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Planar Heptathienoacenes Based on Unsymmetric Dithieno[3,2-*b*:3′,4′-d]thiophene: Synthesis and Photophysical Properties

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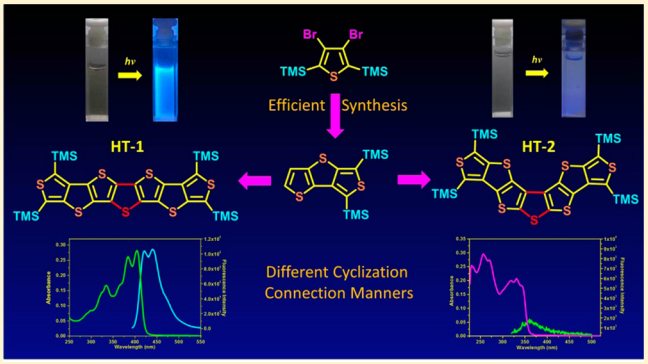
Supporting Information

ABSTRACT: The unsymmetric dithieno[3,2-*b*:3′,4′-*d*]-thiophene (***ts*-DTT**) was efficiently synthesized, and two novel heptathienoacenes with linear and bull's horn shapes were designed and prepared via different ring cyclization connection manners. All intermediates and aimed hepta-thienoacenes were fully characterized by ^{1}H NMR, ^{13}C NMR, and HRMS. Their UV−vis absorption behavior, fluorescence, and electrochemical properties are characterized. In addition, DFT quantum calculation was employed to further understand the electron distribution and the origin of the absorption bands.



Oligothiophenes are one of the most prominent organic semiconducting materials and have been widely studied as active components in organic light-emitting devices (OLEDs),[1] organic field-effect transistors (OFETs),[2] and organic solar cells (OSCs).[3] Fused oligothiophenes based on dithienothiophene (**DTT**) isomers have been well studied in a variety of areas ranging from helicene chemistry to materials science. For example, Rajca[4] and Wang[5] have reported some impressive array of carbon−sulfur[*n*]helicenes based on ***bb*-DTT**, and the helical carbon−sulfur $(C_2S)_n$ oligomers presented moderate curvature character with increasing *n*. However, using a different building block, such as ***tt*-DTT**, Matzger reported a planar and quasi-linearly annulated oligothiophene[6] (**HT-4**, Figure 1a). Recently, our group has reported another building block (***tb*-DTT**), and a bull's horn-shaped oligothienoacene (**HT-5**) with seven fused thiophene rings was successfully prepared as shown in Figure 1 a. It possesses a planar structure and shows strong intermolecular S···C and S···S interactions in the compressed sandwich-herringbone arranged single crystal structures.[7]

Obviously, utilization of different constructing **DTT** building blocks can produce various kinds of fused oligothiophenes. In Figure 1b, there are six **DTT** isomers, but only three of them have been employed for the construction of heptathieno-acenes.[4a,5c,6,7] However, via diverse connection styles as shown in Figure 1 a, heptathienoacenes with varied configurations could also be designed as helical, planar, linear, bull's horn structures, etc. Meanwhile, thiophene-based symmetrical fused oligomers not only limited to heptathienoacenes could be prepared via different ways[2,5b,6−8] as shown in Figure 1c. Generally, two ideas are mainly utilized in the cyclization of the central thiophene ring: (i) forming the C−C bond between the two building blocks first and proceeding in the central thiophene ring cyclization from its corresponding dicarbanions subsequently; (ii) in contrast, introduction of the S bridge between the two thiophene moieties in advance and cyclization

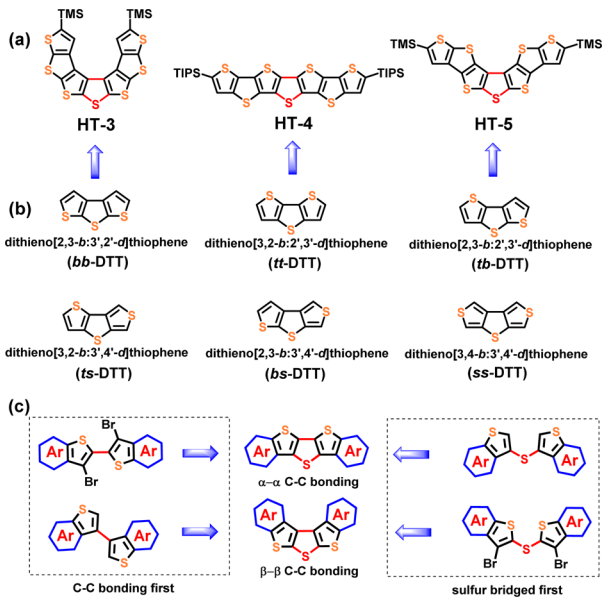


Figure 1. (a) Molecular structures of reported heptathienoacenes in literature; (b) isomers of **DTT** building blocks; (c) different connection manners at the central ring cyclization.

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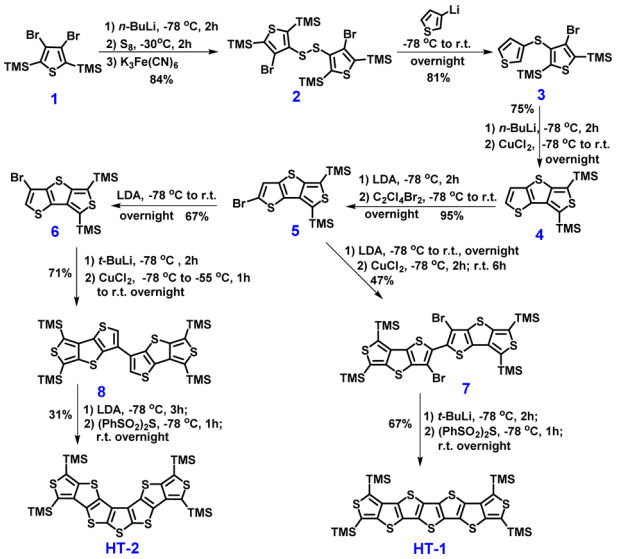
via the C−C coupling subsequently. Interestingly, the connecting positions of the C−C bond and the bridged sulfur atom (at α or β position of the thiophene ring) will greatly influence the structural shape of the final fused oligothiophenes.

Since fused oligothiophenes possess a novel molecular framework, it could produce significantly optical and electronic properties based on the molecular arrangement and the intermolecular interactions, such as S···S and $\pi-\pi$ interactions in solid thin films.[7,9] However, only three skeletons of the heptathienoacenes have been reported to date due to the synthetic challenge. Dithieno[3,2-*b*:3′,4′-*d*]thiophene (***ts*-DTT**) is one of the six **DTT** isomers, which was first reported in 1971 with a low overall yield of 13%.[10] Because of the competition between the Br/Li exchange and deprotonation reactions, many nontarget dicarbanion intermediates may be generated via Janssen's method resulting in a rather low yield of 19% in the final cyclization reaction.[10] It is rare to see a report relative to this unit, not to mention the larger fused oligothiophenes based on it.

In this manuscript, we report an improved and efficient method to prepare ***ts*-DTT** using TMS groups as the solubilizing and blocking/protecting groups in the synthetic process, which will reduce the nontarget dicarbanion intermediates formation and improve the solubility of both reactant and the final **DTT** unit. The yield at the final cyclization reaction is improved from 19% to 75%, and the overall yield reaches 51%. Meanwhile, two novel planar heptathienoacenes (**HT-1** and **HT-2**) with linear and/or bull's horn shapes have been designed and synthesized from ***ts*-DTT** via different connection styles. Their spectroscopic behaviors, electrochemical properties, crystal structure, and quantum calculation are described.

The synthetic routes are outlined in Scheme 1. Starting from 3,4-dibromo-2,5-bis(trimethylsilanyl)thiophene (**1**), via the Br/Li exchange in the presence of *n*-BuLi, the carbanion intermediate could be generated; followed by addition of S_8 and oxidation by $K_3Fe(CN)_6$, the disulfide compound (**2**) could be obtained in a high yield of 84%. Subsequently, the freshly made 3-thiophene lithium is added, and the disulfide precursor (**2**) could be efficiently transferred into the monosulfide (**3**) in a yield of 81%. Then, *n*-BuLi is employed for the Br/Li exchange and selective deprotonation occurs[11] to afford the crucial building block ***ts*-DTT** (**4**) through the $CuCl_2$ oxidation in a yield of 75%. In summary, herein the introduction of TMS as the protecting groups into thiophene precursors is the key to the successful preparation of the important unit ***ts*-DTT** (**4**) due to the improved solubility of the intermediated compound and the reduced possibility of the nontarget dicarbanion intermediates formation, resulting in a significantly elevated yield from 19%[10] to 75% for the ring closure reaction from **3** to **4** in this work. With our method the overall yield to prepare the ***ts*-DTT** reached 52%, which will facilitate the synthetic approaches to organic functional materials with ***ts*-DTT** as the building block.

Scheme 1. Synthetic Routes to Heptathienoacenes (HT-1 and HT-2) Based on *ts*-DTT



Generally, based on the design principle of the fused thiophene mentioned above, two heptathienoacenes could be constructed from this unsymmtric ***ts*-DTT** as shown in Scheme 1. The main idea in this route is to form the dimers via the C−C coupling above all and run ring cyclization subsequently by the S atom. First, LDA-mediated lithiation is introduced in Et_2O to remove the protons at the unprotected α positions in TMS protected ***ts*-DTT** (**4**) and the α-brominated ***ts*-DTT** (**5**) could be generated by quenching the reaction with $C_2Cl_4Br_2$ in 95% isolated yield. Then, the bromine dance reaction of the α-brominated ***ts*-DTT** (**5**) efficiently occurs in the presence of LDA in THF at 0 °C and a β-brominated ***ts*-DTT** intermediate with a carbanion at the α position could be afforded. When $CuCl_2$ is added subsequently to form the C−C bond, a **DTT**-dimer of ***ts*-DTT** (**7**) could be generated in one pot with a yield of 47%. Finally, the ring cyclization of **7** to generate the linear **HT-1** is carried out in the presence of *t*-BuLi and $(PhSO_2)_2S$ with a yield of 67%. However, if the quenching reagent is replaced by methanol in the bromine dance reaction of the α-brominated ***ts*-DTT** (**5**), the β-brominated ***ts*-DTT** (**6**) could be afforded in a yield of 67%. Consequently, another dimer of ***ts*-DTT** (**8**) could be obtained in a yield of 71% through Br/Li exchange in the presence of *t*-BuLi and $CuCl_2$ oxidative coupling reaction. Similarly, via the formation of the dicarbanion intermediate of the corresponding ***ts*-DTT** dimer (**8**) in the presence of LDA, bull's horn shaped heptathienoacene (**HT-2**) is generated by adding $(PhSO_2)_2S$ with a yield of 31%.

Fortunately, the molecular structures of **2**, **3**, **4**, **5** and **HT-2** are confirmed by single-crystal X-ray analysis. The crystals of the crucial building block ***ts*-DTT** (**4**) and one aimed heptathienoacene **HT-2** are shown in Figure 2, and the remaining crystals are shown in Figure S31. The crystal of **4** belongs to orthorhombic space group *Pbcn*. In **4**, all of the three thiophene rings are coplanar (Figure 2c), and the dihedral angle between the two end thiophenes is 4.0°. In the packing of **4** (Figure S31d), there are eight molecules in the unit cell and three kinds of short contacts can be observed as S2···H13B (2.92 Å), C4···H12A (2.85 Å), and H9C···H11A (2.32 Å). As for the **HT-2**, its crystal belongs to orthorhombic space group *Pnma* and all seven thiophene rings are fused together to form a bull's horn-shaped molecule shown in Figure 2b. From the side view in Figure 2d, it is obvious that all thiophene rings are approximately coplanar and the two ***ts*-DTT** arms tend to present slightly bent to the same direction. The average twisted angle between the terminal thiophene ring and the central thiophene ring in **HT-2** single crystal structures is 4.0°; the dihedral angle between the two terminal thiophene rings is 7.0°.

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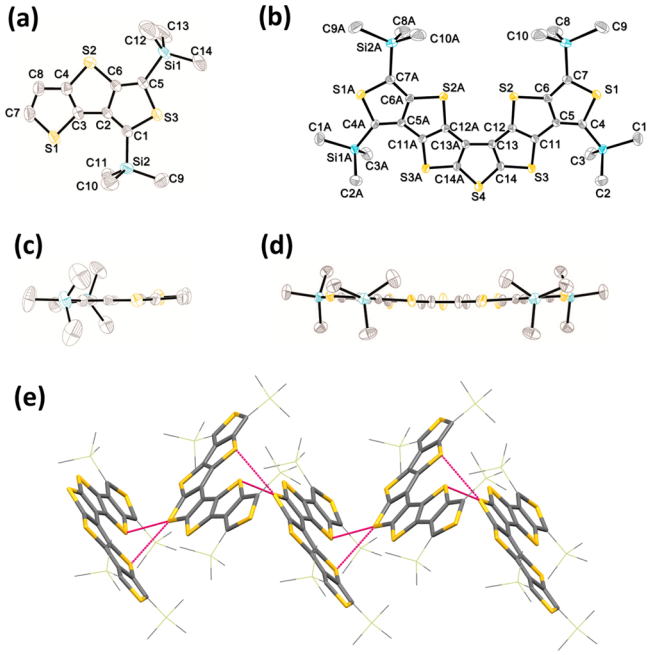

Figure 2. Crystal structures for **4** (a) and **HT-2** (b). Carbon and sulfur atoms are depicted with thermal ellipsoids set at 30%. Side view for **4** (c) and **HT-2** (d). Crystal packing of **HT-2** with S···S interactions (e).

In the packing of **HT-2**, there are four molecules in the unit cell and the molecules tend to only stack as a zigzag type along the *a*-axis due to the sole short contact observed as S···S, 3.45 Å (S2···S4 and S2A···S4) and the two neighbored **HT-2** molecules tend to be vertical with an approximated dihedral angle of 88.2°.

When the single crystal structure of **HT-2** is compared to our previously reported **HT-5**,[7] it is interesting that they are resemble each other in the central [5]thienoacene core, but the ending S atom positions and the quantity of the TMS protecting groups are different. This variation results in slight differences for the two coplanar heptathienoacenes: **HT-2** presents a planar structure that is very slightly bent, but **HT-5** possesses a tiny helical configuration. However, in their stacked graphs, they displayed varied packing styles. Both **HT-2** and **HT-5** show the same S···S interaction, which comes from the same central [5]thienoacene core, but **HT-5** also bears the S···π interaction from the ending sulfur, resulting in a sandwich-herringbone arrangement in its packing graph.[7,12] It is reasonable, because the TMS group possesses a larger space volume and may provide greater steric hindrance. With more TMS groups introduced at the ending thiophenes in **HT-2**, the ending sulfur atoms are buried in between the two TMS groups, which cut off their contact to the neighboring molecules. In short, it indicates that the positions of the annulated sulfur and the substituted groups are important to crystal packing, which may result in varied behaviors in organic electronics characterization.

The UV−vis absorption spectra for ***ts*-DTT** (**4**), **HT-1**, and **HT-2** are shown in Figure 3, and the details are listed in Table 1. Compound **4** as the basic **DTT** unit presents an absorption in the range of 250 to 350 nm with two bands (Band-I: 245−285 nm; Band-II: 285−360 nm), and a broad shoulder is observed at Band II. **HT-1** and **HT-2** bear the same constituents, but the UV−vis absorption activities are greatly different due to the varied sulfur positions and the connection

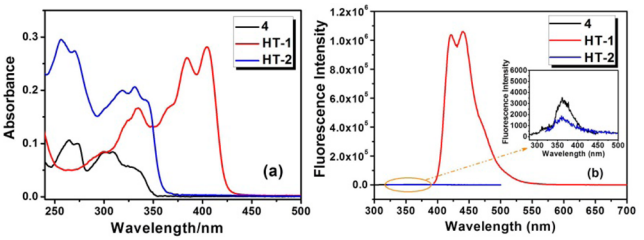

Figure 3. (a) UV/vis spectra for **4**, **HT-1**, and **HT-2** in dichloromethane at room temperature ([C] = 1 × 10^{-5} M). (b) Fluorescence spectra of compound **4** (λ_{ex} = 271 nm), **HT-1** (λ_{ex} = 384 nm), and **HT-2** (λ_{ex} = 310 nm), in dichloromethane at room temperature ([C] = 1 × 10^{-5} M), slit: 1/1.

Table 1. Photophysical and Electrochemical Data[a] for 4 and HT Molecules

compound	λ^{abs}_{max} (nm)	λ^{abs}_{onset} (nm)	λ^{em}_{max} (nm)	E_g (eV)	E_{ox} (V)	HOMO (eV)	LUMO (eV)
4	310	350	362	3.54	1.32	−5.58	−2.04
HT-1	405	422	442	2.94	1.00	−5.36	−2.42
HT-2	332	357	360	3.47	1.13	−5.50	−2.03

[a]Measured in anhydrous CH_2Cl_2/Bu_4F_6NP (0.1 M), [C] = 1× 10^{-3} mol L^{-1}, vs Ag/AgCl. E_{HOMO} = −e[E_{ox} − $E_{(Fc/Fc+)}$ + 4.8]. E_{LUMO} = $E_{g\ (opt)}$ + E_{HOMO}.

styles. With the cross-conjugated thiophene ring in the center for **HT-2**, the main contribution to its UV−vis absorption is the two ***ts*-DTT** arms, so **HT-2** maintains a similar absorption curve shape and presents a two times enhancement of the integrated absorbance relative to **4**. The bathochromic shift of the absorption onset for **HT-2** is rather substantial as 10 nm when compared with **4**. Interestingly, through a different connection manner, the central thiophene in **HT-1** is normally conjugated to the two ***ts*-DTT** arms on each side and results in an extended π-conjugated system in **HT-1**. It presents an obvious bathochromic onset to 428 nm and elevated absorbance intensity. Meanwhile, with the varied connection sequence in the cyclization of the central thiophene, the conjugation was greatly influenced and resulted in different fluorescence properties. The photoluminescence activities of the compound **4**, **HT-1**, and **HT-2** are characterized and **HT-1** shows a much stronger fluorescence than that of compound **4** and **HT-2** as shown in Figure 3b. Consequently, the quantum yield (Φ_F) of **HT-1** is characterized in dichloromethane with quinine sulfate in 0.1 N H_2SO_4 as the control and a Φ_F of 0.44 is obtained in Table S1.[13]

In order to further understand their UV−vis properties, their electronic structures and excited-state calculations of **HT-1** and **HT-2** are performed by using time-dependent density functional theory (TD-DFT) with the B3LYP hybrid function at the 6-31G (d, p) level. The predicted UV−vis spectra are consistent with the experimental curves in Figure S34a−b, and the selected transition contributions are listed in Table S7. It is clear that the absorption Band I at long wavelength of **HT-1** is mainly associated with the HOMO → LUMO transition. However, as for **HT-2**, Band I is not only associated with the HOMO → LUMO, there are also some other contributions originated from mixed transitions, such as H-1 → LUMO, H-1 → L+1, H-2 → LUMO, and H-2 → L+1. In addition, mixed transitions contributed to Band II of both **HT-1** and **HT-2**. The visualized HOMO, LUMO distributions and the calculated major frontier orbital energies are shown in Figure S34c−d.

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Generally, from the visualized LUMO distribution, it is clear that the two *ts*-**DTT** arms display good conjugation with the central thiophene ring in **HT-1**; but a conjugation break is observed at the central sulfur of the thiophene ring in **HT-2** molecule, which explains the absorption differences at the electron distribution level.

Cyclic voltammetry (CV) is utilized to determine the electrochemical properties and irreversible oxidation peaks are observed, but no redox process occurs at negative potential for these compounds. HOMO energy levels of **HT-1** and **HT-2** were calculated as −5.36 eV and −5.50 eV with the onset voltage of the first oxidation potentials, which are close to their corresponding structures reported in literature (**HT-4**, −5.36 eV[6] and **HT-5**, −5.53 eV[7]). It is obvious that the linear **HT-1** and **HT-4** would possess better conjugation and narrower band gaps, but the cross-conjugated bull's horn-shaped **HT-2** and **HT-5** would present lower HOMO energy levels.

In summary, the unsymmetric *ts*-**DTT** building block was efficiently synthesized utilizing TMS as the solubilizing and blocking/protecting groups; the yield of the ring cyclization at the *ts*-**DTT** preparation step was increased to 75%, and the overall yield for the *ts*-**DTT** synthesis reached 51%. Based on this, a linear heptathienoacene (**HT-1**) and a bull's horn-shaped heptathienoacene (**HT-2**) were prepared via different connection styles, which play a key role in the molecular properties, such as UV−vis absorption, fluorescence, and electrochemical properties. Strong S···S interaction was observed in a crystal stacking graph, and the title heptathienoacenes (**HT-1** and **HT-2**) are believed to be promising materials in organic electronics with such a planar structure.

EXPERIMENTAL SECTION

Synthesis of 4,4′-Dibromo-2,2′,5,5′-tetra(trimethylsilanyl)-3,3′-dithienyl Disulfide (2). To a solution of **1** (3.73 g, 1.0 equiv, 9.65 mmol) in dry ethyl ether (50 mL), *n*-BuLi (2.44 M, 3.85 mL, 9.56 mmol, 0.99 equiv) was added dropwise at −78 °C. After this temperature was maintained for 2 h, anhydrous S_8 (371.3 mg, 1.2 equiv, 11.60 mmol) was added under argon. Then, the reaction mixture was maintained at −30 °C for 2 h and then 5 mL of H_2O were added to quench it. Followed by pouring the reaction mixture into 40 mL of saturated $K_3Fe(CN)_6$ solution under vigorously stirring for 6 h, the reaction mixture was washed by saturated $NaHCO_3$ solution (20 mL) and extracted with CH_2Cl_2 (3 × 20 mL), and the organic phase was washed with H_2O (5 mL) and finally 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 as eluent. Then white solid **2** was obtained by precipitation twice from the mixture (CH_2Cl_2−Acetone) (2.74 g, 4.05 mmol, 84%). Mp: 168−170 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.38 (s, 18H), 0.10 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151. 6, 140.9, 140.1, 127.7, 0.2, −0.9; HRMS (MALDI/DHB) *m*/*z* calcd for [$C_{20}H_{36}Br_2S_4Si_4$] 673.9162, found 673.9138; IR (KBr): 2958, 2895 (C−H) cm^{-1}.

Synthesis of 4-Bromo-2,5-di(trimethylsilanyl)-3,3′-dithienyl Sulfide (3). To a solution of 3-bromothiophene (150 mg, 1.2 equiv, 0.920 mmol) in dry ethyl ether (7 mL), *n*-BuLi (2.43 M, 0.34 mL, 0.84 mmol, 1.1 equiv) was added dropwise at −78 °C. After this temperature was maintained for 2 h, anhydrous **2** (518.9 mg, 1.0 equiv, 0.77 mmol) in dry ethyl ether (15 mL) was added dropwise under argon. Then the reaction mixture was maintained at −78 °C for 1 h and then warmed slowly to ambient temperature overnight. After being quenched with CH_3OH, the reaction mixture was washed by saturated $NaHCO_3$ solution (10 mL) and extracted with CH_2Cl_2 (3 × 20 mL), and the organic phase was dried over anhydrous $MgSO_4$. After the solvent was removed in vacuo, the crude product was purified by column chromatography on silica gel with petroleum ether (60−90 °C) as eluent to yield **3** (261.7 mg, 0.62 mmol, 81%) as a white solid. Mp: 46−48 °C. ^{1}H NMR (DMSO-d_6, 400 MHz) δ 6.95 (dd, J_1 = 2.96 Hz, J_2 = 1.28 Hz, 1H), 6.75 (dd, J_1 = 5.04 Hz, J_2 = 1.24 Hz, 1H), 7.56 (dd, J_1 = 5.04 Hz, J_2 = 3.04 Hz, 1H), 0.37 (s, 9H), 0.31 (s, 9H). ^{13}C NMR ($CDCl_3$, 400 MHz): δ 151.6, 141.4, 137.5, 133.3, 127.4, 127.3, 126.1, 119.7, 0.2, −0.8. HRMS (MALDI/DHB) *m*/*z* calcd for [$C_{14}H_{21}Si_2S_3Br$] 419.9522, found 419.9520. IR (KBr): 2958, 2896 (C−H) cm^{-1}.

Synthesis of 5,7-Bis(trimethylsilanyl)dithieno[3,2-*b*:3′,4′-*d*]-thiophene (4). To a solution of **3** (433.4 mg, 1.0 equiv, 1.033 mmol) in dry ethyl ether (30 mL) was added *n*-BuLi (2.49 M, 0.83 mL, 2.07 mmol, 2.0 equiv) dropwise at −78 °C. After this temperature was maintained for 2 h, dry $CuCl_2$ (209.8 mg, 1.5 equiv, 1.55 mmol) was added and the reaction mixture was maintained at −78 °C for 1 h and −55 °C for 1 h and then warmed up slowly to ambient temperature overnight. After being quenched by CH_3OH, the reaction mixture was first filtered by column chromatography on silica gel with petroleum ether (60−90 °C) as eluent. After the solvent was removed in vacuo, the crude product was washed with saturated $NaHCO_3$ solution (10 mL) and extracted with CH_2Cl_2 (3 × 20 mL), and the organic phase was washed with H_2O (5 mL) and finally dried over anhydrous $MgSO_4$. The white product **4** (262.2 mg, 0.77 mmol, 75%) was obtained by column chromatography gel with petroleum ether (60−90 °C) as eluent. Mp: 66−68 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.41 (d, J = 5.2 Hz, 1H), 7.20 (d, J = 5.2 Hz, 1H), 0.50 (s, 9H), 0.43 (s, 9H). ^{13}C NMR ($CDCl_3$, 400 MHz): δ 150.9, 145.3, 144.3, 130.8, 130.5, 128.5, 127.4, 121.4, 0.0, −0.4. HRMS (EI$^+$ 70 eV) *m*/*z* calcd for [$C_{14}H_{20}S_3Si_2$] 340.0266, found 340.0267. IR (KBr): 2957, 2897 (C−H) cm^{-1}.

Synthesis of 2-Bromo-5,7-bis(trimethylsilanyl)dithieno[3,2-*b*:3′,4′-*d*]thiophene (5). *n*-BuLi (2.38 M, 0.22 mL, 0.52 mmol, 1.2 equiv) was added dropwise to diisopropylamine (0.09 mL, 1.4 equiv, 0.62 mmol) in dry ethyl ether (10 mL) at 0 °C. After 0.5 h at 0 °C, the fresh made LDA solution was transferred by syringe into a solution of **4** (147.7 mg, 1.0 equiv, 0.43 mmol) in dry ethyl ether (10 mL) at −78 °C. After 2 h at −78 °C, dry $C_2Cl_4Br_2$ (183.6 mg, 1.3 equiv, 0.56 mmol) was added at −78 °C, and then the reaction mixture was maintained at this temperature for 1 h and warmed up slowly to ambient temperature overnight. After being quenched by CH_3OH at −78 °C, the reaction mixture was washed with saturated $NaHCO_3$ solution (5 mL) and extracted with CH_2Cl_2 (3 × 10 mL), and the organic phase was washed with H_2O (5 mL) and then dried over anhydrous $MgSO_4$. The white product **5** (172.7 mg, 0.41 mmol, 95%) was obtained by column chromatography on silica gel with petrol ether (60−90 °C) as eluent. Mp: 104−106 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.20 (s, 1H), 0.48 (s, 9H), 0.42 (s, 9H). ^{13}C NMR ($CDCl_3$, 400 MHz): δ 149.5, 145.2, 142.7, 131.0, 130.7, 128.9, 124.1, 0.0, −0.4. HRMS (EI$^+$, 70 eV) *m*/*z* calcd for [$C_{14}H_{19}BrS_3Si_2$] 417.9371, found 417.9366. IR (KBr): 2953, 2896 (C−H) cm^{-1}.

Synthesis of 3-Bromo-5,7-bis(trimethylsilanyl)dithieno[3,2-*b*:3′,4′-*d*]thiophene (6). *n*-BuLi (2.42 M, 1.77 mL, 4.29 mmol, 6.0 equiv) was added dropwise to diisopropylamine (0.73 mL, 5.15 mmol, 7.2 equiv) in THF (5 mL) at 0 °C. After 0.5 h at 0 °C, the fresh made LDA solution was transferred by syringe into a solution of **5** (300 mg, 0.72 mmol 1.0 equiv) in THF (10 mL) at −78 °C. Then the reaction mixture was warmed up slowly to ambient temperature overnight. After being quenched by CH_3OH at −78 °C, the reaction mixture was extracted with CH_2Cl_2 (3 × 15 mL), washed with saturated $NaHCO_3$ (10 mL) and water (5 mL), and then dried over $MgSO_4$. After the removal of the solvent under vacuum, the residue was purified by column chromatography on silica gel with petrol ether (60−90 °C) as eluent to yield **6** as a white solid (200 mg, 0.48 mmol, 67%). Mp: 67−69 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.31 (s, 1H), 0.48 (s, 9H), 0.44 (s, 9H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 149.7, 145.6, 145.4, 131.8, 131.6, 128.4, 123.7, 140.4, −0.1, −0.4. HRMS (EI$^+$, 70 eV) *m*/*z* calcd for [$C_{14}H_{19}S_3BrSi_2$] 417.9371, found 417.9375. IR (KBr): 2956, 2896 (C−H) cm^{-1}.

Synthesis of 3,3′-Dibromo- 5,5′,7,7′-tetra(trimethylsilanyl)-2,2′-bis-bidithieno[3,2-*b*:3′,4′-*d*]thiophene (7). *n*-BuLi (2.10 mL, 6.0 equiv, 2.44 M, 5.13 mmol) was added dropwise to diisopropylamine (0.87 mL, 7.2 equiv, 6.16 mmol) in THF (25 mL) at 0 °C. After

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0.5 h at 0 °C, the freshly prepared LDA solution was transferred by syringe into a solution of **5** (358.9 mg, 1.0 equiv, 0.86 mmol) in dry THF (30 mL) at −78 °C. Then the reaction mixture warmed slowly to ambient temperature overnight. The next day, dry $CuCl_2$ (347.53 mg, 3.0 equiv, 2.57 mmol) was added at −78 °C which was maintained for about 2 h, and then the reaction mixture was warmed up slowly to ambient temperature and stirred for 6 h. After being quenched by CH_3OH at −78 °C, the $CuCl_2$ in reaction mixture was filtered by column chromatography on silica gel (200−300 mesh) with petroleum ether (60−90 °C) as eluent. After the solvent was removed in vacuo, the crude product was washed with saturated $NaHCO_3$ solution (5 mL) and extracted with CH_2Cl_2 (3 × 10 mL) and the organic phase was washed with H_2O (5 mL) and then dried over anhydrous $MgSO_4$. The yellow solid **7** (170 mg, 0.20 mmol, 47%) was obtained by column chromatography (silica gel) with petroleum ether (60−90 °C) as eluent. Mp: 252−254 °C. ^1H NMR ($CDCl_3$, 400 MHz): δ 0.51 (s, 18H), 0.46 (s, 18H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 148.8, 146.0, 145.3, 132.9, 131.7, 129.8, 128.8, 0.0, −0.4. HRMS (DART+) m/z $[M + H]^+$ calcd for $[C_{28}H_{37}Br_2S_6Si_4]$ 834.8643, found 834.8658. IR (KBr): 2955, 2895 (C−H) cm^{-1}.

Synthesis of 5,5′,7,7′-Tetra(trimethylsilanyl)-3,2′-bis-bidithieno[3,2-*b*:3′,4′-*d*]thiophene (8). To a solution of **6** (113 mg, 1.0 equiv, 0.27 mmol) in dry ethyl ether (25 mL), *t*-BuLi (0.82 mL, 4.05 equiv, 1.32 M, 1.09 mmol) was added dropwise at −78 °C. After this temperature was maintained for 2 h, dry $CuCl_2$ (109.4 mg, 3.0 equiv, 0.81 mmol) was added at −78 °C, and then the reaction mixture was kept at −55 °C for 1 h and warmed up slowly to ambient temperature overnight. The workup procedure is the same as that for compound **4**, and finally **8** was obtained as a yellow solid (65.0 mg, 0.096 mmol, 71%). Mp: 332−334 °C. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.74 (s, 2H), 0.53 (s, 18H), 0.46 (s, 18H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 150.2, 145.2, 143.0, 130.7, 131.2, 129.7, 128.8, 123.0, 0.0, −0.4. HRMS (DART+) m/z $[M + H]^+$ calcd for $[C_{28}H_{39}S_6Si_4]$ 679.0448, found 679.0435. IR (KBr): 2955, 2895 (C−H) cm^{-1}.

Synthesis of HT-1. To a solution of **7** (84.7 mg, 1.0 equiv, 0.10 mmol) in dry ethyl ether (15 mL), *t*-BuLi (0.31 mL, 4.2 equiv, 1.37 M, 0.43 mmol) was added dropwise at −78 °C under argon. After this temperature was maintained for 2 h, $(PhSO_2)_2S$ (33.4 mg, 1.05 equiv, 0.11 mmol) was added at −78 °C, the reaction mixture was maintained at −78 °C for 1 h and then warmed up slowly to ambient temperature overnight. After being quenched with CH_3OH, the reaction mixture was washed with saturated $NaHCO_3$ solution (10 mL) and extracted with CH_2Cl_2 (3 × 20 mL), and the organic phase was dried over anhydrous $MgSO_4$. After the solvent was removed in vacuo, the crude product was purified by column chromatography on silica gel with petroleum ether (60−90 °C) as eluent, and **HT-1** was obtained as a red solid (48.3 mg, 0.068 mmol, 67%). Mp: >300 °C. ^1H NMR ($CDCl_3$, 300 MHz) δ (ppm) 0.54 (s, 18H), 0.46 (s, 18H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm)149.5, 145.7, 136.4, 133.5, 133.2, 131.5, 130.7, 128.8, 0.1, −0.4. HRMS (DART+) m/z $[M + H]^+$ Calcd for $[C_{28}H_{37}S_7Si_4]$ 709.0012, found 709.0002. IR (KBr): 2955, 2853 (CH) cm^{-1}.

Synthesis of HT-2. *n*-BuLi (2.47 mL, 8.0 equiv, 2.47 M, 0.68 mmol) was added dropwise to diisopropylamine (0.12 mL, 9.6 equiv, 0.82 mmol) in dry ethyl ether (10 mL) at 0 °C. After 0.5 h at 0 °C, the fresh prepared LDA solution was transferred by syringe into a solution of **8** (58.0 mg, 1.0 equiv, 0.085 mmol) in dry ethyl ether (50 mL) at −78 °C. Then the reaction mixture was maintained at −78 °C for 3 h, and $(PhSO_2)_2S$ (33.4 mg, 1.05 equiv, 0.11 mmol) was added at −78 °C; the reaction mixture was then maintained at −78 °C for 1 h and then warmed up slowly to ambient temperature overnight. After being quenched with CH_3OH, the reaction mixture was washed by saturated $NaHCO_3$ solution (10 mL) and extracted with CH_2Cl_2 (3 × 20 mL), and the organic phase was dried over anhydrous $MgSO_4$. After the solvent was removed in vacuo, the crude product was purified by PTLC with petrol ether as the eluent and **HT-2** was obtained as a yellow solid (19 mg, 0.027 mmol, 31%). Mp: (>300) °C; ^1H NMR ($CDCl_3$, 300 MHz): δ (ppm) 0.53 (s, 18H), 0.51 (s, 18H). ^{13}C NMR (DCl_3, 75 MHz): δ 149.9, 145.8, 140.2, 134.8, 131.5, 130.6, 130.2, 129.7, 0.1, −0.2. HRMS (MALDI-FT_DHB) m/z $[M + H]^+$ calcd for $[C_{28}H_{37}S_7Si_4]$ 709.0012, found 708.9996. IR (KBr): 2956, 2897 (C−H) cm^{-1}.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b01506.

^1H NMR, ^{13}C NMR, and HRMS data of all compounds; CV scans and DFT calculation results of **HT-1** and **HT-2**; quantum yield of **HT-1** (PDF)

Crystallographic files of **2**, **3**, **4**, **5**, and **HT-2** (CIF)

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Osken, I.; Gundogan, A. S.; Tekin, E.; Eroglu, M. S.; Ozturk, T. *Macromolecules* **2013**, *46*, 9202−9210.

(2) (a) Xiao, K.; Liu, Y.; Qi, T.; Zhang, W.; Wang, F.; Gao, J.; Qiu, W.; Ma, Y.; Cui, G.; Chen, S. *J. Am. Chem. Soc.* **2005**, *127*, 13281−13286. (b) Gao, J.; Li, R.; Li, L.; Meng, Q.; Jiang, H.; Li, H.; Hu, W. *Adv. Mater.* **2007**, *19*, 3008−3011.

(3) (a) Yu, Q.-C.; Fu, W.-F.; Wan, J.-H.; Wu, X.-F.; Shi, M.-M.; Chen, H.-Z. *ACS Appl. Mater. Interfaces* **2014**, *6*, 5798−5809. (b) Li, Z.; He, G.; Wan, X.; Liu, Y.; Zhou, J.; Long, G.; Zuo, Y.; Zhang, M.; Chen, Y. *Adv. Energy Mater.* **2012**, *2*, 74−77. (c) Liu, Y.; Wan, X.; Wang, F.; Zhou, J.; Long, G.; Tian, J.; You, J.; Yang, Y.; Chen, Y. *Adv. Energy Mater.* **2011**, *1*, 771−775.

(4) (a) Miyasaka, M.; Rajca, A.; Pink, M.; Rajca, S. *J. Am. Chem. Soc.* **2005**, *127*, 13806−13807. (b) Miyasaka, M.; Pink, M.; Rajca, S.; Rajca, A. *Angew. Chem.* **2009**, *121*, 6068−6071.

(5) (a) Rajca, A.; Wang, H.; Pink, M.; Rajca, S. *Angew. Chem., Int. Ed.* **2000**, *39*, 4481−4483. (b) Rajca, A.; Miyasaka, M.; Pink, M.; Wang, H.; Rajca, S. *J. Am. Chem. Soc.* **2004**, *126*, 15211−15222. (c) Li, C.; Shi, J.; Xu, L.; Wang, Y.; Cheng, Y.; Wang, H. *J. Org. Chem.* **2009**, *74*, 408−411.

(6) Zhang, X.; Côté, A. P.; Matzger, A. J. *J. Am. Chem. Soc.* **2005**, *127*, 10502−10503.

(7) Sun, H.; Shi, J.; Zhang, Z.; Zhang, S.; Liang, Z.; Wan, S.; Cheng, Y.; Wang, H. *J. Org. Chem.* **2013**, *78*, 6271−6275.

(8) (a) Xu, L.; Wang, Z.; Xu, K.; Shi, J.; Wang, H. *Lett. Org. Chem.* **2009**, *6*, 474−477. (b) Nenajdenko, V. G.; Gribkov, D. V.; Sumerin, V. V.; Balenkova, E. S. *Synthesis* **2003**, *1*, 0124−0128.

(9) (a) Wang, X.-Y.; Jiang, W.; Chen, T.; Yan, H.-J.; Wang, Z.-H.; Wan, L.-J.; Wang, D. *Chem. Commun.* **2013**, *49*, 1829−1831. (b) Wang, Z.; Shi, J.; Wang, J.; Li, C.; Tian, X.; Cheng, Y.; Wang, H. *Org. Lett.* **2010**, *12*, 456−459.

(10) De Jong, F.; Janssen, M. J. *J. Org. Chem.* **1971**, *36*, 1998−2000.

(11) (a) Ozturk, T.; Ertas, E.; Mert, O. *Tetrahedron* **2005**, *61*, 11055−11077. (b) Ohmae, T.; Nishinaga, T.; Wu, M.; Iyoda, M. *J. Am. Chem. Soc.* **2010**, *132*, 1066−1074.

(12) Bromley, S. T.; Marta, M. T.; Peter, H.; Concepció, R. *J. Am. Chem. Soc.* **2004**, *126*, 6544−6545.

(13) (a) Man, L. L. Z. *Chin. J. Anal. Chem.* **1988**, *8*, 15. (b) Crosby, G. A.; Demas, J. N. *J. Phys. Chem.* **1971**, *75*, 991−1024.

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