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Synthesis of Dithieno[2,3-*b*:4′,3′-*d*]siloles and Their Selective Bromination

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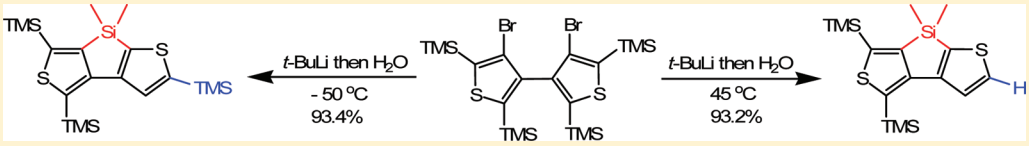
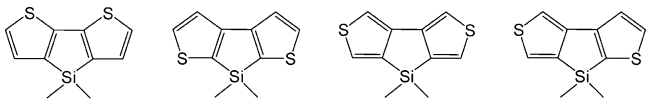
Supporting Information



ABSTRACT: The efficient synthesis of novel unsymmetrical dithienosiloles, 7,7-dimethyl-4,6-di(trimethylsilyl)-dithieno[2,3-*b*:4′,3′-*d*]silole (**1**) and 7,7-dimethyl-2,4,6-tri(trimethylsilyl)-dithieno[2,3-*b*:4′,3′-*d*]silole (**2**) has been developed by intramolecular silole formation with 4,4′-dibromo-2,2′,5,5′-tetrakis(trimethylsilyl)-[3,3′]bithienyl (**3**) as the starting material in the presence of *t*-BuLi. Upon treatment with *N*-bromosuccinimide (NBS) under controlled conditions, dithieno[2,3-*b*:4′,3′-*d*]silole was selectively brominated to produce mono-, di-, and tribrominated dithieno[2,3-*b*:4′,3′-*d*]siloles in good yields. The crystal structures of the title compounds are described.

Silole-based π-conjugated compounds and their derivatives have been actively studied as functional materials because they possess a low-lying LUMO due to the interaction between the σ^* orbitals of their two exocyclic Si−C bonds and the π^* orbital of the butadiene moiety.[1] Among various extended π-conjugated silole systems arising from the fairly good coplanarity of adjacent thiophene rings with sufficient thermal and chemical stability, dithienosiloles (DTS, Scheme 1) are one of the most useful building blocks for the preparation of functional materials.[2] DTSs have been widely used in organic optoelectronic devices such as organic light-emitting diodes (OLEDs),[3] organic field effect transistors (OFETs),[4] and dye-sensitized solar cells (DSSCs).[5]

Scheme 1. Structures of Dithienosiloles



To the best of our knowledge, although the three symmetrical DTS isomers (Scheme 1) based on dithieno[3,2-*b*:2′,3′-*d*]silole (DTS1), dithieno[2,3-*b*:3′,2′-*d*]silole (DTS2), and dithieno[3,4-*b*:4′,3′-*d*]silole (DTS3) have been reported, the synthesis of DTS4 and its derivatives has not been achieved. The method in preparing symmetric dithienosiloles generally involves two key steps, the formation of bithienyl and silylation.[4d,6] Ohshita *et al.*[6a] reported the silole ring formation via the cross-coupling of dilithiobithienyl with dichlorodiphenylsilane in 73% yield in the preparation of DTS1 derivatives. Recently, Marks *et al.*[4d] showed the efficient synthesis of spirocycloalkyl DTS1 by using dilithiobithienyl with 1,1-dichlorosilacycloalkanes. Iyoda *et al.*[7] reported the efficient synthesis of DTS2 and DTS3 via high loading (20%) of Pd catalyst in the intramolecular cyclization reactions of dibromo-dimethyldithienylsilane in the presence of hexamethylditin. Additionally, several intriguing methods for the preparation of benzosiloles need to be highlighted. One interesting method derives from carbanion attack on the silicon atom of a TMS group.[8] Xi *et al.*[9] reported an efficient process involving Pd-catalyzed selective cleavage of a C(sp^3)-Si bond for formation of silole ring. In addition, rhodium-catalyzed synthesis of benzosiloles has also been reported via cleavages of the carbon−silicon bond of trialkylsilyl groups[10] or silicon−hydrogen bonds.[11] In this paper, we report an efficient and novel synthesis of derivatives of dithieno[2,3-*b*:4′,3′-*d*]silole (DTS4), an unknown unsymmetrical isomer of dithienosiloles via intramolecular silole formation of **3** and their highly selective bromination.

In our previous work, we reported that using **3** as substrate in the presence of *t*-BuLi (4 equiv)/$CuCl_2$, a D_2-symmetric derivative of thienosilole (**4**, Scheme 2) was obtained in 55−64% yield.[8d] The formation of **4** included three steps, the ring formation of silole, the thiophene ring-opening alkynylation and S−S bond formation via the $CuCl_2$-promoted coupling. When we quenched the reaction with H_2O instead of $CuCl_2$, instead of forming the functionalized thiol (**5**, Scheme 2) according to the possible mechanism for making **4**,[8d] the unexpected derivatives of DTS4, **1** and **2** were generated in high yields (Scheme 3).

The efficient synthesis of **3** was reported in our previous work.[8d] After Br/Li exchange of **3** with 4.4 equiv of *t*-BuLi in dry ether at −78 °C for 1 h and then −30 °C for 1 h, the

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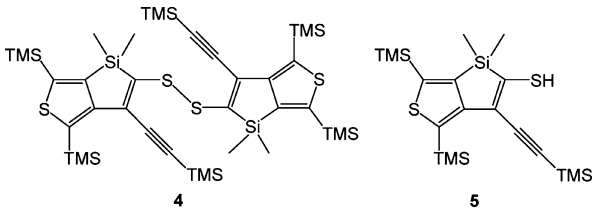
Scheme 2. Structures of Thienosiloles



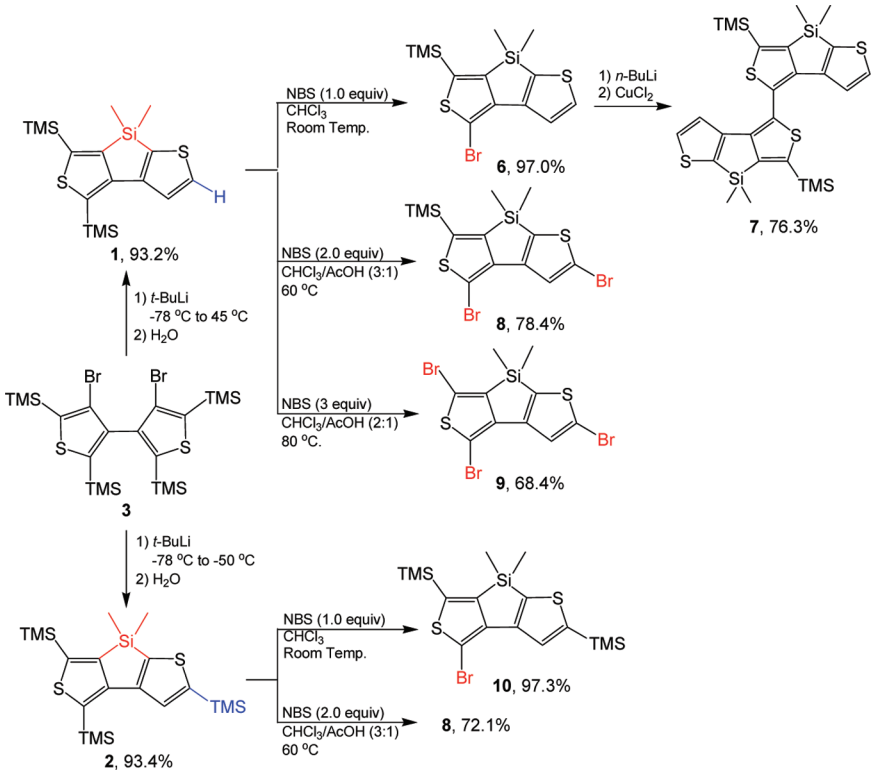
reaction mixture was quenched with H_2O at −30 °C. We obtained a mixture of **1** and **2** in 6.1% and 80.7%, respectively, by GC−MS analysis. The reaction was shown temperature dependence. With increasing the reaction temperature, the yield of **1** increased, and on the contrary, the yield of **2** decreased. When the reaction temperature of Br/Li exchange was set at −78 °C for 1 h and then warmed to 45 °C for 14 h, only **1** was generated in 93.2% isolated yield. In contrast, if the Br/Li exchange was set at −78 °C for 1 h, and then −50 °C for 1 h, only **2** was obtained in 93.4% isolated yield (Scheme 3).

The possible mechanism for the formation of **1** and **2** is shown in Scheme 4. After Br/Li exchange of **3** with *t*-BuLi, a dianionic intermediate **11** was generated, and during the course of reaction, one carbanion in **11** attacked the silicon of TMS on the neighboring thiophene ring to give **12**, a lithium pentaorganosilicate.[8,12] In Klumpp's work,[8a] lithium 2,2′-biphenyldiyltrimethylsilicate was confirmed by NMR studies at −80 °C, which converted reversibly into methyllithium and 9,9-dimethyl-9H,9-silafluorene after raising the temperature. Lammertsma[12] *et al.* even obtained the crystal structure of tetra-alkylammonium pentaorganosilicate. In our case, methyllithium could be removed from **12** to generate intermediate **13** at low temperature (−50 °C). **13** could be quenched with H_2O to form **2**. When **13** was quenched with D_2O, a monodeuterated DTS4, **14** was formed in 91.8% yield. When the reaction temperature was raised up to 45 °C, the possible intermediate **15** could be formed via the attack of a hydroxide anion to the silicon of the TMS group. The hydroxide ion could be generated by the protonation of anion **13** with H_2O. During this procedure, only the TMS group at C-2 position in DTS4 could be removed by hydroxide attack to generate **15**, while the other another two TMS groups at C-4 and C-6 positions remained stable. **15** could be further quenched to generate **1**. When D_2O was employed instead of H_2O, the dideuterated DTS4, **16** could be obtained in 92.3% yield.

When **3** was exposed to 2.2 equiv of *t*-BuLi for Br/Li exchange, meaning that only one bromine in **3** could be removed, intermediate **17** was generated. After quenching with H_2O at 0 °C, the monobrominated [3,3′]bithienyl, **18** was obtained as the main product (79.2%). In addition, a [3,3′]bithienyl, **19** was obtained as the side product in 3.4% yield at same time. The result implies that carbanion in **17** can not attack the silicon of TMS on the neighboring thiophene ring to form the derivative of DTS4. The reason might be due to the steric hindrance between the Br atom and the TMS group on the neighboring thiophene, which keeps the two adjacent thiophene rings deviating from coplane.

Bromination of **1** and **2** is important for material synthesis, in which DTS4 could be further functionalized for "building blocks". When 1.0 equiv of NBS was employed at ambient temperature, 7,7-dimethyl-4-bromo-6-trimethylsilyl-dithieno-[2,3-*b*:4′,3′-*d*]silole (**6**) was formed from **1** in 97.0% yield. An AB spin system in ^{1}H NMR spectrum of **6** was found at 7.91 ppm (d, J = 4.8 Hz) and 7.68 ppm (d, J = 4.8 Hz), meaning that the bromination occurred by substitution of one of two TMS groups in **1**. In order to confirm which TMS group in **1**

Scheme 3. Synthetic Route to 1, 2, and 6−10



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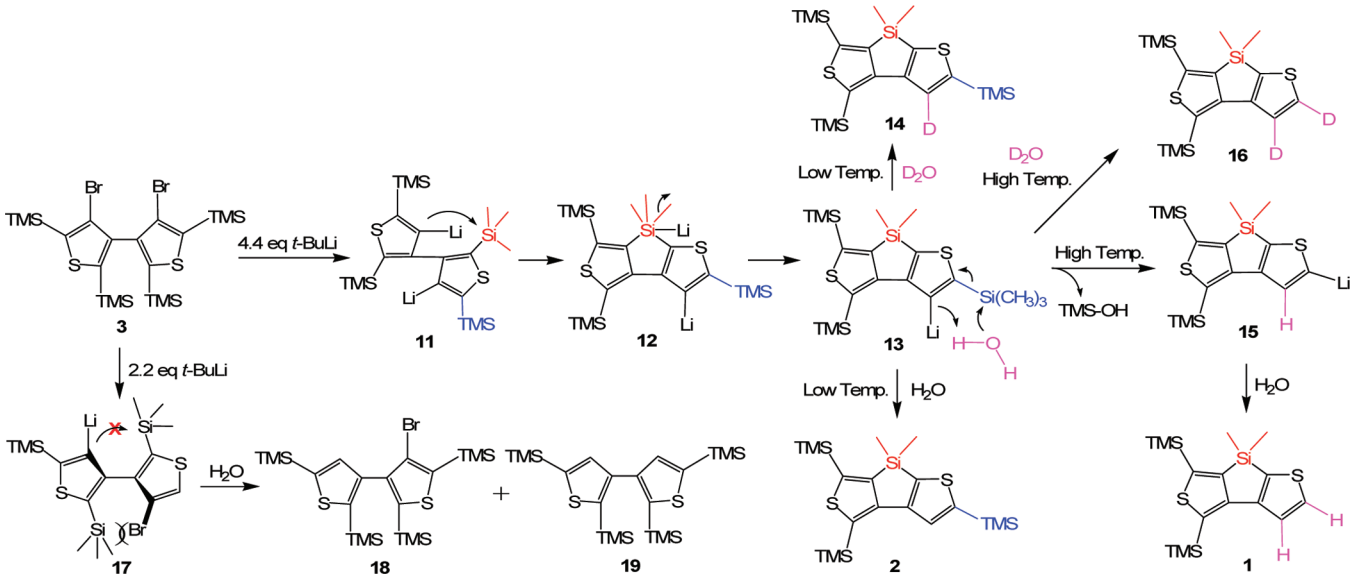
Scheme 4. Possible Mechanism for the Formation of 1 and 2



was first replaced by monobromination, we prepared the dimer of DTS4, **7** in 76.3% yield by Br/Li exchange of **6** and subsequent $CuCl_2$-promoted coupling. The molecular structure of **7** was confirmed by X-ray crystal analysis (Figure 1c), which clearly demonstrated the fact that the monobromination occurred on **1** at C-4 position by replacement of TMS group to generate **6**.

When 2.0 equiv of NBS was employed, 7,7-dimethyl-2,4-dibromo-6-trimethylsilyldithieno[2,3-*b*:4′,3′-*d*]silole (**8**) was obtained from **1** in 78.4% yield. Compared with the structure of **6**, the characteristic AB splitting pattern in the ^{1}H NMR spectrum of **6** disappeared in that of **8**. Instead, only one single peak at 7.87 ppm could be observed. Therefore, the second bromination could be occurred at C-2 position of DTS4 (Scheme 3). The structure of **8** was also confirmed by X-ray analysis (Figure 1e). When 3.0 equiv of NBS were employed, 7,7-dimethyl-2,4,6-tribromo-dithieno[2,3-*b*:4′,3′-*d*]silole (**9**) was obtained from **1** in 68.4% yield. The molecular structure of **9** was confirmed simply by comparison of the ^{1}H NMR spectra of **8** and **9**. The peak at 0.35 ppm in ^{1}H NMR spectrum of **8** disappeared in that of **9**. This fact demonstrated that the TMS group at C-6 position of **8** was replaced by Br to generate **9**.

The monobromination of **2** was carried out by 1.0 equiv of NBS. The bromination occurred on C-4 position of **2** to generate 7,7-dimethyl-4-bromo-2,6-di(trimethylsilyl)dithieno-[2,3-*b*:4′,3′-*d*]silole (**10**) in 97.3% yield. The structure of **10** was confirmed by X-ray crystal analysis (Figure 1f), in which the C-2 position was protected by a TMS group. When 2.0 equiv of NBS was employed, **8** could be obtained from **2** in 72.1% yield. It was demonstrated that the second bromination of **2** occurred on its C-2 position (Scheme 3).

The selective bromination of the aromatic ring of DTS4 suggests different activities on its three α-positions, which produces mono-, di-, and tribrominated dithieno[2,3-*b*:4′,3′-*d*]siloles **6** and **8**−**10** in good yields. The rank of activity of bromination on DTS4 could be illustrated as follows: C-4 position > C-2 position > C-6 position.

Crystal Analyses for 1, 2, 7, 8, and 10. The structures of **1**, **2**, **7**, **8**, and **10** were all confirmed by single-crystal X-ray analysis (Figure 1). The three fused aromatic rings of DTS4 are

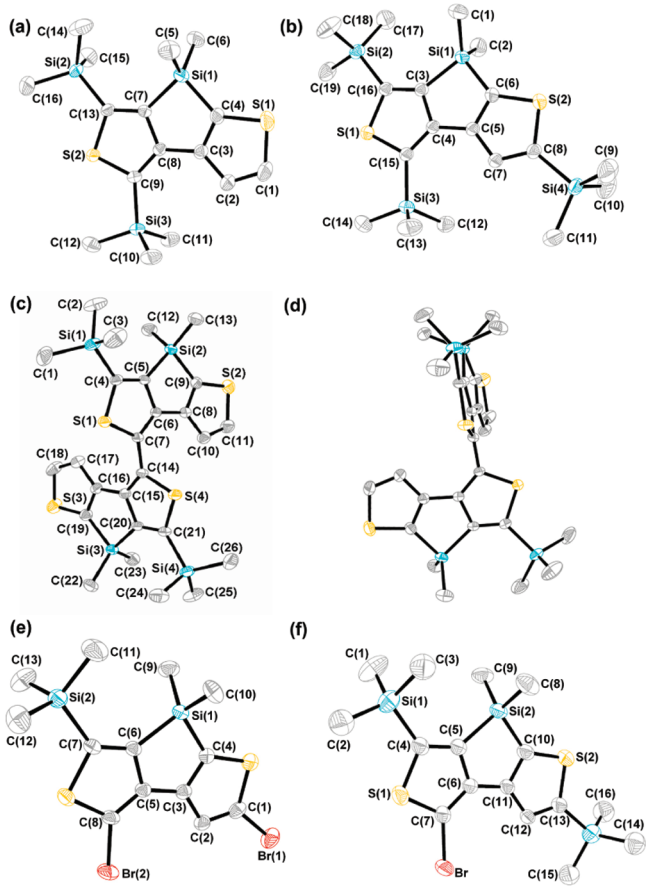


Figure 1. Molecular structures and conformations for **1**, **2**, **7**, **8**, and **10**. Carbon, silicon, and sulfur atoms are depicted with thermal ellipsoids set as the 30% probability level. Hydrogen atoms are omitted for clearity: (a) top view for **1**, (b) top view for **2**, (c) top view for **7**, (d) side view for **7**, (e) top view for **8**, (f) top view for **10**.

basically coplanar in each molecule. **1**, **2**, **8**, and **10** belong to monoclinic space group *P*2(1), monoclinic space group *P*2(1)/*c*, monoclinic space group *P*2(1)/*c*, and triclinic space group *P*-1, respectively. The framework of DTS4 in **1** shows slight

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distortion. The dihedral angle between the two moieties of thiophene is 4.0° and the torsion angle is 6.3° (C2−C3−C8−C9). The cases of **2**, **8**, and **10** are similar to that of **1**; the torsion angles are 2.2° (C7−C5−C4−C15), 0.8° (C2−C3−C5−C8), and 1.4° (C7−C6−C11−C12), respectively. The dihedral angles between the two thiophene moieties are 2.5° for **2**, 0.7° for **8** and 0.9° for **10**, respectively. In the packing of **10**, the two molecules stack orthogonally together. The dihedral angle of two DTS4 moieties is 89.5°.

Compound **7** belongs to orthorhombic space group *P*2(1)2(1)2(1). In **7**, two moieties of DTS4 are nonplanar (Figure 1e,f), the S1−C7−C14−C15 torsion angle is 75.4°, and the S4−C14−C7−C6 torsion angle is 78.4°, but each moiety of DTS4 is approximately coplanar, and the torsions are 4.2° (C7−C6−C8−C10) and 1.2° (C14−C15−C16−C17), respectively. The dihedral angle between the two DTS4 moieties is 73.7°.

In summary, we have demonstrated a novel and efficient method for the preparation of substituted dithieno[2,3-*b*:4′,3′-*d*]siloles, **1** and **2** in high yields by intramolecular silole formation employing **3** as the starting material in presence of *t*-BuLi followed by aqueous quenching. The bromination of **1** and **2** shows high chemoselectivity offering mono-, di-, and tribrominated dithieno[2,3-*b*:4′,3′-*d*]siloles. The title compounds and their brominated deravitives could be important intermediates in synthetic chemistry and organic electronics, such as OLED, OFET, and DSSC.

EXPERIMENTAL SECTION

Synthesis of 7,7-Dimethyl-4,6-di(trimethylsilyl)dithieno[2,3-*b*:4′,3′-*d*]silole (1). To a solution of **3** (6.91 g, 11.3 mmol) in dry ethyl ether (200 mL) was added *t*-BuLi (1.37 M, 36.2 mL, 49.6 mmol, 4.4 equiv) dropwise at −78 °C, and then the reaction mixture was warmed to 45 °C for 14 h. After quenching with water (20 mL), the reaction mixture was extracted with ethyl ether (3 × 50 mL), and the organic phase was dried over anhydrous $MgSO_4$. After the solvent was removed in vacuo, the residue was purified by column chromatography on silica gel with petroleum ether (60−90 °C) as eluent to yield **1** (3.86 g, 93.2%) as a white solid. From the other two reactions on the 3.06 and 1.14 g scales of **3**, 1.69 g (92.2%) and 623 mg (91.3%) of **1** were obtained, respectively. Mp: 137−138 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 (d, J = 4.8 Hz, 1 H), 7.44 (d, J = 4.8 Hz, 1 H), 0.50 (s, 6 H), 0.46 (s, 9 H), δ 0.38 (s, 9 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.0, 154.7, 152.3, 151.0, 140.5, 134.4, 132.1, 123.9, 0.8, 0.4, −1.0. IR (KBr): 2951.6, 2898.0 (C-H) cm^{-1}. HRMS (TOF MS EI$^+$) m/z calcd for $[C_{16}H_{26}Si_3S_2]$ 366.0784, found 366.0788.

Synthesis of 7,7-Dimethyl-2,4,6-tri(trimethylsilyl)dithieno-[2,3-*b*:4′,3′-*d*]silole (2). To a solution of **3** (2.29 g, 3.74 mmol) in dry ethyl ether (80 mL) was added dropwise *t*-BuLi (1.49 M, 11.0 mL, 16.44 mmol, 4.4 equiv) at −78 °C. After being kept at −78 °C for 1 h, the reaction mixture was warmed slowly to −50 °C for 1 h and then quenched with water (50 mL). The workup was same as that for the synthesis of **1**. A white solid **2** (1.53 g, 93.4%) was obtained by column chromatography on silica gel with petroleum ether (60−90 °C) as eluent. From other two reactions on the 171 mg and 955 mg scales of **3**, 110.4 mg (90.2%) and 625.3 mg (91.3%) of **2** were obtained, respectively. Mp: 128−129 °C. ^{1}H NMR(400 MHz, $CDCl_3$): δ 7.54 (s, 1 H), 0.48 (s, 6 H), 0.45 (s, 9 H), 0.36 (s, 9 H), 0.35 (s, 9 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.8, 155.3, 153.9, 151.0, 151.0, 146.6, 131.8, 130.6, 0.8, 0.4, 0.0, −0.9. IR (KBr): 3093.6, 2958.6, 2898.0 (C-H) cm^{-1}. HRMS (TOF MS EI$^+$): m/z calcd for $[C_{19}H_{34}Si_4S_2]$ 438.1179, found 438.1182.

Synthesis of 7,7-Dimethyl-4-bromo-6-trimethylsilyldithieno[2,3-*b*:4′,3′-*d*]silole (6). To a solution of **1** (5.49 g, 14.97 mmol) in chloroform (100 mL) was added NBS (2.67 g, 4.97 mmol, 1.0 equiv) at ambient temperature for 5 h, and then water (30 mL) was added to quench the reaction. The crude product was extracted with chloroform (2 × 30 mL), and the organic layer was dried over anhydrous $MgSO_4$. After solvent was removed in vacuo, the residue was purified by column chromatography with petroleum ether (60−90 °C) on silica gel to yield **6** (5.42 g, 97.0%) as white solid. From another reaction on the 4.06 g scales of **1**, 3.86 g (93.5%) of **6** was obtained. Mp: 54−56 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 (d, J = 4.8 Hz, 1 H), 7.68 (d, J = 4.8 Hz, 1 H), 0.53 (s, 6 H), δ 0.38 (s, 9 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.5, 149.9, 149.3, 147.3, 141.0, 134.8, 122.4, 105.3, 0.43, −0.9. IR (KBr): 2951.0, 2891.1 (C-H) cm^{-1}. HRMS (TFMS ESI): m/z [M + H]$^+$ calcd for $C_{13}H_{18}BrS_2Si_2$ 372.95663, found 372.95697 $[C_{13}H_{18}{}^{79}BrS_2Si_2]$ and 374.9549 $[C_{13}H_{18}{}^{81}BrS_2Si_2]$.

Synthesis of Dimer of DTS4 (7). To a solution of **6** (600 mg, 1.61 mmol) in dry ethyl ether (50 mL) was added *n*-BuLi (2.47 M, 0.65 mL, 1.61 mmol, 1.0 equiv) dropwise at −78 °C, and the reaction mixture was kept at −78 °C for 2 h and then warmed to −60 °C for 0.5 h. After that, dry $CuCl_2$ (324 mg, 2.41 mmol, 1.5 equiv) was added. The reaction mixture was kept at −60 °C for 2 h and then warmed slowly to ambient temperature overnight. The workup was same as that for the synthesis of **1**. A white solid **7** (361 mg, 76.3%) was obtained by column chromatography on silica gel with petroleum ether (60−90 °C) as eluent. From another reaction on the 360.7 mg of **6**, 207.6 mg (73.2%) of **7** was obtained. Mp: 201−203 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42(d, J = 4.4 Hz, 2 H), 6.88 (d, J = 4.8 Hz, 2 H), 0.64 (s, 6H), 0.61(s, 6H), 0.37 (s, 18 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.8 150.9, 148.7, 147.8, 140.1, 134.4, 126.9 122.8 0.6, −0.6, −1.0. IR (KBr): 2950.9, 2890.3 (C-H) cm^{-1}. HRMS (TOF MS EI$^+$): m/z calcd for $[C_{26}H_{34}Si_4S_4]$ 586.0626, found 586.0621.

Synthesis of 7,7-Dimethyl-2,4-dibromo-6-trimethylsilyldithieno[2,3-*b*:4′,3′-*d*]silole (8) from 1. NBS (3.40 g, 19.1 mmol, 2.0 equiv) was added into a solution of **1** (3.50 g, 9.54 mmol) in chloroform/AcOH (60 mL, 3:1, v/v) at ambient temperature. The reaction mixture was heated to 60 °C for 6 h and then quenched with water at ambient temperature. The workup was same as that for the synthesis of **6**. A white solid **8** (3.34 g, 77.8%) was obtained by column chromatography on silica gel with petroleum ether (60−90 °C) as eluent. From other two reactions on the 107.3 mg and 361.7 mg scales of **1**, 93.8 mg (70.8%) and 349.7 mg (78.4%) of **8** were obtained, respectively. Mp: 70−72 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87(s, 1 H), 0.50(s, 6 H), 0.35 (s, 9 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.9, 149.7, 149.3, 146.8, 142.5, 125.3, 120.5, 105.9, 0.4, −1.0. IR (KBr): 2952.3, 2895.4 (C-H) cm^{-1}. HRMS (TFMS ESI): m/z [M + H]$^+$ calcd for $C_{13}H_{17}Br_2S_2Si_2$ 450.8672, found 450.8676 $[C_{13}H_{17}{}^{79}Br_2S_2Si_2]$, 452.8654 $[C_{13}H_{17}{}^{79}Br^{81}Br\ S_2Si_2]$, and 454.8630 $[C_{13}H_{17}{}^{81}Br_2S_2Si_2]$.

Synthesis of 7,7-Dimethyl-2,4-dibromo-6-trimethylsilyldithieno[2,3-*b*:4′,3′-*d*]silole (8) from 2. The procedure of making **8** from **2** is the same to that for the synthesis of **8** from **1**. From the reaction on the 265 mg scale of **2**, 197 mg (72.1%) of **8** was obtained.

Synthesis of 7,7-Dimethyl-2,4,6-tribromodithieno[2,3-*b*:4′,3′-*d*]silole (9). NBS (227 mg, 1.28 mmol, 3.0 equiv) was added to a solution of **1** (156 mg, 0.43 mmol) in chloroform/AcOH (60 mL, 2:1, v/v) at ambient temperature. The reaction mixture was heated to 80 °C for 8 h and then quenched with water at ambient temperature. The workup was same to that for the synthesis of **6**. A pale yellow solid **9** (132 mg, 67.7%) was obtained by column chromatography on silica gel with petroleum ether (60−90 °C) as eluent. From other two reactions on the 103.8 mg and 500 mg scales of **1**, 81.5 mg (63.2%) and 423.9 mg (68.4%) of **9** were obtained, respectively. Mp: 77−79 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75(s, 1 H), 0.50 (s, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.0, 146.8, 144.9, 142.6, 125.3, 121.1, 116.4, 101.1, −3.0. IR (KBr): 2954.5, 2897.0, (C-H) cm^{-1}. HRMS (TOF MS EI$^+$): m/z calcd for $[C_{10}H_7SiS_2Br_3]$ 455.7309, found 455.7315 $[C_{10}H_7SiS_2{}^{79}Br_3]$, 457.7281$[C_{10}H_7SiS_2{}^{79}Br_2{}^{81}Br]$, 459.7263 $[C_{10}H_7SiS_2{}^{79}Br^{81}Br_2]$, and 461.7250 $[C_{10}H_7SiS_2{}^{81}Br_3]$.

Synthesis of 7,7-Dimethyl-4-bromo-2,6-di(trimethylsilyl)-dithieno[2,3-*b*:4′,3′-*d*]silole (10). To a solution of **2** (310.8 mg, 0.71 mmol) in chloroform (10 mL) was added NBS (126.4 mg, 0.71

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mmol, 1.0 equiv) at ambient temperature. After about 4 h, the reaction was quenched with water (20 mL). The workup was the same as that for the synthesis of **6**. A white solid **10** (307.1 mg, 97.3%) was obtained by column chromatography on silica gel with petroleum ether (60−90 °C) as eluent. From another reaction on the 90.0 mg scale of **2**, 87.4 mg (95.6%) of **10** was obtained. Mp: 103−105 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (s, 1 H), 0.53 (s, 6 H), 0.39 (s, 9 H), 0.36 (s, 9 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.2, 151.9, 151.5, 149.3, 147.2, 147.0, 128.6, 105.2, 0.4, 0.0, −0.9. IR (KBr): 2951.8, 2897.0 (C-H) cm^{-1}. HRMS (TFMS ESI): m/z [M + H]$^+$ calcd for $C_{16}H_{26}BrS_2Si_3$ 444.9967, found 444.9968 [$C_{16}H_{26}{}^{79}BrS_2Si_3$] and 446.9947 [$C_{16}H_{26}{}^{81}BrS_2Si_3$].

Synthesis of 7,7-Dimethyl-2,4,6-tri(trimethylsilyl)-(3-^{2}H)-dithieno[2,3-*b*:4′,3′-*d*]silole (14). The procedure of making **14** from **3** was the same as that for the synthesis of **2** from **3**. The only the difference was that D_2O was used instead of H_2O to quench the reaction at −50 °C. From the reaction on the 216 mg scale of **3**, 141 mg (91.8%) of **14** was obtained as a white solid. Mp: 122−124 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.49 (s, 6 H), 0.46 (s, 9 H), 0.37 (s, 9 H), 0.36 (s, 9 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.8, 155.2, 153.8, 151.0, 150.9, 146.6, 131.8, 0.8, 0.3, 0.0, −0.9. IR (KBr): 2956.4, 2852.7 (C-H) cm^{-1}. HRMS (TFMS ES+): m/z [M + H]$^+$ calcd for $C_{19}H_{34}DS_2Si_4$ 440.1320, found 440.1317; [M + Na]$^+$ calcd for $C_{19}H_{33}DNaS_2Si_4$ 462.1139, found 462.1200.

Synthesis of 7,7-Dimethyl-4,6-di(trimethylsilyl)-(2,3-$^2H_2$)-dithieno[2,3-*b*:4′,3′-*d*]silole (16). The procedure of making **16** from **3** was the same to that of making **1** from **3**. The only the difference was that D_2O was employed instead of H_2O. From the reaction on the 308 mg scale of **3**, 171 mg (92.3%) of **14** was obtained as a white solid. Mp: 132−134 °C. ^{1}H NMR(400 MHz, $CDCl_3$): 0.53 (s, 6 H), 0.49 (s, 9 H), δ 0.41 (s, 9 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ156.0, 154.7, 152.3, 151.0, 140.4, 132.0, 0.8, 0.4, −1.0. IR (KBr): 2957.0, 2896.8 (C-H) cm^{-1}. HRMS (TFMS ES+): m/z [M + H]$^+$ calcd for $C_{16}H_{25}D_2S_2Si_3$ 369.0988, found 369.0984.

Synthesis of 3-(2,5-Bis(trimethylsilyl)thiophene-3-yl)-4-bromo-2,5-bis(trimethylsilyl)thiophene (18) and 3-(2,5-Bis-(trimethylsilyl)thiophene-3-yl)-2,5-bis(trimethylsilyl)thiophene (19). The procedure of making **18** from **3** was the same to that of making **1** from **3**. The difference was that 2.2 equiv of *t*-BuLi was employed for Br/Li exchange, and the reaction mixture was quenched with H_2O at 0 °C. From the reaction on the 303 mg scale of **3**, 209 mg (79.2%) of **18** was obtained as a white solid and 7.6 mg (3.4%) of **19** was generated as a side product at the same time. **18**. Mp: 60−62 °C.^{1}H NMR(400 MHz, $CDCl_3$): δ 7.08(s, 1 H), 0.44 (s, 9 H), 0.34 (s, 9 H), 0.09 (s, 9 H), 0.04 (s, 9 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ147.9, 144.8, 144.1, 143.7, 142.2, 138.6, 138.3, 122.4, 0.3, 0.0, −0.2, −0.9. IR (KBr): 2955.0, 2896.8 (C-H) cm^{-1}. HRMS (TFMS ES+): m/z [M + H]$^+$ calcd for [$C_{20}H_{38}{}^{79}BrS_2Si_4$] 533.0675, found 533.0657, calcd for [$C_{20}H_{38}{}^{81}BrS_2Si_4$] 535.0655, found 535.0714. [M + Na]$^+$ calcd for $C_{20}H_{37}{}^{79}BrNaS_2Si_4$ 555.0495, found 555.0499, calcd for $C_{20}H_{37}{}^{81}BrNaS_2Si_4$ 557.0492, found 557.0474. **19**. Mp: 78−80 °C. ^{1}H NMR(400 MHz, $CDCl_3$): δ 7.23(s, 2 H), 0.32 (s, 18 H), 0.07 (s, 18 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.3, 143.6, 141.4, 139.2, 0.3, 0.0. IR (KBr): 2955.0, 2923.6, 2852.7 (C-H) cm^{-1}. HRMS (TFMS ES +): m/z [M + H]$^+$ calcd for $C_{20}H_{39}S_2Si_4$ 455.1570, found 455.1575.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Characterization of all compounds and crystallographic CIF files of **1**, **2**, **7**, and **10**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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