

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/236922476>

# Synthesis and Structure of Bull's Horn-Shaped Oligothiienoacene with Seven Fused Thiophene Rings

ARTICLE *in* THE JOURNAL OF ORGANIC CHEMISTRY · MAY 2013

Impact Factor: 4.72 · DOI: 10.1021/jo4002036 · Source: PubMed

---

CITATIONS

6

---

READS

12

8 AUTHORS, INCLUDING:



Jianwu Shi

Henan University

37 PUBLICATIONS 491 CITATIONS

SEE PROFILE



Hua Wang

Florida International University

41 PUBLICATIONS 204 CITATIONS

SEE PROFILE

# Synthesis and Structure of Bull's Horn-Shaped Oligothiienoacene with Seven Fused Thiophene Rings

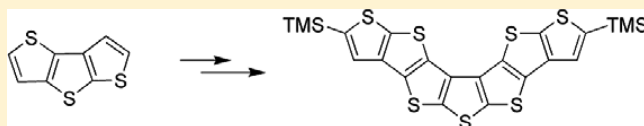
Huiliang Sun,<sup>†</sup> Jianwu Shi,<sup>\*,†</sup> Zilong Zhang,<sup>‡</sup> Sheng Zhang,<sup>†</sup> Zhaoli Liang,<sup>†</sup> Shisheng Wan,<sup>†</sup> Yanxiang Cheng,<sup>\*,‡</sup> and Hua Wang<sup>\*,†</sup>

<sup>†</sup>Key Lab for Special Functional Materials of Ministry of Education, Henan University, Kaifeng 475004, China

<sup>‡</sup>Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, China

## S Supporting Information

**ABSTRACT:** A novel bull's horn-shaped oligothiienoacene with seven fused thiophene rings (**1**) based on dithieno[2,3-*b*:2',3'-*d*]thiophene (**2**) was efficiently synthesized. X-ray diffraction data indicate that **1** possesses an extraordinary compressed sandwich-herringbone arrangement and shows strong intermolecular S...C and S...S interactions. In addition, the UV/vis properties, theoretical calculations, and cyclic voltammetry behaviors of **1** are also described.



Oligothiophenes are among the most extensively studied conjugated organic materials owing to favorable electrical and optical properties for a wide range of new technologies.<sup>1</sup> For example,  $\alpha$ -sexithiophene has been successfully employed as active components in organic light-emitting devices (OLEDs)<sup>2</sup> and organic field-effect transistors (OFETs).<sup>1a,b</sup> In contrast to  $\alpha$ -oligothiophenes with low conjugation through the torsion of single bonds or S-syn defects,<sup>3</sup> the fused oligothiophenes (thienoacenes) possessing chemical stability emerge as a more promising new class of  $\pi$ -conjugated compounds, which combine with extended conjugation and rigid planarity.<sup>4</sup>

Fused oligothiophenes based on two isomers, dithieno[2,3-*b*:3',2'-*d*]thiophene (**3**) and dithieno[3,2-*b*:2',3'-*d*]thiophene (**5**), as building blocks have excited countless studies in a variety of areas ranging from helicene chemistry to materials science. Among them, the synthesis of an impressive array of carbon–sulfur [*n*]helicenes based on **3** has been accomplished by Rajca<sup>5</sup> and Wang.<sup>6</sup> With an increasing of *n*, helical carbon–sulfur (C<sub>2</sub>S)<sub>*n*</sub> oligomers possess moderate curvature characteristics of helicenes,<sup>7</sup> such as **4**, a carbon–sulfur [7]helicene<sup>6b</sup> (Scheme 1). On the basis of **5**, a quasi-linearly annulated oligothiophene (**6**, Scheme 1) was synthesized by Matzger.<sup>4b</sup>

In overall consideration of the fused oligothiophenes, there are three novelties should be attracted. The first one is the novel molecular framework. The second one is their synthetic challenge<sup>5,6</sup> due to solubility problem of fused thiophenes and the strict moisture sensitive conditions in the construction process. The third one is the significantly optical and electronic properties based on the molecular arrangement and intermolecular interactions, such as S...S interactions and  $\pi$ – $\pi$  interactions in solid.<sup>6,8,9</sup>

Herein, we try to present the synthesis of a new and novel [7]thienoacene, **1** (Scheme 2), with bull's horn-shaped molecular structure based on a new building block, dithieno[2,3-*b*:2',3'-*d*]thiophene (**2**). In addition, the selected phys-

icochemical studies including UV/vis properties, theoretical calculations and electrochemical behaviors were also described.

The synthetic route to **1** is shown in Scheme 2. The first work was to make the isomeric dithienothiophene, **2**. In fact, **2** has not received enough attention due to the lack of efficient synthetic methods.<sup>10</sup> In the reported method, an unstable intermediate, 3-(3-bromothiophen-2-yl)thiophene-2-thiol, was employed in making **2** under oxidation of Cu<sub>2</sub>O for the key step of ring cyclization.<sup>10a</sup> In our work, three routes are used for preparation of **2** and its TMS-protected derivative, **10** (Scheme 2). In Route A, direct ring cyclization of 3-bromo-2-(thiophen-3-yl)thiophene (**7**) occurred in 55% yield in the presence of *n*-BuLi and (PhSO<sub>2</sub>)<sub>2</sub>S. Selective deprotonation was observed in this reaction. In Route B, 3-bromo-2-(2-bromothiophen-3-yl)thiophene (**8**)<sup>10a</sup> was made first by bromination of **7**, and then *t*-BuLi was used for Br/Li exchange of **8**, following reaction with (PhSO<sub>2</sub>)<sub>2</sub>S for ring cyclization to generate **2** in 50–55% yield (step c, Scheme 2). 2,5-Bis(trimethylsilyl)-dithieno[2,3-*b*:2',3'-*d*]thiophene (**10**) was synthesized from **2** via TMS-protection in the presence of LDA and TMS-Cl in high yield of 92–94% (step d, Scheme 2). Route C has two steps; the first one is the TMS-protection of **8**, in which 3-bromo-2-(2-bromo-5-(trimethylsilyl)thiophen-3-yl)-5-(trimethylsilyl)-thiophene (**9**) was obtained in the presence of LDA and TMS-Cl with high yield as 89–94%. The second step is the ring cyclization of **9** to generate **10** in presence of *n*-BuLi and (PhSO<sub>2</sub>)<sub>2</sub>S with 55–60% yield.

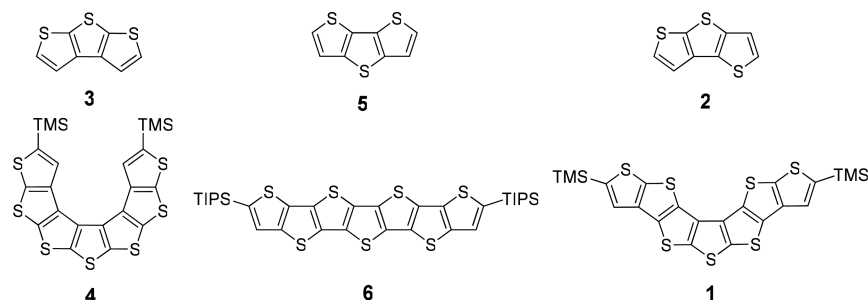
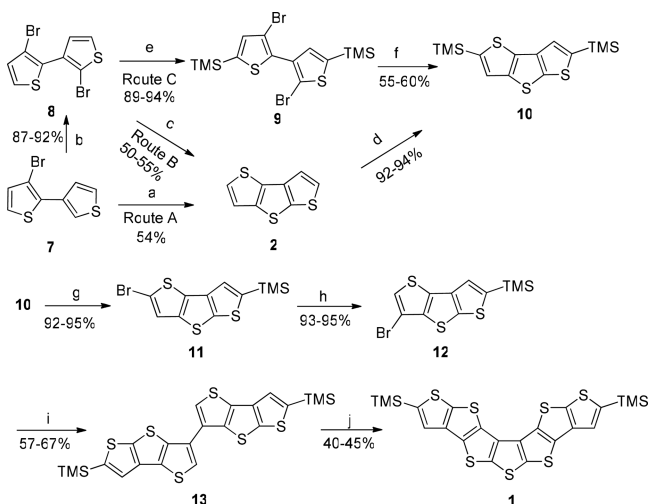
Compound **10** is an important intermediate for making title compound. The highly selective bromination of **10** was observed in the presence of NBS in a mixture solvent, AcOH–CHCl<sub>3</sub> (1:8, v/v). 5-Bromo-2-trimethylsilyl-dithieno[2,3-*b*:2',3'-*d*]thiophene (**11**) was generated efficiently in 92–95% yield (step g, Scheme 2). Then, the bromine dance

Received: February 1, 2013

Published: May 20, 2013



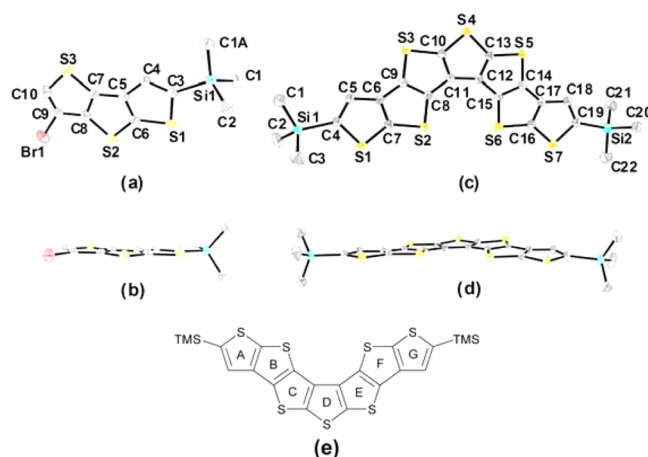
Scheme 1. Molecular Structures of [3]Thienoacenes and [7]Thienoacenes

Scheme 2. Synthetic Route to **1**<sup>a</sup>

<sup>a</sup>Reagents and conditions: (a) (i) *n*-BuLi (2.05 equiv), Et<sub>2</sub>O, -78 °C; (ii) (PhSO<sub>2</sub>)<sub>2</sub>S (1.0 equiv), -78 °C to rt, overnight; (b) NBS (1.05 equiv), AcOH-CHCl<sub>3</sub> (1:1), rt; (c) (i) *t*-BuLi (4.1 equiv), Et<sub>2</sub>O, -78 °C; (ii) (PhSO<sub>2</sub>)<sub>2</sub>S (1.0 equiv), -78 °C to rt, overnight; (d) (i) LDA (2.2 equiv), Et<sub>2</sub>O, 0 °C; (ii) TMSCl (4.0 equiv), -78 °C; (e) (i) LDA (2.05 equiv), Et<sub>2</sub>O, -78 °C; (ii) TMSCl (4.0 equiv), -78 °C; (f) (i) *n*-BuLi (2.05 equiv), Et<sub>2</sub>O, -78 °C; (ii) (PhSO<sub>2</sub>)<sub>2</sub>S (1.0 equiv), -78 °C to rt, overnight; (g) NBS (1.05 equiv), AcOH-CHCl<sub>3</sub> (1:8), rt; (h) (i) LDA (1.5 equiv), THF, 0 °C; (ii) (i) Pd[P<sup>*t*</sup>Bu<sub>3</sub>]<sub>2</sub> (0.6 equiv), K<sub>3</sub>PO<sub>4</sub> (2.1 equiv), toluene, 90 °C; (j) (i) LDA (2.5 equiv), THF, -78 °C; (ii) (PhSO<sub>2</sub>)<sub>2</sub>S (1.0 equiv), -78 °C to rt, overnight.

reaction of **11**<sup>6b,11</sup> efficiently occurred in the presence of LDA in THF at 0 °C to generate 6-bromo-2-trimethylsilyl-dithieno[2,3-*b*:3',2'-*d*]thiophene (**12**) in 93–95% yield. Pd-mediated reductive C–C homocoupling of **12** occurred to give 2,2'-di(trimethylsilyl)-6,6'-bis-dithieno[2,3-*b*:2',3'-*d*]thiophene (**13**) in 57–67% yield. LDA-mediated lithiation was introduced to remove the protons at the unprotected  $\alpha$  positions in **13**, and the formed dilithiated **13** was reacted with (PhSO<sub>2</sub>)<sub>2</sub>S to give the bull's horn-shaped [7]thienoacene, **1**, in 40–45% yield.

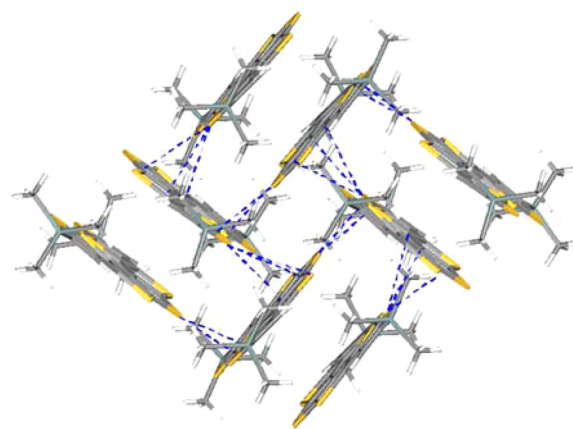
The structures of **12** and **1** are confirmed by single-crystal X-ray analysis (Figure 1). In **12**, all the thiophene rings are completely coplanar (Figure 1a,b). In the packing of **12**, the molecules show layer-by-layer assembly. The distance between the two layers is about 3.630 Å. There are four molecules in one cell and some short contacts can be observed as C4...C9, 3.630 Å; C6...S3, 3.649 Å; and S2...S3, 3.843 Å. The crystal of **1** belongs to monoclinic *P2*(1)/*c*. In **1**, all seven thiophene rings are fused together to form a bull's horn-shaped molecule (Figure 1c); its molecular framework is different from another



**Figure 1.** Molecular structures and conformations for **12** and **1**. (a) Top view for **12**; (b) side view for **12**; (c) top view for **1**; (d) side view for **1**; (e) molecular structure of **1**. Carbon, oxygen, silicon, and sulfur atoms are depicted with thermal ellipsoids set at the 30% probability level. All hydrogen atoms are omitted for clarity.

two [7]thienoacene isomers, helical **4** and linear **6**. There are five rings (ring-B to ring-F) in the middle of **1**, forming [5]helicene-like structure with a little bit of twisting. The dihedral angle between ring-B and ring-F is 8.65° (Figure 1e).

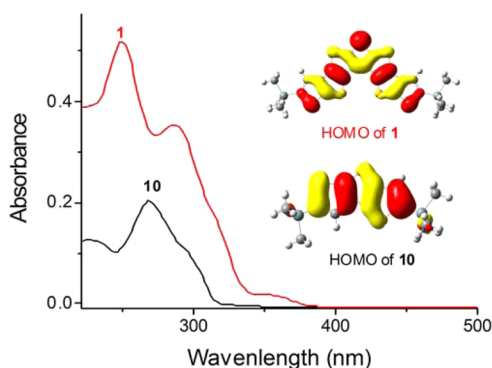
Compound **1** possesses a little bit distorted molecular geometry, leading to a packing of sandwich-herringbone arrangement in its crystal (Figure 2).<sup>12</sup> Multiple short interactions including S...S and S... $\pi$  interactions can be observed. For example, the distances of S2...S4, 3.541 Å;



**Figure 2.** Sandwich-herringbone arrangement with C...S and S...S interactions in the crystal packing of **1**.

S4...S6, 3.345 Å; S1...C8, 3.489 Å; S1...C9, 3.523 Å; S1...C10, 3.477 Å; S1...C11, 3.494 Å are found, respectively. Such multiple short interactions are important for thiophene-based organic semiconductors in the research of high field-effect mobility.<sup>9,12,13</sup> Further, **1** has an approximately coplanar molecular structure, which may show similar electronic properties to that of annulated  $\alpha$ -oligothiophenes, a linear pentathienoacene and heptathienoacene reported by Zhu<sup>14</sup> and Matzger.<sup>4c</sup>

UV/vis spectra for **1** and **10** in chloroform are shown in Figure 3. The integrated absorbance of **1** is more than twice



**Figure 3.** UV/vis spectra of **1** and **10** in chloroform at room temperature ( $[C] = 1 \times 10^{-5}$  M). (Insets) HOMOs for **1** and **10** at the B3LYP/6-31G\*\* level of theory.

that of **10**. Compound **1** has  $\pi$ -electron delocalization including both helical distortion and possible conjugation through the sulfur atoms with a maximum absorption peak at 288 nm and a low shoulder peak at 355 nm. The short conjugation gives an absorption peak at 268 nm for **10**. The bathochromic shift for **1** is rather substantial, considering that **1** and **10** possess molecular connectivities of homologous cross-conjugated  $\pi$ -systems. The optical band gap ( $E_g$ ) of 2.7 eV for **1** and 3.54 eV for **10** were obtained by extrapolating the long-wavelength absorption edges,  $\lambda_{\text{onset}}$  ( $E_g = 1240/\lambda_{\text{onset}}$  eV), respectively.

In order to further understand these absorption properties, the theoretical calculations of **1** and **10** with density functional theory (DFT) method at the B3LYP/6-31G\*\* level have been carried out (Supporting Information). Table 1 lists the electronic absorption spectral data of **1** and **10**. It is clear that the maximum absorption peak of **1** mainly arises from the excitation from H to L+1, and the maximum absorption peak of **10** originates from the excitation from H-1 to L+1. From both

**Table 1.** Electronic Absorption Spectra of **1** and **10** Calculated by the DFT Method at the TDDFT//B3LYP/6-31G\*\* Level Related to the Strongest UV/Vis Absorptions Observed Experimentally

compound	electronic transition	wavelengths <sup>a</sup> (nm)	<i>f</i>	main configurations <sup>b</sup>	
<b>1</b>	S <sub>0</sub> →S <sub>1</sub>	297	0.0110	H→L	0.51
	S <sub>0</sub> →S <sub>2</sub>	292 (288) <sup>c</sup>	0.3809	H→L+1	0.51
<b>10</b>	S <sub>0</sub> →S <sub>1</sub>	308	0.1496	H→L	0.67
	S <sub>0</sub> →S <sub>2</sub>	295	0.0533	H-1→L	0.58
	S <sub>0</sub> →S <sub>3</sub>	286 (268) <sup>c</sup>	0.2984	H-1→L+1	0.60

<sup>a</sup>Calculated in chloroform. <sup>b</sup>HOMO and LUMO are abbreviated as H and L, respectively. <sup>c</sup>Data in chloroform from experiment.

theoretical calculations and experimental results, the bathochromic shift in absorption spectrum of **1** indicates that the increased thiophene units enhance the  $\pi$  conjugation in the backbone resulting in narrowing of the optical band gap. Compared with the UV/vis properties of the other two annulated oligothiophenes, **4** and **6**, reported in the literature, **1** shows bathochromic shift compared to **4** peaked at 267 nm,<sup>6b</sup> and hypsochromic shift compared to **6** peaked at 375 and 396 nm,<sup>15</sup> respectively. Interestingly, the absorption properties of these three [7]thienoacenes, **1**, **4** and **6**, are distinctly affected by their molecular configurations, which implies that the conjugated extent of bull's horn-shaped **1** is larger than that of helical **4** and lower than that of linear **6**.

Cyclic voltammetry of **1** gives two reversible waves at  $E_1^\circ = +0.73$  and  $E_2^\circ = +1.14$  V (vs Fc/Fc<sup>+</sup>, see Supporting Information), most likely corresponding to oxidation to the radical cation and dication,<sup>5b</sup> respectively. Its highest occupied molecular orbital (HOMO) energy level is estimated as -5.53 eV based on the oxidation onset referred to the Fc/Fc<sup>+</sup> couple. The HOMO level of **1** is lower than that of **6** (HOMO at -5.36 eV,  $E_1^\circ = +0.56$  V vs Fc/Fc<sup>+</sup>),<sup>15b</sup> which implies that **1** has better stability than **6**. From the frontier molecular orbital in **1** as shown in the inset in Figure 3, all the sulfur atoms have contributions to HOMO, while the sulfur atoms have no contributions to HOMO for **6**.<sup>15</sup> Thus, it can be concluded that the combination mode of thiophene units in the annulated oligothiophenes not only has a distinct effect on the absorption properties but also plays an important role on the energy level of HOMO and its stability.

In summary, a novel bull's horn-shaped [7]thienoacene, **1**, has been effectively developed based on **2** as a building block. This work provides a new and novel member in the family of oligothiophenes. According to the experimental results and theoretical calculations, it was found that the combination mode of thiophene units plays an important role on molecular configuration and its physicochemical properties. From the observation of both strong S...C and S...S interactions in solid and its quasi-planarity, we believe that **1** may show high performance with good environmental stability as a semiconductor in organic electronics.<sup>13</sup>

## EXPERIMENTAL SECTION

### Synthesis of Dithieno[2,3-*b*:2',3'-*d'*]thiophene (**2**, Route A).

To a solution of **7** (1.12 g, 4.6 mmol) in anhydrous Et<sub>2</sub>O (150 mL), *n*-BuLi (2.35 M, 4.01 mL, 2.05 equiv) was added dropwise at -78 °C. After keeping at -78 °C for 2 h, anhydrous (PhSO<sub>2</sub>)<sub>2</sub>S (1.52 g, 4.83 mmol, 1.05 equiv) was added, then the reaction mixture was warmed slowly to ambient temperature overnight. The reaction mixture was quenched with H<sub>2</sub>O (30 mL), extracted with Et<sub>2</sub>O (2 × 40 mL), and then washed with H<sub>2</sub>O (2 × 40 mL). After drying over MgSO<sub>4</sub>, the solvent was removed in vacuo. The residue was purified by column chromatography on silica gel with PE (60–90 °C) as eluent to yield **2** (0.46 g, 50%) as a white solid. From the other reaction on a 2.16 g scale of **7**, 0.93 g (54%) of **2** was obtained. Mp: 52–53 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.40 (d, *J* = 5.2 Hz), 7.36 (d, *J* = 5.2 Hz), 7.32 (d, *J* = 5.2 Hz), 7.27 (d, *J* = 5.2 Hz). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  141.6, 139.2, 137.7, 130.9, 128.2, 125.5, 120.4, 118.6.

### Synthesis of Dithieno[2,3-*b*:2',3'-*d'*]thiophene (**2**, Route B).

To a solution of **8** (3.39 g, 10.4 mmol) in anhydrous Et<sub>2</sub>O (150 mL), *t*-BuLi (1.85 M, 23 mL, 4.10 equiv) was added dropwise at -78 °C. After keeping at -78 °C for 2 h, anhydrous (PhSO<sub>2</sub>)<sub>2</sub>S (3.41 g, 10.9 mmol, 1.05 equiv) was added, then the reaction mixture was warmed slowly to ambient temperature overnight. The workup is the same to that in Route A, and 1.19 g (53%) of **2** was obtained. From two other



reactions on a 3.61 and 4.05 g scale of **8**, 2.07 g (55%) and 2.10 g (50%) of **2** were obtained, respectively.

**Synthesis of 3-Bromo-2-(2-bromo-5-(trimethylsilyl)-thiophen-3-yl)-5-(trimethylsilyl)thiophene (9).** *n*-BuLi (2.32 M, 15.0 mL, 46.6 mmol, 2.2 equiv) was added dropwise to diisopropylamine (7.9 mL, 55.9 mmol, 2.64 equiv) in anhydrous Et<sub>2</sub>O (20 mL) at 0 °C. After keeping at 0 °C for 0.5 h, the prepared LDA solution was transferred by syringe into a solution of **8** (6.87 g, 21.2 mmol) with anhydrous Et<sub>2</sub>O. After keeping at 0 °C for 2 h, the reaction mixture was cooled to −78 °C, then trimethylchlorosilane (13.4 mL, 84.8 mmol, 4.0 equiv) was added dropwise. The reaction was warmed slowly to ambient temperature overnight. The workup is the same to that in making **2**, 8.94 g (90.1%) of **9** was obtained as a white solid. From two other reactions on 5.44 and 6.79 g scale of **8**, 7.41 g (94.2%) and 8.77 g (89.3%) of **9** were obtained, respectively; Mp: 67–68 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.18 (s, 1H), 7.15 (s, 1H), 0.34 (s, 9H), 0.32 (s, 9H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 141.7, 141.5, 136.8, 136.2, 136.0, 134.4, 117.0, 111.4, 0.3, 0.4. IR (KBr): 2962.3, 3011.2 (C–H) cm<sup>−1</sup>. MS (EI, 70 eV): *m/z* = 467.95 (70) [M<sup>+</sup>], 452.92 (100) [M<sup>+</sup> − 15]. HRMS (EI<sup>+</sup> 70 eV) *m/z* calcd for [C<sub>14</sub>H<sub>20</sub>Si<sub>2</sub>S<sub>2</sub>Br<sub>2</sub>] 465.8912, found 465.8909.

**Synthesis of 2,5-Bis(trimethylsilyl)dithieno[2,3-*b*:2',3'-*d*]thiophene (10, Route C).** To a solution of **9** (2.00 g, 4.1 mmol) in anhydrous Et<sub>2</sub>O (150 mL), *n*-BuLi (2.50 M, 3.6 mL, 2.2 equiv) was added dropwise at −78 °C. After keeping at −78 °C for 2 h, anhydrous (PhSO<sub>2</sub>)<sub>2</sub>S (1.35 g, 4.3 mmol, 1.05 equiv) was added, then the reaction mixture was warmed slowly to ambient temperature overnight. The workup is the same to that in making **2**, 0.79 g (58%) of **10** was obtained as a white solid. From two other reactions on 1.00 and 3.00 g scale of **9**, 0.43 g (60%) and 1.20 g (55%) of **10** were obtained, respectively. Mp: 82–83 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.41 (s, 1H), 7.34 (s, 1H), 0.38 (d, *J* = 1.2 Hz, 18H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 144.0, 144.7, 143.8, 141.1, 139.3, 135.2, 126.3, 124.6, 0.1. IR (KBr): 2953.3, 2896.2, 2855.5 (C–H) cm<sup>−1</sup>. HRMS (EI<sup>+</sup> 70 eV) *m/z* calcd for [C<sub>14</sub>H<sub>20</sub>Si<sub>2</sub>S<sub>3</sub>] 340.0266, found 340.0268.

**Synthesis of 2,5-Bis(trimethylsilyl)dithieno[2,3-*b*:2',3'-*d*]thiophene (10) from 2.** *n*-BuLi (2.38 M in hexane, 0.92 mL, 2.02 mmol, 2.2 equiv) was added dropwise to diisopropylamine (0.42 mL, 3.03 mmol, 3.3 equiv) in Et<sub>2</sub>O (20 mL) at 0 °C. After keeping at 0 °C for 0.5 h, the prepared LDA solution was transferred by syringe into a solution of **2** (0.20 g, 1.01 mmol) with anhydrous Et<sub>2</sub>O. After keeping at 0 °C for 15 min, the reaction mixture was cooled to −78 °C, then trimethylchlorosilane (0.50 mL, 4.0 equiv) was added dropwise. The reaction warmed slowly to ambient temperature overnight. The workup is the same to that in making **2**, 0.32 g (92%) of **10** was obtained as a white solid. From two other reactions on 0.62 and 0.87 g scale of **2**, 0.97 g (93%) and 1.41 g (94.1%) of **10** were obtained, respectively.

**Synthesis of 5-Bromo-2-trimethylsilyl-dithieno[2,3-*b*:2',3'-*d*]thiophene (11).** Compound **10** (0.60 g, 1.76 mmol) was dissolved in 120 mL CHCl<sub>3</sub>–HOAc (*v/v* = 8:1), NBS (0.33 g, 1.85 mmol, 1.05 equiv) was added in small portions. The reaction mixture was stirred at room temperature for 2 h, then quenched with 40 mL water. After extracting with chloroform (3 × 20 mL), washing with saturated NaHCO<sub>3</sub> solution (20 mL) and water (20 mL), the organic layer was dried over anhydrous MgSO<sub>4</sub>, then the solvent was removed under vacuum. The residue was purified by column chromatography on silica gel with PE (60–90 °C) as eluent to yield **11** (0.59 g, 92.2%) as a white solid. From two other reactions on 1.28 and 1.15 g scales of **10**, 1.19 g (93.4%) and 1.12 g (95.3%) of **11** were obtained, respectively. Mp: 84–86 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.35 (s, 1H), 7.24 (s, 1H), 0.38 (s, 9H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 145.8, 148.5, 140.2, 139.7, 130.5, 123.4, 123.1, 111.5, −0.06. IR (KBr): 2854.5, 2960.3 (C–H) cm<sup>−1</sup>. HRMS (EI<sup>+</sup> 70 eV) *m/z* calcd for [C<sub>11</sub>H<sub>11</sub>SiS<sub>3</sub>Br] 345.8976, found 345.8977.

**Synthesis of 6-Bromo-2-trimethylsilyl-dithieno[2,3-*b*:3',2'-*d*]thiophene (12).** *n*-BuLi (2.46 M in hexane, 0.56 mL, 1.37 mmol, 1.5 equiv) was added dropwise to diisopropylamine (0.24 mL, 1.69 mmol, 1.8 equiv) in THF (7 mL) at 0 °C. After keeping 15

min at 0 °C, the prepared LDA solution was transferred by syringe into a solution of **11** (0.3178 g, 0.91 mmol) in THF (40 mL) at 0 °C. After 3 h at 0 °C, methanol (excess) was added to quench the reaction. The workup is the same to that in making **11**, 0.30 g (95%) of **12** was obtained as a white solid. From two other reactions on the 1.07 and 1.27 g scales of **11**, 1.00 g (93.6%) and 1.21 g (95.7%) of **12** were obtained, respectively. Mp: 67–69 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.39 (s, 1H), 7.24 (s, 1H), 0.38 (s, 9H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 145.7, 144.2, 142.9, 140.01, 129.8, 124.5, 121.7, 102.9. IR (KBr): 2847.6, 2957.6, 2933.2 (C–H) cm<sup>−1</sup>. HRMS (EI<sup>+</sup> 70 eV) *m/z* calcd for [C<sub>11</sub>H<sub>11</sub>SiS<sub>3</sub>Br] 345.8976, found 345.8978.

**Synthesis of 2,2'-Di(trimethylsilyl)-6,6'-bis-dithieno[2,3-*b*:2',3'-*d*]thiophene (13).** Compound **12** (0.04 g, 0.1 mmol, 1.0 equiv), K<sub>3</sub>PO<sub>4</sub> (0.05 g, 0.24 mmol, 2.1 equiv) and Pd[P<sup>*t*</sup>Bu<sub>3</sub>]<sub>2</sub> (0.034 g, 0.067 mmol, 0.6 equiv) in toluene (3 mL) was heated at 90 °C in a Schlenk vessel. After keeping 5 h at 90 °C, the reaction mixture was cooled to ambient temperature. The usual aqueous workup with ethyl ether was carried out. The white product **13** (0.017 g, 57.2%) was obtained by column chromatography on silica gel with petrol ether (60–90 °C) as eluent. From two other reactions on 0.0973 and 0.1320 g scales of **12**, 0.0483 g (64.2%) and 0.0652 g (67.4%) of **13** were obtained, respectively. Mp: 183–184 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.67 (s, 2H), 7.46 (s, 2H), 0.39 (s, 18H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 145.7, 144.0, 140.3, 139.2, 130.5, 128.8, 124.7, 120.9, 0.04. IR (KBr): 2950.1, 2884.3 (C–H) cm<sup>−1</sup>. HRMS (MALDI) *m/z* calcd for [C<sub>22</sub>H<sub>22</sub>Si<sub>2</sub>S<sub>6</sub>] 533.95788, found 533.9578.

**Synthesis of Bull's Horn-Shaped Oligothienoacene (1).** *n*-BuLi (0.9419 M in hexane, 0.21 mL, 0.2 mmol, 2.3 equiv) was added dropwise to diisopropylamine (0.04 mL, 0.3 mmol, 3.5 equiv) in Et<sub>2</sub>O (5 mL) at 0 °C. After 1.5 h at 0 °C, the prepared LDA solution was transferred by syringe into a solution of **13** (0.046 g, 0.087 mmol) in Et<sub>2</sub>O (20 mL) at 0 °C. After 4 h at 0 °C, dry (PhSO<sub>2</sub>)<sub>2</sub>S (0.1894 g, 0.60 mmol, 1.05 equiv) was added at −78 °C, then the reaction mixture was kept at −78 °C for 3 h and then warmed up slowly to ambient temperature overnight. The workup is the same to that in making **2**, and 0.0193 g (40%) of **1** was obtained as a white solid. From two other reactions on 0.063 g and 0.11 g scales of **13**, 0.03 g (43%) and 0.05 g (45%) of **1** were obtained, respectively. Mp 259–260 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 7.66 (s, 2 H), 0.25 (s, 18 H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): δ 145.0, 143.5, 141.1, 140.1, 139.6, 130.4, 129.5, 128.1, 0.0. IR (KBr): 2952.6, 2892.8 (C–H) cm<sup>−1</sup>. HRMS (MALDI) *m/z* calcd for [C<sub>22</sub>H<sub>20</sub>Si<sub>2</sub>S<sub>7</sub>] 563.9148, found 563.9151.

## ■ ASSOCIATED CONTENT

### ⑤ Supporting Information

Experimental details, NMR, HRMS, CV, IR spectra and X-ray crystallographic data. The crystallographic data of **1** and **12** in CIF were deposited with CCDC 920144 and 920145, respectively. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## ■ AUTHOR INFORMATION

### Corresponding Author

\*E-mail: [jwshi@henu.edu.cn](mailto:jwshi@henu.edu.cn), [yanxiang@ciac.jl.cn](mailto:yanxiang@ciac.jl.cn), [hwang@henu.edu.cn](mailto:hwang@henu.edu.cn).

### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

We thank Professor Hegui Gong from Shanghai University for helpful discussion, and Mr. Pengtao Ma for crystal measurements. This research was supported by NSFC (21270255, 51273055, 20972041, 50803015) and Programs for SRFDP (20124103110004) and PCS IRT1126.

## ■ REFERENCES

- (1) (a) Xu, B.; Fichou, D.; Horowitz, G.; Garnier, F. *Adv. Mater.* **1991**, *3*, 150. (b) Katz, H. E. *J. Mater. Chem.* **1997**, *7*, 369. (c) Caras-Quintero, D.; Bauerle, P. *Chem. Commun.* **2004**, 926. (d) Heeney, M.; Bailey, C.; Genevicius, K.; Shkunov, M.; Sparrowe, D.; Tierney, S.; McCulloch, I. J. *Am. Chem. Soc.* **2005**, *127*, 1078.
- (2) Uchiyama, K.; Akimichi, H.; Hotta, S.; Noge, H.; Sakaki, H. *Synth. Met.* **1994**, *63*, 57.
- (3) DiCésare, N.; Belletête, M.; Donat-Bouillud, A.; Leclerc, M.; Durocher, G. *Macromolecules* **1998**, *31*, 6289.
- (4) (a) Liu, Y.; Sun, X.; Di, C.; Liu, Y.; Du, C.; Lu, K.; Ye, S.; Yu, G. *Chem.-Asian J.* **2010**, *5*, 1550. (b) Zhang, X.; Cote, A. P.; Matzger, A. J. *Am. Chem. Soc.* **2005**, *127*, 10502. (c) Zhang, L.; Tan, L.; Wang, Z.; Hu, W.; Zhu, D. *Chem. Mater.* **2009**, *21*, 1993. (d) Liu, Y.; Wang, Y.; Wu, W.; Liu, Y.; Xi, H.; Wang, L.; Qiu, W.; Lu, K.; Du, C.; Yu, G. *Adv. Funct. Mater.* **2009**, *19*, 772.
- (5) (a) Rajca, A.; Wang, H.; Pink, M.; Rajca, S. *Angew. Chem., Int. Ed.* **2000**, *39*, 4481. (b) Rajca, A.; Miyasaka, M.; Pink, M.; Wang, H.; Rajca, S. *J. Am. Chem. Soc.* **2004**, *126*, 15211. (c) Miyasaka, M.; Rajca, A.; Pink, M.; Rajca, S. *J. Am. Chem. Soc.* **2005**, *127*, 13806. (d) Miyasaka, M.; Pink, M.; Rajca, S.; Rajca, A. *Angew. Chem., Int. Ed.* **2009**, *48*, 5954.
- (6) (a) Wang, Z.; Shi, J.; Wang, J.; Li, C.; Tian, X.; Cheng, Y.; Wang, H. *Org. Lett.* **2010**, *12*, 456. (b) Li, C.; Shi, J.; Xu, L.; Wang, Y.; Cheng, Y.; Wang, H. *J. Org. Chem.* **2009**, *74*, 408.
- (7) (a) Zmolek, P. B.; Sohn, H.; Gantzel, P. K.; Trogler, W. C. *J. Am. Chem. Soc.* **2001**, *123*, 1199. (b) Frapper, G.; Saillard, J.-Y. *J. Am. Chem. Soc.* **2000**, *122*, 5367.
- (8) (a) Bromley, S. T.; Mas-Torrent, M.; Hadley, P.; Rovira, C. *J. Am. Chem. Soc.* **2004**, *126*, 6544. (b) Xue, J.; Forrest, S. R. *Appl. Phys. Lett.* **2001**, *79*, 3714.
- (9) Shi, J.; Li, Y.; Jia, M.; Xu, L.; Wang, H. *J. Mater. Chem.* **2011**, *8*, 17612.
- (10) (a) De Jong, F.; Janssen, M. J. *J. Org. Chem.* **1971**, *36*, 1998. (b) Archer, W. J.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1982**, *3*, 301. (c) Šafarik, J.; Koružnjak, J.; Karminski-Zamola, G. *Molecules* **2005**, *10*, 279.
- (11) (a) Schnürch, M.; Spina, M.; Khan, A. F.; Mihovilovic, M. D.; Stanetty, P. *Chem. Soc. Rev.* **2007**, *36*, 1046. (b) Nenajdenko, V. G.; Gribkov, D. V.; Sumerin, V. V. *Synthesis* **2003**, 124. (c) He, M.; Zhang, F. *J. Org. Chem.* **2007**, *72*, 442.
- (12) (a) Tan, L.; Zhang, L.; Jiang, X.; Yang, X.; Wang, L.; Wang, Z.; Li, L.; Hu, W.; Shuai, Z.; Li, L.; Zhu, D. *Adv. Funct. Mater.* **2009**, *19*, 272. (b) Qi, T.; Guo, Y.; Liu, Y.; Xi, H.; Zhang, H.; Gao, X.; Liu, Y.; Lu, K.; Du, C.; Yu, G.; Zhu, D. *Chem. Commun.* **2008**, 6227.
- (13) (a) Murphy, A. R.; Fréchet, J. M. J. *Chem. Rev.* **2007**, *107*, 1066. (b) Reese, C.; Bao, Z. *Mater. Today* **2007**, *10*, 20. (c) Shao, W.; Dong, H.; Jiang, L.; Hu, W. *Chem. Sci.* **2011**, *2*, 590.
- (14) Xiao, K.; Liu, Y. Q.; Qi, T.; Zhang, W.; Wang, F.; Gao, J. H.; Qiu, W. F.; Ma, Y. Q.; Cui, G. L.; Chen, S. Y.; Zhan, X. W.; Yu, G.; Qin, J. G.; Hu, W. P.; Zhu, D. B. *J. Am. Chem. Soc.* **2005**, *127*, 13281.
- (15) (a) Osuna, R. M.; Zhang, X.; Matzger, A. J.; Hernández, V.; López Navarrete, J. T. *J. Phys. Chem. A* **2006**, *110*, 5058. (b) Arago, J.; Viruela, P. M.; Oti, E.; Osuna, R. M.; Vercelli, B.; Zotti, G.; Hernandez, V.; Navarrete, J. T. L.; Henssler, J. T.; Matzger, A. J.; Suzuki, Y.; Yamaguchi, S. *Chem.—Eur. J.* **2010**, *16*, 5481.

## ■ NOTE ADDED AFTER ASAP PUBLICATION

This paper was published ASAP on June 3, 2013. Manuscript title and main text were updated. The revised paper was reposted on June 5, 2013.