

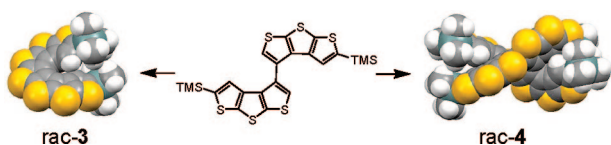
Syntheses and Crystal Structures of Fused Thiophenes: [7]Helicene and Double Helicene, a D<sub>2</sub>-Symmetric Dimer of 3,3'-Bis(dithieno[2,3-*b*:3',2'-*d*]thiophene)

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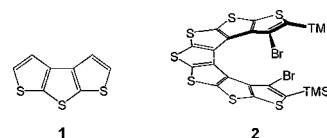
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The efficient synthesis of (TMS)<sub>2</sub>-[7]helicene (**rac-3**) and double helicene, a D<sub>2</sub>-symmetric dimer of 3,3'-bis(dithieno[2,3-*b*:3',2'-*d*]thiophene) (**rac-4**) was developed. The crystal structures of **3** and **4** show both strong intermolecular  $\pi$ - $\pi$  interactions and S...S interactions. UV/vis spectra reveal that both **3** and **4** show significant  $\pi$ -electron delocalization.

In carbohelicene chemistry, *ortho*-fused aromatic compounds show aesthetic and miraculous structures, which have attracted organic chemists for many years. Recently, [*n*]helicenes display extraordinary optical and electronic properties in the field of organic functional materials<sup>1,2</sup> and their synthetic methods have also been developed.<sup>3,4</sup> As an important part of heterohelicenes,

annelated oligothiophenes have received more and more attentions recently, because such kind of materials provide significantly improved properties in organic electronics.<sup>5</sup> Dithieno[2,3-*b*:3',2'-*d*]thiophene (**1**), as one of the six possible isomeric dithienothiophenes has attracted considerable attention in preparation,<sup>6</sup> has been used as the building blocks for higher homologues of helicenes. The series work on the synthesis of carbon-sulfur helicenes has been reported by Rajca,<sup>7</sup> and a few reviews on the preparation of such helicenes are also published.<sup>7-10</sup> The first and representative member in this family is tetrafunctionalized [7]helicene (**2**), which containing two Br and two TMS groups was reported in 2000.<sup>7a</sup> Low yield (1.7%) in making **2** with 3,4-dibromothiophene as starting material limits its application in materials science and the synthesis of higher homologues of helicenes.



Herein, we describe the efficient synthesis of (TMS)<sub>2</sub>-[7]helicene (**rac-3**) and double helicene, a D<sub>2</sub>-symmetric dimer of 3,3'-bis(dithieno[2,3-*b*:3',2'-*d*]thiophene) (**rac-4**), and their crystal structures. The synthetic route to them is shown in Scheme 1. The starting material is 2,5-bis-trimethylsilyl-dithieno[2,3-*b*:3',2'-*d*]thiophene (**5**). The efficient synthesis of **5** (ca. 45% total yield with 3-bromothiophene as starting material) was reported in our previous work.<sup>6b</sup>

**Syntheses of 3 and 4.** 5-Bromo-2-trimethylsilyl-dithieno[2,3-*b*:3',2'-*d*]thiophene (**6**) is obtained in 89–94% yield via the treatment of NBS directly with **5** in a mixture solvent (HOAc-CHCl<sub>3</sub>). At this step, one of two TMS groups in **5** is removed and bromination is acted in situ at same time. The next step is bromine dance reaction,<sup>6a,12</sup> which is the key step in the synthetic route to **3** and **4**. The high efficient bromine

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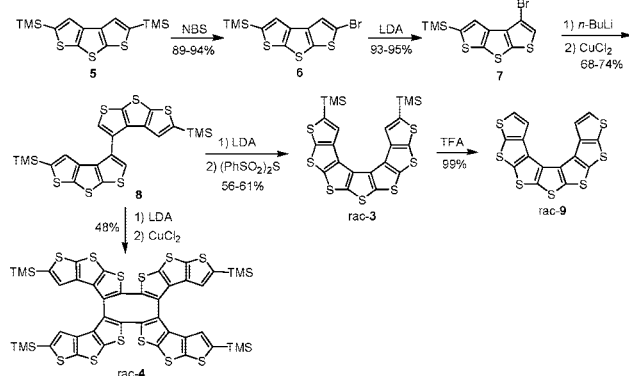
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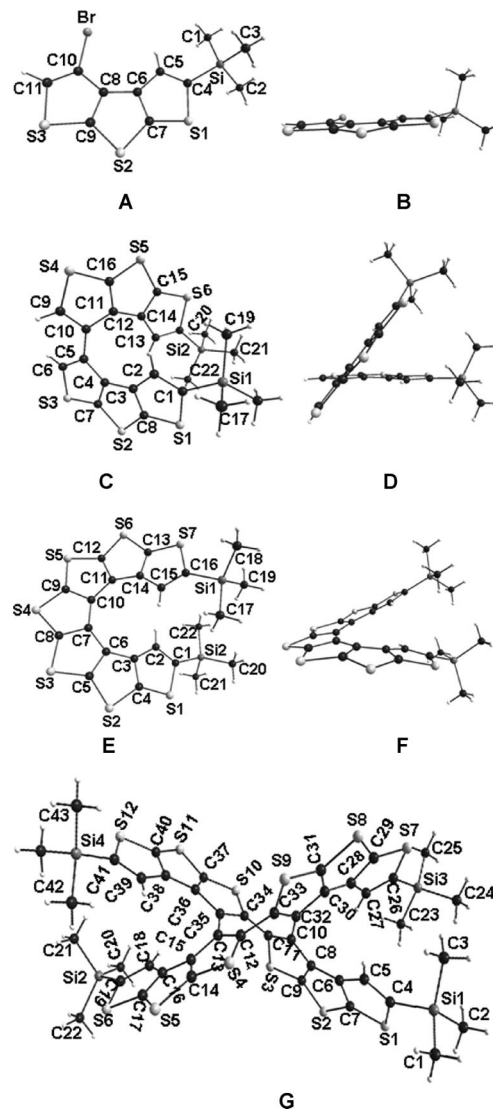
SCHEME 1. Synthetic Route to rac-3 and rac-4<sup>a</sup>

<sup>a</sup> NBS = *N*-bromosuccinimide, LDA = lithium diisopropylamide, TMS = trimethylsilyl, TFA = trifluoroacetic acid.

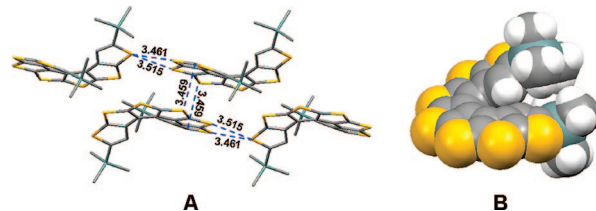
dance reaction is observed to **6** by using LDA in THF at 0 °C to generate 4-bromo-2-trimethylsilylthiophene (**7**) in 93–95% yield. Following the Li/Br exchange on **7**, the resultant aryllithium species is oxidized with CuCl<sub>2</sub> to afford 5,5'-di(trimethylsilyl)-3,3'-bis(dithieno[2,3-*b*:3',2'-*d*]thiophene) (**8**) in 68–74% yield. LDA-mediated lithiation is introduced to remove the protons on α positions in **8** to give dilithiated **8**. Dilithiated **8** is an amazing intermediate. On the one hand, the reaction of dilithiated **8** with bis(phenylsulfonyl)sulfide gives the annelated product [7]helicene: rac-**3** in 56–61% yield. On the other hand, dilithiated **8** could be oxidized with CuCl<sub>2</sub> to generate rac-**4** in 48% yield. The method in making **4** is similar to that of tetra[2,3-thienylene]s in Marsella's work<sup>13,14</sup> and our previous work.<sup>6b</sup> **4** is a novel D<sub>2</sub>-symmetric dimer of 3,3'-bis(dithieno[2,3-*b*:3',2'-*d*]thiophene), and a novel eight membered cyclic compound. With TFA to remove the TMS groups in rac-**3**, almost quantitative yield of rac-**9** could be generated. Therefore, compounds rac-**3** and rac-**4** are obtained in ca. 36% and ca. 29% isolated yields, respectively in four steps with **5** as starting material. From 3-bromothiophene as starting material, the overall yields for rac-**3** and rac-**4** could be ca. 16% and ca. 13% isolated yields, respectively in eight steps. <sup>1</sup>H and <sup>13</sup>C NMR spectra show the expected 2-fold symmetry for **3**, **8**, **9** and 4-fold symmetry for **4** (see Supporting Information). **6** and **7** are isomers with significant difference in both <sup>1</sup>H and <sup>13</sup>C NMR spectra.

**Crystal Analyses for 3 and 4.** The structures of **7**, **8**, rac-**3** and rac-**4** are all confirmed by Single-crystal X-ray analysis (Figure 1). In **7**, all the thiophene rings are approximately coplanar. The C10–C8–C6–C5 torsion angle is 0.9°. In **8**, two moieties of dithieno[2,3-*b*:3',2'-*d*]thiophene are nonplanar, the C6–C5–C10–C9 torsion is 50.6° and the H6–C6–C9–H9 torsion is 65.6°, but each moiety is approximately coplanar with torsions of 2.6° (C2–C3–C4–C5) and 4.2° (C10–C11–C12–C13), respectively. The dihedral angle between the two planes of moieties is 52.0° and the distance between H2A···H13A is 3.25 Å.

With the formation of the middle thiophene ring from **8** to **3**, the molecule of **3** is compressed with a helical structure (Figure 2B). The distance between H2A···H15A is changed to 2.36 Å and the two H atoms are pointing away from each



**FIGURE 1.** Molecular structure and conformation for **3**, **4**, **7** and **8**. (A) top view for **7**, (B) side view for **7**, (C) top view for **8**, (D) side view for **8**, (E) top view for **3**, (F) side view for **3** and (G) side view for **4**.

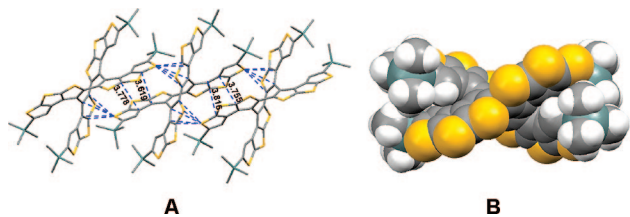


**FIGURE 2.** π-π interaction and S-S interaction in crystal packing of rac-**3**. (A) crystal packing; (B) spacefill mode.

other (Figure 1). The repulsion of the facing terminal thiophene rings, causes an interplanar angle between the terminal thiophene rings, 43.0°, which is smaller than 54.1° of **2**,<sup>7a</sup> due to the steric hindrance decreased from the two Br atoms to two H atoms. The angles between the least-squares planes of neighboring thiophene rings are between 5.0° and 9.6°. With the middle thiophene ring as a reference, the inner (C15, C14, C11, C10, C7, C6, C3, C2) helix climbs 2.18 Å and turns in-plane by 266°, and the analogous values for **2** are 2.92 Å and 260°,<sup>7a</sup> respectively.

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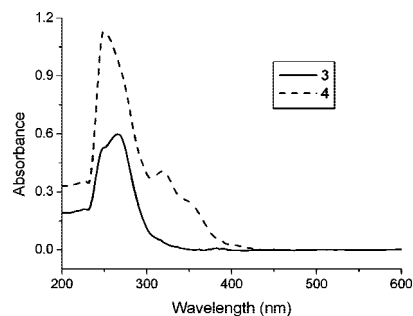
**FIGURE 3.**  $\pi$ - $\pi$  interaction and S- $\pi$  interaction in crystal packing of macrocyclic dimer, rac-**4**. (A) crystal packing; (B) spacefill mode.

Crystal packing of rac-**3** (Figure 2A) reveals exist of  $\pi$ - $\pi$  interaction between (*R*)-**3** and (*S*)-**3**, the distances of C8...C12, C9...C11, C9...C12, S4...C13, S5...C7 and S5...C10 are 3.776, 3.666, 3.829, 3.459, 3.855 and 3.751 Å, respectively. The interactions of S atoms include the interaction of neighboring enantiomers (the distance of S1...S5 and S1...S6 are 3.515 and 3.461 Å, respectively) and interaction between (*R*)-**3** and (*S*)-**3** (the distance of S3...S6 and S4...S6 are 3.902 and 3.666 Å, respectively).

The structure of **4** is a macrocyclic dimer of 3,3'-bis-(dithieno[2,3-*b*:3',2'-*d*]thiophene) possessed approximately a  $D_2$  point group of symmetry (Figure 1).<sup>15</sup> The central cyclooctatetraene ring has a 'saddle' form with an average dihedral angle of 53.9°, smaller than that in tetra-*o*-phenylene derivatives<sup>15a,16</sup> but bigger than that in tetra[2,3-thienylene]-(TMS)<sub>4</sub>.<sup>6b</sup> In rac-**4**, the sterically hindered biaryls correspond to bis(dithieno[2,3-*b*:3',2'-*d*]thiophene) moieties, and each of the moieties has a chiral axis with opposite configurations. Each of the four dithieno[2,3-*b*:3',2'-*d*]thiophenes is approximately coplanar, torsions are 2.66° (C5-C6-C8-C10), 3.07° (C13-C15-C16-C18), 7.05° (C27-C28-C30-C32) and 3.49° (C35-C36-C38-C39), respectively. The distances of H5A...H27A and H18A...H39A are 3.311 and 3.499 Å, respectively. Therefore, **4** shows somewhat of double-helix like configuration, in which two [7]helicene-like structures linked together pointing away from each other (Figure 1). On the other hand, two helix of the sulfur-containing the edges of **4** embraced together to form the double helix (see spacefill mode in Figure 3B).

Crystal packing of rac-**4** reveals two types of short contacts (Figure 3A). The first one is  $\pi$ - $\pi$  interaction between (*R*)-**4** and (*S*)-**4**, the distances of C14...C16, C14...C18, C15...C17, C28...C31, C29...C30 are 3.778, 3.719, 3.619, 3.775 and 3.816 Å, respectively. The second one is from the S atoms on terminal thiophene rings interact with the  $\pi$ -system of the neighboring **4**. Two arms in **4** give two S atoms and another two arms provide two interacted  $\pi$ -systems. For example, the distances of S7...S10, S7...C34, S7...C35, S7...C36 and S7...C37 are 3.575, 3.552, 3.466, 3.333 and 3.348 Å, respectively.

**UV/Vis Spectra for 3 and 4.** The UV/vis spectra for **3** and **4** in chloroform are shown in Figure 4. The integrated absorbance in **4** is approximately twice that of **3**. **3** has  $\pi$ -electron delocalization including both helical distortion and possible conjugation through the sulfur atoms with maximum absorption peak at 267 nm. **4** has four approximately planar dithieno[2,3-*b*:3',2'-*d*]thiophenes, which are cross-conjugated together with two absorption peaks at 247, 349 nm and a



**FIGURE 4.** UV-vis spectra of **3** and **4** in chloroform at room temperature ( $[C] = 1 \times 10^{-5}$  M).

shoulder peak at 354 nm. The bathochromic shift for **4** is rather substantial, due to its increased  $\pi$ -electron delocalization.

In summary, the synthesis of novel fused thiophenes: racemic carbon-sulfur helicene **3** and racemic  $D_2$ -symmetric dimer **4** was efficiently developed. The crystal structures of **3** and **4** show both strong  $\pi$ - $\pi$  interactions and S...S interactions. Such short intermolecular contacts (especially, S...S) are known to facilitate high carrier mobilities in organic semiconductors.<sup>7d,17-20</sup> Therefore, **3** and **4** might be a novel compound with special properties in organic functional materials. Both module **3** and **4** are chiral, so the enantiomer of **3** could be used for making higher carbon-sulfur helicene.<sup>6a</sup> Both enantiomers of **3** and **4** might be used as chiral catalysts.<sup>21</sup> The more work about **3** and **4** are in progress.

## Experimental Section

**5-Bromo-2-trimethylsilylanyl-dithieno[2,3-*b*:3',2'-*d*]thiophene (6).** **5** (0.5000 g, 1.47 mmol) was dissolved in 30 mL  $\text{CHCl}_3$ , NBS (0.3135 g, 1.76 mmol, 1.20 equiv) was dissolved in 18 mL  $\text{HOAc-CHCl}_3$  ( $v/v = 4:5$ ) and added dropwise under good stirring at ambient temperature. After stirring for 2 h, the reaction mixture was quenched with 60 mL water and extracted with chloroform ( $3 \times 15$  mL), then washed with saturated  $\text{NaHCO}_3$  (20 mL) and water (20 mL). The organic layer was dried over anhydrous  $\text{MgSO}_4$ . After the solvent was removed under vacuum, the residue was purified by recrystallization from  $\text{CHCl}_3\text{-CH}_3\text{OH}$  to yield **6** (0.4550 g, 89.1%). From other two reactions on the 0.9826 and 1.9727 g scales of **5**, 0.9370 g (93.5%) and 1.8767 g (93.3%) of **6** were obtained, respectively. Mp 78–79 °C.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.40 (s, 1 H), 7.38 (s, 1H), 0.37 (s, 9 H),  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  144.9, 143.5, 140.3, 138.1, 136.8, 124.7, 122.1, 112.6, -0.1. IR (KBr): 2952.6, 2923.8, 2889.4, 2840.4 (C-H)  $\text{cm}^{-1}$ . MS (EI, 70 eV):  $m/z = 345.89$  (42) [ $\text{M}^+$ ], 330.86 (100) [ $\text{M}^+ - 15$ ].

**4-Bromo-2-trimethylsilylanyl-dithieno[2,3-*b*:3',2'-*d*]thiophene (7).** *n*-BuLi (2.186 M in hexane, 0.11 mL, 0.24 mmol, 1.5 equiv) was added dropwise to diisopropylamine (0.04 mL, 0.28 mmol, 1.8 equiv) in THF (5 mL) at 0 °C. After 1 h at 0 °C, the prepared LDA solution was transferred by syringe into a solution of **6** (0.0551 g, 0.16 mmol) in THF (10 mL) at -78 °C. After 10 h at -78 °C, methanol (excess) was added to quench the reaction. The reaction mixture was extracted with  $\text{CHCl}_3$  ( $3 \times 15$  mL) and washed with saturated NaCl (30 mL) and water (30 mL), and then dried over  $\text{MgSO}_4$ . After the removal of the solvent under vacuum, the residue

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was purified by column chromatography on silica gel with petrol ether (60–90 °C) as eluent to yield **7** (0.0523 g, 94.9%) as a white solid. From other two reactions on the 0.3436 and 1.8317 g scales of **6**, 0.3223 g (93.8%) and 1.7079 g (93.2%) of **7** were obtained, respectively. Mp 79–81 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 7.75 (s, 1 H), 7.28 (s, 1H), 0.39 (s, 9 H), <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): δ 144.8, 144.6, 139.7, 139.3, 136.4, 124.6, 123.7, 102.8, –0.1. IR (KBr): 2952.6, 2923.8, 2892.8, 2855.1 (C–H) cm<sup>–1</sup>. MS (EI, 70 eV): *m/z* = 345.88 (40) [M<sup>+</sup>], 330.85 (90) [M<sup>+</sup> – 15].

**5,5'-Di(trimethylsilyl)-3,3'-bis-dithieno[2,3-*b*:3',2'-*d*]thiophene (8).** To a solution of **7** (0.0992 g, 0.29 mmol) in dry ethyl ether (10 mL), *n*-BuLi (2.34 M, 0.13 mL, 0.29 mmol, 1.05 equiv) was added dropwise at –78 °C. After keeping at –78 °C for 3 h, dry CuCl<sub>2</sub> (0.1920 g, 1.43 mmol, 5.00 equiv) was added. The reaction mixture was kept at –78 °C for 3 h, then warmed up slowly to ambient temperature overnight. The reaction mixture was quenched with water, extracted with ethyl ether (3 × 20 mL). The organic layer was washed with water (3 × 25 mL) and then dried over MgSO<sub>4</sub>. The white product **8** (0.0563 g, 74.3%) was obtained by column chromatography on silica gel with petrol ether (60–90 °C) as eluent. From other reaction on the 0.6023 g scale of **7**, 0.3137 g (67.6%) of **8** was obtained. Mp 183–185 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 7.45 (s, 2 H), 6.79 (s, 2 H), 0.14 (s, 18 H), <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): δ 144.2, 143.5, 140.1, 139.9, 136.7, 128.7, 126.0, 124.8, –0.3. IR (KBr): 2950.7, 2890.9 (C–H) cm<sup>–1</sup>. HRMS (TOF MS EI<sup>+</sup>) *m/z* calcd for [C<sub>22</sub>H<sub>22</sub>Si<sub>2</sub>S<sub>6</sub>] 533.9584, found 533.9586.

**[7]Helicene: (rac-3).** *n*-BuLi (2.51 M in hexane, 0.50 mL, 1.26 mmol, 2.2 equiv) was added dropwise to diisopropylamine (0.22 mL, 1.58 mmol, 2.7 equiv) in Et<sub>2</sub>O (15 mL) at 0 °C. After 1.5 h at 0 °C, the prepared LDA solution was transferred by syringe into a solution of **8** (0.3071 g, 0.57 mmol) in Et<sub>2</sub>O (35 mL) at 0 °C. After 3 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 reaction mixture was quenched with water, extracted with ethyl ether (3 × 40 mL) and then washed with saturated NaCl (45 mL) and water (45 mL). After drying over MgSO<sub>4</sub>, the solvent was removed under vacuum. The residue was purified by column chromatography on silica gel with petrol ether (60–90 °C) as eluent to yield *rac*-**3** (0.1993 g, 61.4%) as a white solid. From other two reactions on the 0.3001 and 0.3028 g scales of **8**, 0.1849 g (58.4%) and 0.1780 g (55.6%) of *rac*-**3** were obtained, respectively. Mp

259–261 °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 (TOF MS EI<sup>+</sup>) *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.

**D<sub>2</sub>-Symmetric Dimer (rac-4).** *n*-BuLi (2.64 M in hexane, 0.19 mL, 5.14 mmol, 4.05 equiv) was added dropwise to diisopropylamine (0.09 mL, 0.62 mmol, 4.8 equiv) in Et<sub>2</sub>O (6 mL) at 0 °C. After 1 h at 0 °C, the prepared LDA solution was transferred by syringe into a solution of **8** (0.0679 g, 0.13 mmol) in Et<sub>2</sub>O (15 mL) at 0 °C. After 4.5 h at 0 °C, dry CuCl<sub>2</sub> (0.17 g, 1.3 mmol, 10 equiv) was added at –78 °C, then the reaction mixture was kept at –78 °C for 4 h and warmed up slowly to ambient temperature overnight. The reaction mixture was quenched with water, extracted with ethyl ether (3 × 15 mL). The organic layer was washed with saturated NaCl (25 mL) and water (2 × 25 mL), and then dried over MgSO<sub>4</sub>. The yellow product *rac*-**4** was obtained by precipitation twice (CHCl<sub>3</sub>–CH<sub>3</sub>OH) (0.0327 g, 48.4% yield). From other reaction on the 0.1521 g of **8**, 0.0749 g (49.4%) of *rac*-**4** was obtained. Mp > 300 °C. <sup>1</sup>H NMR (benzene-*d*<sub>6</sub>, 400 MHz): δ 6.50 (s, 4 H), –0.08 (s, 36 H), <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): δ 143.6, 143.0, 140.6, 137.3, 134.9, 134.8, 128.1, 126.5, –0.4. IR (KBr): 2953.2, 2920.4, 2893.2, 2850.5 (C–H) cm<sup>–1</sup>. HRMS (TOF MS EI<sup>+</sup>) *m/z* calcd for [C<sub>44</sub>H<sub>40</sub>Si<sub>4</sub>S<sub>12</sub>] 1063.8856, found 1063.8848.

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**Supporting Information Available:** Experimental details, NMR, HRMS spectra and X-ray crystallographic data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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