giving **20I23I**. The second route (Route B) first involved the elimination of the iodide anion via a SN mechanism to form the carbocation, followed by intramolecular nucleophilic substitution by the sulfur atom forming the sulfonium intermediate, liberating the methyl group by nucleophylic attack by the iodide anion to give 4*b*,9*b*-dihydrobenzothieno[3,2-*b*]benzothiophene (**23III**). A crystal structure of **23III** was obtained, which showed a racemic mixture of R,R and S,S (see SI).

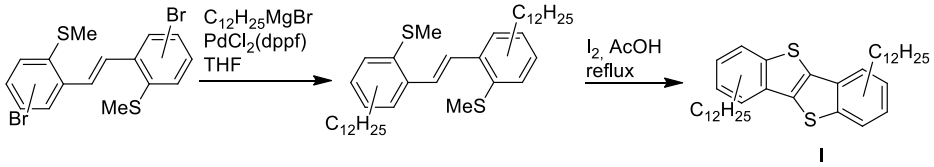
If Route A is favored for 3,4, and 5-bromostilbene, sterical hindranceof bromine atom promotes Route B for 6-bromostilbene, by preventing iodine addition.

It is worth mentioning that when the isolated intermediates **20II** to **22II** are subjected to cyclization conditions they finaly gave the corresponding **20I** to **22I** compounds. Conversely, **23III** does not react under the same reaction conditions, i.e. excess iodine in AcOH for 2 days.

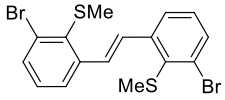
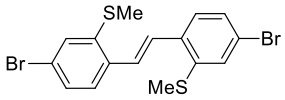
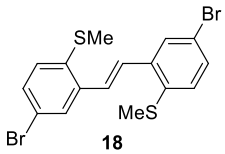
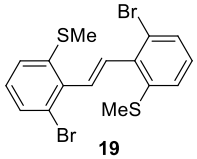
Moreover, the neat compound **23III** does not thermaly aromatize, as evidenced by thermogravimetric analysis, (see SI) before sublimation above 225 °C. It forms a deadend that significantly reduces the yield of **23I**.

A coupling reaction[27] could have been used to substitute dibromo compounds **20**, **21**, **22**, or **23** with didodecyl side chains. However, the poor yield of the ring closing step prompted us to explore a different synthetic pathway, i.e. the introduction of didodecyl substituents by the Kumada reaction[28] prior to cyclization (Table 2). Dibromostilbenes **16**, **17**, **18**, and **19** were treated with an excess of dodecylmagnesium bromide, with a catalytic amount of $PdCl_2$(dppf) in THF giving **24**, **25**, **26**, and **27** respectively in yields ranging from 13 to 82 %.

TABLE 2. Synthesis of didodecylstilbenes and didodecylbenzothienobenzothiophenes

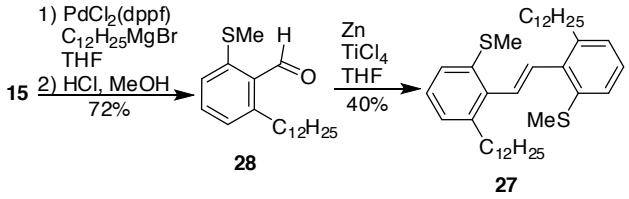


I

Entry	Br-stilbene	C_{12}-Stilbene	[%][a]	BTBT (**I**)	**I** [%][a]
E	 **16**	**24**	62	**1**	67
F	 **17**	**25**	66	**2**	3
G	 **18**	**26**	82	**3**	53
H	 **19**	**27**	13	**4**	33

[a] Isolated yield.

The poor yield obtained for the synthesis of stilbene **27** was possibly due to steric hindrance and/or close proximity of the sulphur atoms that could coordinate and deactivate the palladium catalyst. An alternative route was specifically developed for the synthesis of the stilbene **27**. Starting from **15**, Kumada coupling with an excess of dodecylmagnesium bromide with a catalytic amount of $PdCl_2(dppf)$ in THF, follow by treatment with HCl 6M in methanol afforded **28** in 72 % yield. Subsequent McMurry coupling led to the target stilbene **27** in 40 % yield. (Scheme 3)



SCHEME 3. Synthesis of stilbene **27**

Finally, the stilbene derivatives **24**, **25**, **26**, and **27** were treated with excess iodine[16] to induce a ring closing reaction, forming the desired didodecyl benzothienothiophenes **1**, **2**, **3**, or **4** in 67 %, 3 %, 53 %, and 33 % yield respectively. In sharp contrast to the cyclization of dibromostilbenes **16**, **17**, **18**, and **19**, no uncyclized and/or dihydro derivatives were observed for these cyclizations. No plausible explanation has been found for the low yield of product **2**.

The reported pathways allow the synthesis of 1,6-, 3,8-, and 4,9-didodecyl benzothiophene **1**, **3**, and **4** in overall yields of 18 %, 32 %, and 5 % respectively. Importantly for further physical characterization, the final cyclization step was performed on the half-gram scale. The reaction conditions and work-up used here indicate that the production of these compounds could easily be scaled up. Our synthetic pathway to 2,7-didodecyl benzothiophene **2** is inefficient with an overall yield of 0.8 % in comparison to prior work. Better results are obtained by acylation of benzothiophene, followed by Wolff-Kishner reduction,[5,8] or by Sonogashira coupling on 2,7-diiodobenzothiophene, followed by reduction[5].

There are several noteworthy observations. Firstly, the yields are globally superior (entries E,G,H) to those found for the cyclization of dibromostilbenes (entries A,B,C). This is likely due to the electron donating character of the alkyl side chains. Secondly, the comparison of entries B and F is instructive. The yield of the cyclization step of dibromostilbene **17** and didodecyl stilbene **25** remains very poor when performed under the same reaction conditions. This lack of reactivity is puzzling since neither steric, nor electronic factors could be invoked, i. e. the substituents are in the meta position and their electronic effects are opposite. Thirdly, a

comparison of entries C and G lead to the suprising conclusion that the didodecyl stilbene **26** is dramatically more reactive that its counterpart **18**, under same experimental conditions. Again no direct explanation could be proposed but we must stress that the reactions were repeated at least one time and that the yields are reproducible. Lastly, the unknown didodecyl benzothienothiophenes **1**, **3**, and **4** were synthesized in contrasting yields. Interestingly, the 3,8 isomer **3** is the easiest to prepare in large amount.

Experimental Section

General Methods. ^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were collected at room temperature in $CDCl_3$ unless otherwise noted. High resolution mass spectra (HRMS) under electron impact ionization (+ mode) were obtained on an instrument combining six sectors of $cE_1B_1cE_2qcE_3B_2cE_4$ geometry (E_i stands for electric sector, B_i for magnetic sector, q for a quadrupole collision cell and c for conventional collision cells). Melting points are uncorrected. A silica gel (40 μm average particle size) was used for column chromatography. Anhydrous, reagent grade CH_3CN, DMF, MeOH, and absolute EtOH were used as received. 2,4-Dinitrophenylhydrazine was used as visualization reagent for the detection of aldehydes. Sodium thiomethoxide[20] was prepared following the literature procedure.

1-Bromo-3-iodo-2-(methylthio)benzene (6). Following a reported procedure,[17] a solution of 1-bromo-3-iodobenzene (**5**) (2.56 mL, 20.0 mmol) in anhydrous THF (40 mL) at –100 °C was treated with LDA (15 mL, 2 M in THF/n-heptane/ethylbenzene, 30.0 mmol) over 1 h. After stirring for 30 min at –100 °C, dimethyldisulfide (2.88 mL, 32.0 mmol) was added dropwise, and the mixture was stirred for 1 h at – 100 °C. A saturated solution of NH_4Cl was added, and the mixture was stirred for 10 min. Ethyl acetate was added, and the organic layer was separated, dried over $MgSO_4$, and concentrated under vacuum. The resulting residue was subjected to

column chromatography [silica, n-hexane] to afford an off-white solid (5.25 g, 93 %): m.p.: 47–48 °C; ^{1}H NMR δ 2.46 (s, 3H), 6.79 (t, J = 7.9 Hz, 1H, H_5), 7.65 (dd, J = 7.9 and 1.2 Hz, 1H), 7.88 (dd, J = 7.9 and 1.2 Hz, 1H); ^{13}C NMR δ 19.2, 109.6, 129.7, 131.1, 133.7, 139.3, 141.2; EI-HRMS obsd 327.8407, calc 327.8418 (C_7H_6BrIS).

3-Bromo-2-(methylthio)benzaldehyde (7). Following a reported procedure,[18] a solution of **6** (2.82 g, 0.01 mol) in anhydrous THF (30 mL) at – 78 °C was treated with iPrMgCl (5.5 mL, 2 M in Et_2O, 0.011 mol). After stirring for 3 h at – 78 °C, DMF (1.26 mL, 0.015 mol) was added dropwise, and the mixture was stirred for 1 h at – 78 °C, and then allowed to warm overnight to room temperature. A saturated solution of NH_4Cl was added, and the mixture was stirred for 10 min. Ethyl acetate was added, and the organic layer was separated, dried over $MgSO_4$, and concentrated under vacuum. The resulting residue was subjected to column chromatography [silica, n-hexane/ethyl acetate (95:5)] to afford a pale yellow oil (1.78 g, 77%): ^{1}H NMR δ 2.46 (s, 3H), 7.35 (m, 1H), 7.89 (m, 2H), 10.76 (s, 1H); ^{13}C NMR δ 20.4, 127.6, 130.1, 132.6, 138.4, 139.9, 140.6, 192.6; EI-HRMS obsd 229.9411, calc 229.9400 (C_8H_7BrOS).

4-Bromo-2-(methylthio)benzaldehyde (9). A solution of 4-bromo-2-fluorobenzaldehyde (**8**) (5 g, 24.6 mmol) in anhydrous DMF (15 mL) at 0 °C was treated with freshly prepared NaSMe (1.9 g, 27.1 mmol). After stirring 1 h at 0 °C, the mixture was allowed to warm to room temperature overnight, and then cooled to 0 °C. Crushed ice was added, and the precipitate was filtered, washed with water, and dried. Crystallization in hexane afforded a yellow solid (3.61g, 63 %): m.p.: 88–89 °C; ^{1}H NMR δ 2.51 (s, 3H), 7.40–7.44 (m, 2H), 7.65 (d, J = 8 Hz, 1H), 10.18 (s, 1H); ^{13}C NMR δ 15.4, 127.5, 127.8, 129.7, 131.3, 134.4, 145.5, 190.2; EI-HRMS obsd 229.9393, calc 229.9401 (C_8H_7BrOS). ^{1}H NMR data are identical to those reported in literature.[19]

5-Bromo-2-(methylthio)benzaldehyde (11). Following a reported procedure,[23] a solution of 5-bromo-2-fluorobenzaldehyde (**10**) (5 g, 24.6 mmol) in anhydrous DMF (15 mL) was treated with freshly prepared NaSMe (1.9 g, 27.1 mmol). After stirring 1 h, crushed ice was added, and the precipitate was filtered, washed with water, and dried. Crystallization in hexane afforded a yellow solid (4.94 g, 87%): mp.: 90–91 °C; ^{1}H NMR δ 2.50 (s, 3H), 7.21 (d, J = 8.5 Hz, 1H), 7.64 (dd, J = 8.5 and 2.3 Hz, 1H), 7.92 (d, J = 2.3 Hz, 1H), 10.21 (s, 1H); ^{13}C NMR δ 15.7, 118.2, 127.4, 134.1, 135.2, 136.6, 142.4, 189.8; EI-HRMS obsd 229.9400, calc 229.9401 (C_8H_7BrOS). ^{1}H NMR data are identical to those reported in literature.[23]

2-Bromo-6-fluorobenzaldehyde (13). Following a reported procedure,[17] a solution of 1-bromo-3-fluorobenzene (**12**) (6.00 mL, 54.6 mmol) in anhydrous THF (100 mL) at –100 °C was treated with LDA (30 mL, 2 M in THF/n-heptane/ethylbenzene, 60.0 mmol) over 1 h. After stirring for 30 min at –100 °C, dimethyldisulfide (6.43 mL, 89 mmol) was added dropwise, and the mixture was stirred for 1 h at – 100 °C. A saturated solution of NH_4Cl was added, and the mixture was stirred for 10 min. Ethyl acetate was added, and the organic layer was separated, dried over $MgSO_4$, and concentrated under vacuum. The resulting residue was subjected to column chromatography [silica, n-hexane] to afford an colorless oil (9.06 g, 82%): ^{1}H NMR δ 7.16 (m, 1H), 7.41 (td, J = 8.0 and 5.0 Hz, 1H), 7.50 (dt, J = 8.0 and 0.9 Hz, 1H); ^{13}C NMR δ 116.3 (d, ^2J = 22 Hz), 122.8 (d, J = 9 Hz), 125.3 (d, J = 3 Hz), 130.1 (d, J = 4 Hz), 135.3 (d, J = 10 Hz), 163.1 (d, ^1J = 266 Hz), 188.5 (d, J = 2 Hz); EI-HRMS obsd 201.9429, calc 201.9429 (C_7H_4OFBr).

6-Bromo-2-(methylthio)benzaldehyde (14). Following a reported procedure,[23] a solution of 2-bromo-6-fluorobenzaldehyde (**13**) (5 g, 24.6 mmol) in anhydrous DMF (15 mL) was treated with freshly prepared NaSMe (1.9 g, 27.1 mmol). After stirring 1 h, crushed ice was added, and

the precipitate was filtered, washed with water, and dried. Crystallization in hexane afforded a yellow solid (3.43 g, 60%): mp.: 90–93 °C; ^{1}H NMR δ 2.45 (s, 3H, SMe), 7.26 (m, 1H), 7.33 (m, 1H), 7.42 (m, 1H), 10.53 (s, J = 0.7 Hz, 1H, CHO); ^{13}C NMR δ 15.5, 13.7, 128.9, 129.0, 129.6, 133.6, 147.0, 192.7; EI-HRMS obsd 229.9395, calc 229.9401 (C_8H_7BrOS).

1-Bromo-2-dimethoxymethyl-3-(methylthio)benzene (15). A solution of 6-bromo-2-(methylthio)benzaldehyde (**14**) (3.82 g, 16.0 mmol) and trimethyl orthoformate (3.62 mL, 33.0 mmol) in methanol (80 mL) was treated with 1 drop of concentrated H_2SO_4, and the mixture was refluxed for 1 h. A saturated solution of K_2CO_3 was added to pH = 9. Ethyl acetate was added and the organic layer was separated, dried over $MgSO_4$, and concentrated under vacuum to afford a colorless oil (4.25 g, 96 %): ^{1}H NMR δ 2.42 (s, 3H), 3.48 (s, 6H), 5.85 (s, 1H), 7.05–7.20 (m, 2H), 7.33 (dd, J = 7.7 and 1.2 Hz 1H); ^{13}C NMR δ 16.1, 55.6, 106.8, 124.3, 124.6, 129.3, 129.6, 132.9, 141.1; EI-HRMS obsd 275.9811, calc 275.9819 ($C_{10}H_{13}BrO_2S$).

3,3'-dibromo-2,2'-dimethylthio-trans-stilbene (16). Following a procedure for McMurry coupling,[15] a suspension of Zn (1.97 g, 30.0 mmol) in anhydrous THF (40 mL) at 0 °C was treated dropwise with $TiCl_4$ (3.30 mL, 30.0 mmol), and the resulting mixture was heated at reflux for 1 h. After cooling to 0 °C, a solution of **7** (2.32 g, 10.0 mmol) in anhydrous THF (20 mL) was added, and the resulting mixture was heated at reflux overnight. After cooling to room temperature, the mixture was poured in saturated solution of $NaHCO_3$ (100 mL) and dichloromethane (100 mL) and stirred for 3 h. The mixture was filtered through a Celite pad, washed with hot chloroform, and the layers of the filtrate were separated. The aqueous layer was extracted with dichloromethane, and the combined organic layer was dried over $MgSO_4$ and concentrated under vacuum. Recrystallization from *n*-hexane affords a white solid (1.34 g, 61 %): m.p.: 131–137 °C; ^{1}H NMR δ 2.36 (s, 6H), 7.22 (t, J = 7.9 Hz, 2H), 7.65 (d, J = 7.9 Hz, 2H),

7.70 (d, J = 7.8 Hz, 2H), 7.83 (s, 2H); ^{13}C NMR δ 19.4, 125.8, 129.8, 131.0, 132.0, 132.7, 136.1, 143.5; EI-HRMS obsd 427.8905, calc 427.8904 ($C_{16}H_{14}Br_2S_2$).

4,4'-dibromo-2,2'-dimethylthio-trans-stilbene (17). The coupling was performed with 3.00 g (13 mmol) of **9** following the above procedure for **16**. Recrystallization from *n*-hexane affords a white solid (2.00 g, 70 %): mp.: 178–186 °C (184–186 °C, xylene)[29]; ^{1}H NMR δ 2.48 (s, 6H), 7.30 (dd, J = 8.3 and 1.9 Hz, 2H), 7.33 (s, 2H), 7.36 (d, J = 1.9 Hz, 2H), 7.45 (d, J = 8.3 Hz, 2H, H_6+$H_{6'}$); ^{13}C NMR δ 16.3, 122.2, 127.1, 127.5, 128.5, 128.9, 135.0, 139.5; EI-HRMS obsd 427.8892, calc 427.8904 ($C_{16}H_{14}Br_2S_2$).

5,5'-dibromo-2,2'-dimethylthio-trans-stilbene (18). The coupling was performed with 3.00 g (13 mmol) of **11** following the above procedure for **16**. Recrystallization from *n*-hexane affords a white solid (2.31 g, 84 %): m.p.: 216–224 °C; ^{1}H NMR δ 2.46 (s, 6H), 7.15 (d, J = 8.4 Hz, 2H), 7.36 (s, 2H), 7.38 (dd, J = 8.4 and 2.1 Hz, 2H), 7.70 (d, J = 2.1 Hz, 2H); ^{13}C NMR δ 19.7, 119.6, 127.7, 128.8, 129.0, 131.1, 136.6, 138.1; EI-HRMS obsd 427.8892, calc 427.8904 ($C_{16}H_{14}Br_2S_2$).

6,6'-dibromo-2,2'-dimethylthio-trans-stilbene (19). The coupling was performed with 3.00 g (13 mmol) of **14** following the above procedure for **16**. Recrystallization from *n*-hexane affords a white solid (2.49 g, 87 %): m.p.: 127–135 °C; ^{1}H NMR δ 2.46 (s, 6H), 6.99 (s, 2H), 7.09 (t, J = 7.8 Hz, 2H), 7.16 (dd, J = 7.8 and 0.7 Hz, 2H), 7.43 (dd, J = 7.7 and 1.1 Hz, 2H); ^{13}C NMR δ 16.5, 123.9, 124.1, 128.5, 129.3, 133.4, 135.4, 140.5; EI-HRMS obsd 427.8918, calc 427.8904 ($C_{16}H_{14}Br_2S_2$).

1,6-Dibromo[1]benzothieno[3,2-*b*][1]benzothiophene (20I). A solution of **16** (500 mg, 1.19 mmol) in AcOH (80 mL) at reflux was treated with powdered iodine (9.64 g, 38.0 mmol).

The resulting mixture was heated at reflux for 2 days. After cooling to room temperature, the mixture was poured in sodium dithionite solution (100 mL), and the solid collected by filtration. The filtered material was subjected overnight to high vacuum. The resulting residue was subjected to column chromatography [silica, hot n-hexane] to afford **20I** as an off-white solid (128 mg, 27%) followed by 7-bromo-2-(3-bromo-2-(methylthio)phenyl)benzo[*b*]thiophene (**20-II**) as an off-white solid (182 mg, 37 %). **20I** : m.p.: 280–282 °C; ^{1}H NMR (1,1,2,2-tetrachloroethane-d_2, 400 MHz, 100 °C) δ 7.43 (t, J = 7.8 Hz, 2H), 7.65 (dd, J = 7.7 and 0.9 Hz, 2H), 7.93 (dd, J = 7.9 and 0.9 Hz, 2H); ^{13}C NMR (1,1,2,2-tetrachloroethane-d_2, 100 MHz, 100 °C) δ 116.9, 120.3, 126.3, 128.1, 133.9, 134.3, 143.6; EI-HRMS obsd 395.8261, calc 395.8277 ($C_{14}H_6Br_2S_2$). **20-II** : mp.: 92–94 °C; ^{1}H NMR δ 2.29 (s, 3H), 7.19 (t, J = 7.9 Hz, 1H), 7.24 (t, J = 7.8 Hz, 1H), 7.47 (dd, J = 7.7 and 1.4 Hz, 1H), 7.48 (dd, J = 7.7 and 0.9 Hz, 2H), 7.50 (s, 1H), 7.68 (dd, J = 8.0 and 1.4 Hz, 1H), 7.73 (dd, J = 7.9 and 0.9 Hz, 1H); ^{13}C NMR δ 19.7, 115.3, 122.7, 125.0, 125.7, 127.3, 129.3, 130.7, 132.2, 133.7, 136.5, 140.3, 140.5, 142.0, 143.6; EI-HRMS obsd 411.8581, calc 411.8591 ($C_{15}H_{10}Br_2S_2$).

2,7-Dibromo[1]benzothieno[3,2-*b*][1]benzothiophene (21I). The cyclization was performed with a solution of **17** (495 mg, 1.17 mmol) following the above procedure for **20I**. The resulting residue was subjected to column chromatography [silica, hot n-hexane] to afford **21I** as an off-white solid (23 mg, 5 %) followed by 6-bromo-2-(4-bromo-2-(methylthio)phenyl)benzo[*b*]thiophene (**21-II**) (256 mg, 53 %): **21I** : m.p.: 280 °C (299–300 °C, AcOH)[29]; ^{1}H NMR (1,1,2,2-tetrachloroethane-d_2, 400 MHz, 100 °C) δ 7.63 (dd, J = 8.4 and 1.7 Hz, 2H), 7.77 (d, J = 8.4 Hz, 2H), 8.11 (d, J = 1.5 Hz, 2H); ^{13}C NMR (1,1,2,2-tetrachloroethane-d_2, 100 MHz, 100 °C) δ 119.2, 122.6, 126.7, 128.7, 131.8, 133.6, 144.0; EI-HRMS obsd 395.8274, calc 395.8277 ($C_{14}H_6Br_2S_2$). **21-II** : mp.: 149–151 °C; ^{1}H NMR δ 2.45 (s, 3H), 7.28

(d, J = 8.0 Hz, 1H), 7.32 (dd, J = 8.0 and 1.8 Hz, 1H), 7.38 (d, J = 1.8 Hz, 1H), 7.41 (d, J = 0.5 Hz, 1H), 7.46 (dd, J = 8.5 and 1.7 Hz, 1H), 7.66 (d, J = 8.5 Hz, 1H), 7.98 (d, J = 1.7 Hz, 1H); ^{13}C NMR δ 16.0, 118.4, 123.3, 124.1, 124.6, 124.9, 127.7, 127.8, 127.9, 131.2, 132.1, 138.5, 140.7, 140.9, 141.6; EI-HRMS obsd 411.8602, calc 411.8590 ($C_{15}H_{10}Br_2S_2$).

3,8-Dibromo[1]benzothieno[3,2-*b*][1]benzothiophene (22I). The cyclization was performed with a solution of **18** (282 mg, 0.67 mmol) following the above procedure for **20I**. The resulting residue was subjected to column chromatography [silica, hot cyclohexane] to afford **22** as an off-white solid (10 mg, 4 %) followed by 5-bromo-2-(5-bromo-2-(methylthio)phenyl)benzo[*b*]thiophene (**22-II**) (256 mg, 40 %): **22I** : m.p.: 239–241 °C; ^{1}H NMR (1,1,2,2-tetrachloroethane-d_2, 400 MHz, 100 °C) δ 7.59 (dd, J = 8.6 and 1.7 Hz, 2H), 7.84 (d, J = 8.6 Hz, 2H), 8.08 (d, J = 1.7 Hz, 2H); ^{13}C NMR (1,1,2,2-tetrachloroethane-d_2, 100 MHz, 100 °C) δ 119.6, 124.6, 125.4, 128.6, 134.5, 136.1, 141.2; EI-HRMS obsd 395.8272, calc 395.8277 ($C_{14}H_6Br_2S_2$). **22II** : m.p.: 116–118 °C; ^{1}H NMR δ 2.41 (s, 3H), 7.15 (d, J = 8.5 Hz, 1H), 7.38 (d, J = 0.5 Hz, 1H), 7.44 (dd, J = 8.6 and 2.0 Hz, 1H), 7.47 (dd, J = 8.5 and 2.2 Hz, 1H), 7.57 (d, J = 2.2 Hz, 1H), 7.69 (d, J = 8.6 Hz, 1H), 7.94 (d, J = 1.8 Hz, 1H); ^{13}C NMR δ 16.2, 118.3, 118.5, 123.4, 123.9, 126.4, 127.2, 127.7, 131.9, 133.5, 134.3, 137.6, 138.8, 141.2, 141.7; EI-HRMS obsd 411.8590, calc 411.8590 ($C_{15}H_{10}Br_2S_2$).

4,9-Dibromo[1]benzothieno[3,2-*b*][1]benzothiophene (23I). The cyclization was performed with 242 mg (0.576 mmol) of **19** following the above procedure for **20I**. The resulting residue was subjected to column chromatography [silica, hot cyclohexane] to afford an off-white solid (46 mg, 20 %) followed by 4,9-dibromo-4*b*,9*b*-dihydrobenzothieno[3,2-*b*]benzothiophene (**23III**) (64 mg, 28 %). **23I** : m.p.: 252–260 °C; ^{1}H NMR (1,1,2,2-tetrachloroethane-d_2, 400 MHz, 100 °C) δ 7.34 (t, J = 7.6 Hz, 2H), 7.71 (d, J = 7.6 Hz, 2H), 7.95 (d, J = 7.9 Hz, 2H); ^{13}C

NMR (1,1,2,2-tetrachloroethane-d_2, 100 MHz, 100 °C) δ 116.4, 122.8, 126.2, 128.5, 129.7, 132.6, 143.6; EI-HRMS obsd 395.8278, calc 395.8277 ($C_{14}H_6Br_2S_2$). **23III** : mp.: 226–228 °C; ^{1}H NMR δ 5.96 (s, 2H), 7.04 (t, J = 7.7 Hz, 2H), 7.12 (d, J = 7.6 Hz, 2H), 7.21 (d, J = 7.7 Hz, 1H); ^{13}C NMR δ 60.9, 120.5, 120.8, 127.9, 130.5, 138.1, 143.2; EI-HRMS obsd 397.8447, calc 397.8434 ($C_{14}H_8Br_2S_2$).

3,3'-Didocecyl-2,2'-dimethylthio-trans-stilbene (24). Following a general procedure for Kumada coupling,[28] a solution of **16** (438 mg, 1 mmol) and $PdCl_2$(dppf) (146 mg, 0.2 mmol) in anhydrous THF (20 mL) at 0 °C was treated dropwise with 1-dodecylmagnesium bromide (10 mL, 0.5 M in THF, 5 mmol), and the mixture was heated at reflux for 12 h. After cooling to room temperature, a saturated solution of NH_4Cl was added, and the mixture was stirred for 10 min. The mixture was filtered through a Celite pad, and the layers of the filtrate were separated. The aqueous layer was extracted with dichloromethane, and the combined organic layer was dried over MgSO4 and concentrated under vacuum. The resulting residue was subjected to column chromatography [silica, n-hexane/CH_2Cl_2 (85/15)] to afford an off-white solid (380 mg, 62 %): m.p.: 77–79 °C; ^{1}H NMR δ 0.88 (t, J = 6.2 Hz, 6H), 1.25–1.34 (m, 36H), 1.59 (m, 4H), 2.23 (s, 6H), 2.93 (t, J = 7.6 Hz, 4H), 7.18 (dd, J = 7.4 and 0.9 Hz, 2H), 7.29 (t, J = 7.59 Hz, 2H), 7.63 (dd, J = 7.8 and 0.9 Hz, 2H), 7.85 (s, 2H); ^{13}C NMR δ 14.2, 20.2, 22.8, 29.5, 29.7, 29.8 (5X), 32.0, 32.1, 35.5, 124.7, 128.5, 129.0, 130.3, 134.8, 142.1, 147.4; EI-HRMS obsd 608.4464, calc 608.4449 ($C_{40}H_{64}S_2$).

4,4'-Didocecyl-2,2'-dimethylthio-trans-stilbene (25). The Kumada coupling was performed with 438 mg (1 mmol) of **17** following the above procedure for **24**. The resulting residue was subjected to column chromatography [silica, n-hexane/CH_2Cl_2 (85/15)] to afford an off-white solid (402 mg, 66 %): m.p.: 93–98 °C; ^{1}H NMR δ 0.88 (t, J = 6.3 Hz, 6H), 1.25–1.34

(m, 36H), 1.62 (m, 4H), 2.46 (s, 6H), 2.59 (t, J = 7.7 Hz, 4H), 7.02 (dd, J = 7.9 and 1.4 Hz, 2H), 7.11 (d, J = 1.4 Hz, 2H), 7.44 (s, 2H), 7.56 (d, J = 7.9 Hz, 2H); ^{13}C NMR δ 14.1, 16.9, 22.7, 29.3, 29.4, 29.5, 29.6 (2X), 29.7, 31.4, 31.9, 35.8, 126.1, 126.2, 126.9, 127.7, 135.6, 136.5, 143.0; EI-HRMS obsd 608.4427, calc 608.4449 ($C_{40}H_{64}S_2$).

5,5'-Didocecyl-2,2'-dimethylthio-trans-stilbene (26). The Kumada coupling was performed with 438 mg (1 mmol) of **18** following the above procedure for **24**. The resulting residue was subjected to column chromatography [silica, petroleum ether/CH_2Cl_2 (90/10)] to afford an off-white solid (500 mg, 82 %): m.p.: 73–75 °C; ^{1}H NMR δ 0.88 (t, J = 6.9 Hz, 6H), 1.25–1.34 (m, 36H), 1.63 (m, 4H), 2.45 (s, 6H), 2.61 (t, J = 7.6 Hz, 4H), 7.08 (dd, J = 8.0 and 1.7 Hz, 2H), 7.26 (d, J = 8.0 Hz, 2H), 7.45 (d, J = 1.7 Hz, 2H), 7.49 (s, 2H); ^{13}C NMR δ 14.1, 17.2, 22.7, 29.4 (2X), 29.5, 29.6 (2X), 29.7, 31.5, 31.9, 35.6, 126.4, 127.8, 128.2, 128.3, 133.8, 137.1, 140.9; EI-HRMS obsd 608.4457, calc 608.4449 ($C_{40}H_{64}S_2$).

6,6'-Didocecyl-2,2'-dimethylthio-trans-stilbene (27). *Route A:* The Kumada coupling was performed with 438 mg (1 mmol) of **19** following the above procedure for **24**. The resulting residue was subjected to column chromatography [silica, n-hexane/CH_2Cl_2 (85/15)] to afford an off-white solid (80 mg, 13 %): m.p.: 78–82 °C; ^{1}H NMR δ 0.88 (t, J = 6.5 Hz, 6H), 1.22–1.38 (m, 36H), 1.61 (m, 4H), 2.44 (s, 6H), 2.83 (t, J = 7.8 Hz, 4H), 6.74 (s, 2H), 7.03-7.09 (m, 4H), 7.20 (t, J = 7.7 Hz, 2H); ^{13}C NMR δ 14.1, 16.1, 22.7, 29.4, 29.7 (5X), 29.8, 31.6, 31.9, 33.8, 122.0, 125.8, 127.3, 131.9, 135.6, 138.3, 141.8; EI-HRMS obsd 608.4459, calc 608.4449 ($C_{40}H_{64}S_2$). *Route B:* The McMurry coupling was performed with 1.45 g (5 mmol) of **28** following the above procedure for **24**. Column chromatography [silica, petroleum ether/CH_2Cl_2 (80/20)] affords an off-white solid (609 mg, 40 %).

2-Dodecyl-6-(methylthio)benzaldehyde (28). Following a general procedure for Kumada coupling,[28] a solution of **15** (1.83g, 6.6 mmol) and $PdCl_2$(dppf) (483 mg, 0.66 mmol) in anhydrous THF (30 mL) at 0 °C was treated dropwise with 1-dodecylmagnesium bromide (33 mL, 0.5 M in THF, 16.5 mmol), and the mixture was heated at reflux for 12 h. After cooling to room temperature, 6 M aqueous HCl (20 mL) was added and the mixture was stirred for 10 min. The mixture was filtered through a Celite pad, and the layers of the filtrate were separated. The aqueous layer was extracted with dichloromethane, and the combined organic layer was dried over $MgSO_4$ and concentrated under vacuum. The resulting residue was subjected to column chromatography [silica, petroleum ether/CH_2Cl_2 (60/40)] to afford an off-white solid (1.53 g, 72 %). m.p.: 60–64 °C; ^{1}H NMR δ 0.88 (t, J = 6.5 Hz, 3H), 1.22–1.38 (m, 18H), 1.61 (m, 2H), 2.46 (s, 3H), 2.95 (t, J = 7.6 Hz, 1H), 7.02 (dd, J = 7.6 and 0.7 Hz, 1H), 7.19 (d, J = 8.0 Hz, 1H), 7.40 (d, J = 7.8 Hz, 1H), 10.58 (s, 1H); ^{13}C NMR δ 14.1, 16.1, 22.7, 29.3, 29.4, 29.5 (2X), 29.6 (3X), 31.9, 32.9, 33.2, 123.3, 126.9, 130.3, 133.0, 144.2, 147.8, 191.2; EI-HRMS obsd 320.2176, calc 320.2174 ($C_{20}H_{32}OS$).

1,6-Didodecyl[1]benzothieno[3,2-*b*][1]benzothiophene (1). The cyclization was performed with 263 mg (0.43 mmol) of **24** following the above procedure for **20**. The resulting residue was subjected to column chromatography [silica, hot n-hexane] to afford an off-white solid (166 mg, 67 %): m.p.: 86.3 °C; ^{1}H NMR δ 0.87 (t, J = 6.9 Hz, 6H), 1.19–1.45 (m, 36H), 1.85 (m, 4H), 2.92 (t, J = 7.6 Hz, 4H), 7.22 (dd, J = 7.5 and 0.8 Hz, 2H), 7.41 (t, J = 7.5 Hz, 2H), 7.74 (dd, J = 7.8 and 0.8 Hz, 2H); ^{13}C NMR δ 14.1, 22.7, 29.3 (2X), 29.5, 29.6 (2X), 29.7 (3X), 31.9, 34.8, 119.2, 124.3, 125.2, 133.2, 133.5, 138.2, 141.9; EI-HRMS obsd 576.3806, calc 576.3823 ($C_{38}H_{56}S_2$).

2,7-Didodecyl[1]benzothieno[3,2-*b*][1]benzothiophene (2). The cyclization was performed with 312 mg (0.51 mmol) of **25** following the above procedure for **20**. The resulting residue was subjected to column chromatography [silica, hot n-hexane] to afford an off-white solid (10 mg, 3 %): m.p.: 117.4 °C (121–123 °C, hexane)[5]; ^{1}H NMR δ 0.87 (t, J = 6.9 Hz, 6H), 1.25–1.38 (m, 36H), 1.69 (m, 4H), 2.75 (t, J = 7.8 Hz, 4H), 7.26 (dd, J = 8.1 and 1.3 Hz, 2H), 7.70 (d, J = 1.3 Hz, 2H), 7.75 (d, J = 8.1 Hz, 2H); ^{13}C NMR δ 14.1, 22.7, 29.3 (2X), 29.5, 29.6 (3X), 29.7 (2X), 31.7, 31.9, 121.0, 123.3, 125.8, 131.2, 132.5, 140.0, 142.4; EI-HRMS obsd 576.3816, calc 576.3823 ($C_{38}H_{56}S_2$). These data are identical to those reported in the literature.[5]

3,8-Didodecyl[1]benzothieno[3,2-*b*][1]benzothiophene (3). The cyclization was performed with 414 mg (0.94 mmol) of **26** following the above procedure for **20**. The resulting residue was subjected to column chromatography [silica, hot n-hexane] to afford an off-white solid (287 mg, 53 %): m.p.: 106.5 °C; ^{1}H NMR δ 0.88 (t, J = 6.9 Hz, 6H), 1.25–1.38 (m, 36H), 1.71 (m, 4H), 2.76 (t, J = 7.6 Hz, 4H), 7.23 (dd, J = 8.3 and 1.5 Hz, 2H), 7.66 (d, J = 1.5 Hz, 2H), 7.81 (d, J = 8.3 Hz, 2H); ^{13}C NMR δ 14.1, 22.7, 29.4 (2X), 29.5, 29.6 (2X), 29.7 (2X), 31.8, 36.0, 121.0, 123.6 (2X), 126.0, 133.4, 139.4, 140.0; EI-HRMS obsd 576.3828, calc 576.3823 ($C_{38}H_{56}S_2$).

4,9-Didodecyl[1]benzothieno[3,2-*b*][1]benzothiophene (4). The cyclization was performed with 480 mg (0.79 mmol) of **27** following the above procedure for **20**. The resulting residue was subjected to column chromatography [silica, hot n-hexane] to afford an off-white solid (151 mg, 33 %): m.p.: 89 °C; ^{1}H NMR δ 0.87 (t, J = 6.9 Hz, 6H), 1.20–1.60 (m, 36H), 1.80 (m, 4H), 3.13 (t, J = 7.9 Hz, 4H), 7.25 (d, J = 7.6 Hz, 2H), 7.33 (t, J = 7.5 Hz, 2H), 7.78 (d, J = 7.8 Hz, 2H); ^{13}C NMR δ 14.1, 22.7, 29.6 (2X), 29.7 (4X), 31.2, 31.9, 34.7, 121.1, 124.9 (2X), 131.7, 131.9, 137.4, 143.1; EI-HRMS obsd 576.3812, calc 576.3823 ($C_{38}H_{56}S_2$).

Associated content

Supporting information

Crystallographic information and copies of ^{1}H NMR and ^{13}C NMR spectra for all products. This material is available free of charge via the Internet at http://pubs.acs.org. CCDC 936655 contains 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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