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Diseleno[2,3-b:3',2'-d]selenophene and Diseleno[2,3-b:3',2'-d] thiophene: Building Blocks for the Construction of [7]Helicenes

Wan Xu,[†] Longlong Wu,[†] Maohong Fang, Zhiying Ma, Zhen Shan, Chunli Li,*[®] and Hua Wang*

Engineering Research Center for Nanomaterials, Henan University, Kaifeng 475004, P.R. China

Supporting Information

ABSTRACT: New building blocks, 2,5-di(trimethylsilanyl)diseleno-[2,3-*b*:3',2'-*d*]selenophene ((TMS)₂-**DSS**) and 2,5-di(trimethylsilanyl)diseleno[2,3-*b*:3',2'-*d*]thiophene ((TMS)₂-**DST**), for helicenes were obtained from selenophene with total yields of 54 and 61%. From (TMS)₂-**DSS** and (TMS)₂-**DST**, selenophene-based hetero[7]helicenes, 5,5'-di(trimethylsilanyl)benzo[1,2-*b*:3,4-*b*']bis(diseleno[2,3-*b*:3',2'-*d*]thiophene) (*rac*-1), and 5,5'-di(trimethylsilanyl)benzo[1,2-*b*:3,4-*b*']bis(diseleno[2,3-*b*:3',2'-*d*]selenophene) (*rac*-2) were prepared. The



overall yields from selenophene were approximately 6.5 and 6.1%, respectively. Intermolecular interactions such as C–Se, C–S, and Se–Se were observed in the crystal packings of *rac*-1 and *rac*-2. In addition, the absorption behaviors of *rac*-1 and *rac*-2 were investigated.

Helicenes are defined as ortho-fused aromatic compounds, which have interesting π -conjugated helical structures and are widely applied in asymmetric catalysis, molecular recognition, and circularly polarized luminescence materials.¹ Helicenes are generally divided into carbohelicenes and heterohelicenes.² Thiahelicene is a kind of carbon–sulfur helicene that contains all sulfur atoms down the lateral edge of molecular scaffolds, and all thiophene units cross-conjugated and fused to form helical structure.³ Rajca et al. have synthesized a series of thiahelicenes such as [5]-, [7]-, [9]-, and [11]thiahelicenes.^{3b,4} Wang et al. have reported a series of studies about the synthesis of carbon–sulfur helicenes, double helicenes, and triple helicenes.^{1,3b,5} They have also successfully modulated the position of the absorption peaks of carbon–sulfur double helicenes by changing their spacer group.¹

Selenophene is a close analogue of thiophene. In general, substitution of sulfur with selenium leads to many differences. The atom size of selenium is larger than that of sulfur (covalent radii are 1.20 and 1.05 Å, respectively), and selenium is more polarizable because of the larger number of electrons.⁶ In the solid state, selenium-containing compounds often undergo increased Se–Se interactions, which confer ordering on molecular scale and result in well-aligned solid-state packing and show excellent charge-transport properties.^{6,7}

However, limited research has been accorded to selenophene derivatives than thiophene derivatives, especially in its synthesis and organic functional materials, because the preparation of these derivatives is difficult.^{6,8} As such, replacing sulfur with selenium remains a big challenging, yet at the same time is a rewarding endeavor. By comparison, bearing larger atom size, less electronegativity, and more polarization, selenium leads to obvious differences in numbers of properties.⁶ Inspired by the specificity of selenium, we investigate the synthesis of selenophene-based helicenes and develop their key synthetic routes and processing conditions. In addition, we hope to

modulate the inner helix climb and turn in-plane of benzohetero[7]helicene by changing the number of selenophenes.

In this study, we use diseleno[2,3-b:3',2'-d]selenophene (**DSS**) and diseleno[2,3-b:3',2'-d]thiophene (**DST**) as building blocks for helicenes. We likewise report the synthesis and crystal structures of two new kinds of selenophene-based helicenes, namely, *rac*-1 and *rac*-2. The UV–vis absorption spectral behaviors of *rac*-1 and *rac*-2 are also described.

Synthesis of (TMS)₂-**DSS, (TMS)**₂-**DST,** *rac*-1, and *rac*-2. The synthetic route of $(TMS)_2$ -**DSS** and $(TMS)_2$ -**DST** is shown in Scheme 1. Through bromination, trimehtylsilanyl (TMS) protection, bromine dance, CuCl₂ oxidative coupling, and cyclization with selenium and bis(phenylsulfonyl)sulfide ((PhSO₂)₂S), (TMS)₂-**DSS**, and (TMS)₂-**DST** were obtained from selenophene with total yields of 54 and 61%.

2,5-Dibromoselenophene (3) was prepared from selenophene according to the literature method.⁹ Following Br/Li exchange of 3 with n-BuLi, chlorotrimethylsilane was added to produce 5-bromo-2-trimethylsilanylselenophene (4) with a yield of 94%. Highly efficient bromine dance reaction was observed in 4 using lithium diisopropylamide (LDA) to generate 4-bromo-2-trimethylsilanylselenophene (5) with 95% yield. Following Li/Br exchange in 5 with n-BuLi, resultant aryllithium was oxidized with CuCl₂ to afford 5,5'-di(trimethylsilanyl)-3,3'-diselenophene (6) with 88% yield. n-BuLi was introduced to deprotonate in 6 to give dilithiated 6. The reaction of dilithiated 6 with selenium gave the mixture of $(TMS)_2$ -**DSS** and 2,5-di(trimethylsilanyl)-diseleno[2,3-c:3',2'-e][1,2]diseleninecyclohexadienes (7). Separating the $(TMS)_2$ -DSS and 7 mixture is problematic owing to their similar solubility and polarity. However, 7 can be successfully converted into

Received: June 2, 2017 Published: September 27, 2017 Scheme 1. Synthetic Route to (TMS)₂-DSS and (TMS)₂-DST^a



^aReagents and conditions: (a) NBS (2.2 equiv), CHCl₃, rt; (b) (i) *n*-BuLi (1.0 equiv), Et₂O, $-78 \degree C/2$ h; (ii) TMSCl (1.5 equiv), $-78 \degree C/0.5$ h; (c) (i) LDA (1.3 equiv), THF, $-78 \degree C/6$ h; (d) (i) *n*-BuLi (1.0 equiv), Et₂O, $-78 \degree C/2$ h; (ii) CuCl₂ (2.0 equiv), $-55 \degree C/2$ h to rt; (e) (i) *n*-BuLi (2.1 equiv), Et₂O, $0 \degree C/2$ h; (ii) Se (5.0 equiv), $-55 \degree C/2$ h to rt; (f) Cu(5.0 equiv), 145 °C/0.5 h; (g) (i) *n*-BuLi (2.1 equiv), Et₂O, $0 \degree C/2$ h; (ii) (PhSO₂)₂S (1.02 equiv), $-78 \degree C/2$ h.

Scheme 2. Synthetic Route to rac-1 and rac- 2^{a}



^aReagents and conditions: (a) NBS (1.05 equiv), CHCl₃/HOAc (8/1), 0 °C/2 h; (b) (i) *n*-BuLi (1.05 equiv), Et₂O, -78 °C/2 h; (ii) DMF (2.0 equiv), -78 °C/1 h; (c) TiCl₄ (5.0 equiv), Zn (10.0 equiv), pyridine (5.0 equiv), THF; (d) *hv*, iodine (0.5 equiv), toluene.

 $(TMS)_2$ -DSS by heating a mixture of 7 and Cu nanopowder at 140–150 °C for several minutes without solvent. The preparation yield of $(TMS)_2$ -DSS from 6 is about 75%. In addition, $(TMS)_2$ -DST can be prepared through reaction of dilithiated 6 and $(PhSO_2)_2S$ with 85% yield.

In the synthesis of *rac-***1** and *rac-***2**, oxidative photocyclization of 1,2-diarylethylenes is the crucial step (Scheme 2). 2-Bromo-5-(trimethylsilanyl)diseleno-[2,3-b:3',2'-d]thiophene (8a) and 2-bromo-5-(trimethylsilanyl)diseleno[2,3-b:3',2'-d]selenophene (8b) could be obtained with yields of 90 and 83% by treating $(TMS)_2$ -DST and $(TMS)_2$ -DSS with NBS in a mixture solvent (HOAc-CHCl₃),^{5a} respectively. Following Li/Br exchange on 8a and 8b with n-BuLi, N,N-dimethylformamide (DMF) was added to produce 5-trimethylsilanyl-diseleno [2,3-b:3',2'-d]thiophene-2-carbaldehyde (9a) and 5-trimethylsilanyldiseleno [2,3-b:3',2'-d]selenophene-2-carbaldehyde (9b). After intermolecular McMurry reaction of 9a and 9b using TiCl₄/Zn/ pyridine, bis(2-trimethylsilanyldiseleno[2,3-b:3',2'-d]thiophene-5-yl)ethane (10a) and bis(2-trimethylsilanyldiseleno-[2,3-b:3',2'-d] selenophene-5-yl)ethane (10b) were obtained with yields of 41 and 56%, respectively. Following oxidative photocyclization of 10a and 10b in the presence of iodine in

dry benzene via irradiation of 450 W Hg medium pressure lamp, *rac*-1 and *rac*-2 were prepared with yields of 40 and 35%, respectively. From selenophene, the steps for creating *rac*-1 and *rac*-2 with yields of 6.5 and 6.1%, respectively, are shown as follows.

Crystallographic Analysis for (TMS)₂-DSS, rac-1, and *rac*-2. The molecular structures of (TMS)₂-DSS, *rac*-1, and *rac*-2 are all confirmed through single-crystal analysis (Figure 1). In $(TMS)_2$ -DSS, two $(TMS)_2$ -DSS molecules pair together. All selenophene rings are approximately coplanar (Figure 1A,B). The C25-C27-C13-C14 and C20-C22-C23-C16 torsion angles are 5.4 and 4.3°, respectively. The interplanar angle of two $(TMS)_2$ -DSS molecules is 84.8°. With the formation of the benzene ring from 10a, rac-1 is compressed with helical structure (Figure 1C-E). The distance between H5A-H20A is 2.96 Å, which is larger than that of H2-H17 in bis(trimethylsilanyl)benzohexathia[7]helicene (2.72 Å).^{5b} Repulsion of the facing terminal selenophene rings results in an interplanar angle of 51.8° between the terminal selenophene rings, which is larger than that of the terminal thiophene units in bis(trimethylsilanyl)benzohexathia[7]helicene.^{5b} Angles between the least-squares planes of neighboring rings are between 3.4

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Figure 1. Molecular structures for $(TMS)_2$ -**DSS**, *rac*-1, and *rac*-2 and space-filled mode for *rac*-1 and *rac*-2. (A) Molecular structure for $(TMS)_2$ -**DSS**, (B) side view for $(TMS)_2$ -**DSS**, (C) molecular structure for *rac*-1, (D) side view for *rac*-1, (E) space-filled mode for *rac*-1, (F) molecular structure for *rac*-2, (G) side view for *rac*-2, and (H) space-filled mode for *rac*-2. Carbon, selenium, sulfur, and silicon atoms are depicted with thermal ellipsoids set at the 30% probability level, and all hydrogen atoms are omitted for clarity.

and 12.3°. With the benzene ring as reference, the inner (C5, C6, C8, C11, C12, C16, C19, C20) helix climbs 2.94 Å and turns in-plane by 318.9°, which is larger than those in bis(trimethylsilanyl)benzohexathia[7]helicene.^{5b} This difference may be explained by the average bond length of C–Se (1.88 Å) in *rac*-1 being longer than that of C–S (1.73 Å), and the average bond angle of C–Se–C (86.1°) being smaller than that of C–S–C (90.1°) in bis(trimethylsilanyl)benzohexathia[7]-helicene.^{5b} Crystal packing of *rac*-1 (Figure S41) reveals that each *rac*-1 molecule interacts with six adjacent molecules through intermolecular C–Se (3.58, 3.57, and 3.52 Å), C–S (3.44 Å), and Se–Se (3.75 Å) interactions.

With the formation of benzene ring from 10b, *rac-2* is compressed into the helix (Figure 1F–H). The distance between H5A–H20A is 3.15 Å, which is larger than that in *rac-1*. The interplanar angle between terminal selenophene rings is 49.0° , which is smaller than that in *rac-1*. The angles between the least-squares planes of neighboring rings are between 7.5 and 10.8°. With the benzene ring as reference, the inner (C5, C6, C8, C10, C15, C16, C19, C20) helix climbs 2.98 Å and turns in-plane by 324.9° , which are larger than that in *rac-1*. The average bond length of C–Se is 1.88 Å, and the average bond

angle of C–Se–C is 86.0°. Crystal packing of *rac-2* (Figure S41) reveals that each *rac-2* molecule interacts with five adjacent molecules through intermolecular C–Se (3.55, 3.60 Å) and Se–Se (3.73, 3.76 Å) interactions. From bis(trimethylsilanyl)-benzohexathia[7]helicene^{Sb} to *rac-1* and *rac-2*, the inner helix climbs and turns in-plane gradually and becomes larger. The result shows that modification of the inner helix that climbs and turns in-plane of benzohetero[7]helicene, including thiophene and selenophene, can be achieved by changing the number of thiophenes and selenophenes.

The UV–vis absorption spectra for $(TMS)_2$ -DST, $(TMS)_2$ -DSS, *rac*-1, and *rac*-2 are shown in Figure 2. $(TMS)_2$ -DST and $(TMS)_2$ -DSS have similar absorption behavior with maximum absorption peak at 288 nm. *Rac*-1 and *rac*-2 have similar absorption behavior compared with that of bis(trimethylsil-anyl)benzohexathia[7]helicene (absorption peaks at 264, 332, and 347 nm).^{5b} *Rac*-1 and *rac*-2 are significantly red-shifted compared to bis(trimethylsilanyl)benzohexathia[7]helicene and show two major absorption bands in the ranges of 280–325 nm (Band-I) and 325–385 nm (Band-II). In Band-I, *rac*-1 shows a maximum absorption peak at 289 nm. *Rac*-1 has π -electron delocalization, including helical distortion and possible conjugation



Figure 2. UV–vis absorption spectra of $(TMS)_2$ -**DST**, $(TMS)_2$ -**DSS**, *rac*-1, and *rac*-2 in dichloromethane at room temperature ([C] = 1 × 10^{-5} M).

through the selenium and sulfur atoms with two major absorption peaks at 349 and 363 nm in Band-II.

To obtain the effects of molecular structure and electron distribution on spectroscopic properties of rac-1 and rac-2, electronic structure and excited-state calculations of these compounds were determined using Gaussian 09.14 Visualized HOMO and LUMO distributions and calculated frontier orbital energies for rac-1 and rac-2 are presented in Supporting Information (Figure S34). The predicted UV-vis spectra are consistent with experimental curves (Figure S35), and transition contributions are listed (Table S1). The absorption peak of 289 nm in Band-I is characterized mainly by the contributions of HOMO \rightarrow LUMO+10, HOMO-1 \rightarrow LUMO+5, and HOMO \rightarrow LUMO+3. The absorption peaks of 349 and 363 nm in Band-II are characterized mainly by the contributions of HOMO-1 \rightarrow LUMO and HOMO \rightarrow LUMO, respectively. Rac-2 has π -electron delocalization including helical distortion and possible conjugation through selenium atoms with two major absorption peaks at 353 and 366 nm in Band-II and shows a maximum absorption peak at 288 nm and a shoulder peak at 310 nm in Band-I. The absorption and shoulder peaks in Band-I are characterized mainly by the contributions of HOMO-3 \rightarrow LUMO+2 and HOMO \rightarrow LUMO+3, respectively. Absorption peaks in Band-II are characterized mainly by the contributions of HOMO \rightarrow LUMO and HOMO-1 \rightarrow LUMO. In Band-II, slight bathochromic shifts can be observed from rac-1 to rac-2; however, rac-1 and rac-2 are significantly red-shifted compared to bis(trimethylsilanyl)benzohexathia[7]helicene.^{5E}

In addition, we have evaluated the transition states between two chiral states using DFT calculations. We directly consider simplified models of the molecules, named as *rac*-1-H and *rac*-2-H, in which the TMS groups in *rac*-1 and *rac*-2 are replaced by hydrogen atoms. As presented in Figures S36 and S37, the isomerization barriers of *rac*-1-H and *rac*-2-H are estimated to be 35.4 and 37.7 kcal/mol, respectively.

In conclusion, from selenophene, $(TMS)_2$ -DSS and $(TMS)_2$ -DST were used as building blocks for helicenes. Using these molecules, two new kinds of selenophene-based helicenes, namely, *rac*-1 and *rac*-2, were successfully prepared. Single-crystal analysis shows the predicted two-fold symmetry for *rac*-1 and *rac*-2 and the existence of multiple short contacts, including C–Se, C–S, and Se–Se interactions. From bis(trimethylsilanyl)benzohexathia[7]helicene^{5b} to *rac*-1 and *rac*-2, the inner helix climbs and turns in-plane gradually and becomes larger, and the UV–vis absorption spectra red shifts with increasing of selenophene number. $(TMS)_2$ -DSS and $(TMS)_2$ -DST can be used not only as building blocks for selenophene-based helicenes but also for preparation of new types of organic functional materials based on selenophene.¹⁰ The current work provides a foundation for the development of selenophene chemistry.

EXPERIMENTAL SECTION

General Procedures and Materials. Ether and tetrahydrofuran (THF) for use on vacuum line were freshly distilled from sodium/ benzophenone prior to use. *t*-BuLi (pentane) and *n*-BuLi (hexane) were obtained from Energy Chemical prior to use, and their concentrations were determined by titration with *N*-pivaloyl-*o*-toluidine.¹¹ Column chromatography was carried out on silica gel (300–400 mesh). Analytical thin-layer chromatography was performed on glass plates of silica gel GF-254 with detection by UV. Standard techniques for synthesis under inert atmosphere, using gasbag and Schlenk glassware equipped with an 8 mm PTFE vacuum stopcock, were employed. All starting materials and reagents were commercially available.

¹H NMR and ¹³C NMR spectra were recorded on 300 or 400 MHz NMR instruments using CDCl₃ as solvent. IR spectra were obtained using an FT-IR instrument. HRMS analysis was carried out on a mass spectrometer equipped with DART-Positive. Melting point determination was taken on a Melt-Temp apparatus and was uncorrected. The X-ray crystallographic analyses were performed using crystals of compounds $(TMS)_2$ -DSS, rac-1, and rac-2 with sizes of $0.43 \times 0.16 \times$ 0.14, 0.41 \times 0.12 \times 0.09, and 0.34 \times 0.25 \times 0.06 mm, respectively. The intensity data were collected with the ω scan mode (296 K) on a diffractometer with a CCD detector using Mo K α radiation (λ = 0.71073 Å). The data were corrected for Lorentz and polarization effects, and absorption corrections were performed using SADABS program.¹² The crystal structures were solved using the SHELXTL program and refined using full-matrix least-squares.¹³ Further details are in the deposited CIF files. Slow evaporation of solutions of (TMS)₂-DSS, rac-1, and rac-2 in CHCl₃-CH₃OH (1:3, 2:3, 1:1, v/v) was employed for growing single crystals. The predicted absorption spectra were computed within the TD-DFT/PCM approaches based on B3LYP/6-31g* level. HOMO and LUMO distributions and isomerization barriers of rac-1-H and rac-2-H (i.e., the TMS replaced by hydrogen atom) were at the B3LYP/6-31g* level.

Synthesis of 2,5-Dibromoselenophene (3). Selenophene (1.76 g, 13.4 mmol) was dissolved in CHCl₃ (45 mL); NBS (5.26 g, 29.6 mmol, 2.2 equiv) was added in one portion, and afterward, the orange solution was stirred at room temperature for about 10 h. The reaction mixture was quenched with H₂O at room temperature, extracted with CH₂Cl₂ (3 × 15 mL), and then washed with saturated Na₂S₂O₃ (20 mL) and water (2× 20 mL). After being dried over MgSO₄, the solvent was removed under vacuum. The residue was purified by column chromatography on silica gel with petroleum ether (60–90 °C) as eluent to yield 3 (3.54 g, 91%) as a light yellow liquid. From another reaction on the 5.21 g scale of selenophene, 10.33 g (90%) of 3 was obtained: ¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.00 (s, 2H) (these data are agreement with the analyses reported in the literature).¹⁵

Synthesis of 2-Bromo-5-(trimethylsilanyl)selenophene (4). To a solution of 3 (1.95 g, 6.8 mmol) in dry ethyl ether (30 mL) was added *n*-BuLi (2.9 mL, 2.3 M in hexane, 6.7 mmol, 1.0 equiv) dropwise at -78 °C. After being kept at -78 °C for 2 h, TMSCI (1.3 mL, 10.2 mmol, 1.5 equiv) was added at -78 °C, and then the reaction mixture was kept at -78 °C for 0.5 h and warmed up slowly to ambient temperature overnight. The reaction mixture was quenched with H₂O at -78 °C, extracted with CH₂Cl₂ (3 × 20 mL), and then washed with H₂O (3× 25 mL). After being dried over MgSO₄, the solvent was removed under vacuum. The residue was purified by column chromatography on silica gel with petroleum ether (60–90 °C) as eluent to yield 4 (1.78 g, 94%) as a light yellow liquid. From another

reaction on the 11.71 g scale of 3, 10.43 g (91%) of 4 was obtained: ¹H NMR (CDCl₃, 400 MHz) δ (ppm) 7.28 (d, *J* = 3.6 Hz, 1H), 7.21 (d, *J* = 3.6 Hz, 1H), 0.29 (s, 9H) (these data are agreement with the analyses reported in the literature).¹⁵

Synthesis of 4-Bromo-2-(trimethylsilanyl)selenophene (5). n-BuLi (1.7 mL, 2.5 M in hexane, 4.3 mmol, 1.3 equiv) was added dropwise to diisopropylamine (0.7 mL, 5.0 mmol, 1.5 equiv) in THF (5 mL) at 0 °C. After 0.5 h at 0 °C, the prepared LDA solution was transferred by syringe into a solution of 4 (0.9361 g, 3.3 mmol) in THF (40 mL) at -78 °C. After 6 h at -78 °C, methanol was added to quench the reaction. The reaction mixture was extracted with CH₂Cl₂ $(3 \times 15 \text{ mL})$ and washed with saturated NaCl (20 mL) and H₂O $(2 \times 20 \text{ mL})$ and then dried over MgSO₄. After the removal of the solvent under vacuum, the residue was purified by column chromatography on silica gel with petroleum ether (60-90 °C) as eluent to yield 5 (0.8882 g, 95%) as a light yellow liquid. From another reaction on the 4.1059 g scale of 4, 3.7149 g (90%) of 5 was obtained: ^{1}H NMR (CDCl₃, 400 MHz) δ (ppm) 8.10 (s, 1 H), 7.41 (s, 1H), 0.31 (s, 9 H) (these data are agreement with the analyses reported in the literature).

Synthesis of 5,5'-Di(trimethylsilanyl)-3,3'-diselenophene (6). To a solution of 5 (0.8720 g, 3.1 mmol) in dry ethyl ether (20 mL) was added n-BuLi (1.2 mL, 2.5 M in hexane, 3.0 mmol, 1.0 equiv) dropwise at -78 °C. After being kept at -78 °C for 2 h, dry CuCl₂ (0.8310 g, 6.2 mmol, 2.0 equiv) was added. The reaction mixture was kept at -55 °C for 2 h and then warmed up slowly to ambient temperature overnight. The reaction mixture was quenched with methanol at -78 °C, extracted with CH₂Cl₂ (3 × 15 mL), and then washed with H_2O (3× 20 mL). After being dried over MgSO₄, the solvent was removed under vacuum. The residue was purified by column chromatography on silica gel with petroleum ether (60-90 °C) as eluent to yield 6 (0.5500 g, 88%) as a light yellow solid: mp 68-69 °C. From another reaction on the 3.3088 g scale of 5, 2.1660 g (91%) of **6** was obtained: ¹H NMR (CDCl₃, 400 MHz) δ (ppm) 8.28 (s, 2H), 7.76 (s, 2H), 0.35 (s, 18H); 13 C NMR (CDCl₃, 100 MHz) δ 148.63, 142.35, 136.51, 129.87, 0.29; HRMS (DART-Positive) m/z $[M + H]^+$ calcd for C₁₄H₂₃Se₂Si₂ 406.9663; found 406.9662; IR (KBr) 3124, 3026, 2947, 2892 cm⁻¹

Synthesis of 2,5-Di(trimethylsilanyl)diseleno[2,3-b:3',2'-d]thiophene ((TMS)₂-DST). n-BuLi (0.76 mL, 2.4 M in hexane, 1.9 mmol, 2.1 equiv) was added dropwise into a solution of 6 (0.3598 g, 0.9 mmol) in Et₂O (30 mL) at 0 $^{\circ}$ C, and then the reaction mixture was kept for 2 h. (PhSO₂)₂S (0.2851 g, 0.9 mmol, 1.02 equiv) was added at -78 °C; the reaction mixture was kept at -78 °C for 2 h and then warmed up slowly to ambient temperature overnight. The reaction mixture was quenched with methanol at -78 °Č, extracted with CH_2Cl_2 (3 × 15 mL), and then washed with water (3 × 10 mL). After being dried over MgSO4, the solvent was removed under vacuum. The residue was purified by column chromatography on silica gel with petroleum ether (60-90 °C) as eluent to yield (TMS)₂-DST (0.3284 g, 85%): mp 76-78 °C. From another reaction on the 1.70 g scale of 6, 1.49 g (82%) of (TMS)₂-DST was obtained: ¹H NMR (CDCl₃, 300 MHz) δ (ppm) 7.76 (s, 2H), 0.36 (s, 18H), ¹³C NMR (CDCl₃, 75 MHz) δ 150.61, 143.69, 143.54, 127.76, 0.24; HRMS (DART-Positive) m/z [M + H]⁺ calcd for C₁₄H₂₁SSe₂Si₂ 436.9232; found 436.9229; IR (KBr) 3037, 2956, 2894 cm⁻¹

Synthesis of 2,5-Di(trimethylsilanyl)diseleno[2,3-b:3',2'-d]selenophene ((TMS)₂-DSS). *n*-BuLi (3.3 mL, 2.4 M in hexane, 7.8 mmol, 2.1 equiv) was added dropwise into a solution of 6 (1.5026 g, 3.7 mmol) in Et₂O (30 mL) at 0 °C, and then the reaction mixture was kept for 2 h. Dry Se (metals basis) (1.4675 g, 18.6 mmol, 5.0 equiv) was added at -78 °C; the reaction mixture was kept at -55 °C for 2 h and then warmed up slowly to ambient temperature overnight. The reaction mixture was quenched with methanol at -78 °C, extracted with CH₂Cl₂ (3 × 25 mL), and then washed with water (3 × 30 mL). After being dried over MgSO₄, the solvent was removed under vacuum. The residue was purified by column chromatography on silica gel with petroleum ether (60–90 °C) as eluent to yield the mixture of (TMS)₂-DSS and 7. The mixture and Cu nanopowder were heated to 145 °C without use of any solvent for 0.5 h; (TMS)₂-DSS (1.3413 g) as a light yellow solid was obtained, and the preparation yield of $(TMS)_2$ -DSS from 6 was 75%: mp 125–127 °C. From another reaction on the 0.1061 g scale of 6, 0.0909 g (72%) of $(TMS)_2$ -DSS was obtained. ¹H NMR (CDCl₃, 400 MHz) δ (ppm) 7.79 (s, 2H), 0.36 (s, 18H); ¹³C NMR (CDCl₃, 100 MHz) δ 152.15, 145.61, 141.29, 129.24, 0.27; HRMS (DART-Positive) m/z [M + H]⁺ calcd for C₁₄H₂₁Se₃Si₂ 484.8672; found 484.8670; m/z [M + NH₃]⁺ calcd for C₁₄H₂₃Se₃Si₂N 500.8859; found 500.8621; IR (KBr) 3040, 2950, 2897 cm⁻¹.

Synthesis of 2-Bromo-5-(trimethylsilanyl)diseleno[2,3b:3',2'-d]thiophene (Selenophene) (8a, 8b). (TMS)₂-DST (0.3284 g, 0.76 mmol) was dissolved in CHCl₃ (20 mL), and NBS (0.1420 g, 0.80 mmol, 1.05 equiv) was dissolved in 16 mL of HOAc- $CHCl_3$ (v/v = 1/3) and added dropwise under stirring at 0 °C. After being stirred for 2 h, the reaction mixture was guenched with H₂O and extracted with CH_2Cl_2 (3 × 10 mL) and then washed with saturated NaHCO₃ (20 mL) and water (2 \times 20 mL). The organic layer was dried over anhydrous MgSO₄. After the solvent was removed under vacuum, the residue was washed with 3×5 mL of hexane to yield 8a (0.3001 g, 90%) as a reddish brown oil: ¹H NMR (CDCl₃, 300 MHz) δ (ppm) 7.68 (s, 1H), 7.63 (s, 1H), 0.37 (s, 9H); ¹³C NMR (CDCl₃, 75 MHz) δ 151.33, 143.93, 142.43, 139.76, 138.37, 127.41, 125.20, 114.68, 0.20; HRMS (DART-Positive) m/z [M + H]⁺ calcd for C11H12BrSSe2Si 442.7938; found 442.7933; IR (KBr) 3037, 2952, 2854 cm⁻¹.

8b: reddish brown oil in yield of 83% (0.0930 g); ¹H NMR (CDCl₃, 300 MHz) δ (ppm) 7.71 (s, 1H), 7.65 (s, 1H), 0.36 (s, 9H); ¹³C NMR (CDCl₃, 75 MHz) δ 152.84, 145.88, 142.09, 140.57, 136.02, 128.95, 126.75, 115.48, 0.23; HRMS (DART-Positive) m/z [M + H]⁺ calcd for C₁₁H₁₂BrSe₃Si 490.7382; found 490.7378; IR (KBr) 2945, 2852 cm⁻¹.

Synthesis of 5-Trimethylsilanyldiseleno[2,3-b:3',2'-d]thiophene(selenophene)-2-carbaldehyde (9a, 9b). n-BuLi (0.3 mL, 2.4 M in hexane, 0.75 mmol, 1.05 equiv) was added dropwise to 8a (0.3167 g, 0.72 mmol) in THF (30 mL) at -78 °C. After 2 h at -78 °C, DMF (0.1 mL, 1.44 mmol, 2.0 equiv) was added at -78 °C and kept for 0.5 h, then the reaction mixture warmed up slowly to ambient temperature overnight. The reaction mixture was quenched with H₂O and extracted with CH₂Cl₂ (3×15 mL). The organic layer was washed with saturated NaHCO₃ (20 mL) and water $(2 \times 20 \text{ mL})$ and then dried over MgSO₄. The residue was purified by column chromatography on silica gel with petroleum ether (60–90 °C)/ CH_2Cl_2 (v/v = 2/1) as eluent to yield **9a** (0.2017 g, 72%) as a brown solid: mp 126-128 °C; ¹H NMR (CDCl₃, 300 MHz) δ (ppm) 9.84 (s, 1H), 8.28 (s, 1H), 7.79 (s, 1H), 0.38 (s, 9H); ¹³C NMR (CDCl₃, 75 MHz) δ 184.12, 152.67, 150.62, 148.57, 144.37, 144.11, 141.21, 131.01, 127.26, 0.19; HRMS (DART-Positive) $m/z [M + H]^+$ calcd for C12H13OSSe2Si 392.8782; found 392.8779; IR (KBr) 2950, 2843, 1661 cm⁻

9b: brown solid in yield of 60% (0.1351 g); mp 143–145 °C; ¹H NMR (CDCl₃, 300 MHz) δ (ppm) 9.82 (s, 1H), 8.28 (s, 1H), 7.82 (s, 1H), 0.38 (s, 9H); ¹³C NMR (CDCl₃, 75 MHz) δ 183.74, 153.82, 152.08, 147.88, 145.88, 143.55, 142.03, 132.19, 128.67, 0.21; HRMS (DART-Positive) m/z [M + H]⁺ calcd for C₁₂H₁₃OSe₃Si 440.8226; found 440.8227; IR (KBr) 2966, 2902, 1646 cm⁻¹.

Synthesis of Bis(2-trimethylsilanyldiseleno[2,3-b:3',2'-d]thiophene(selenophene)-5-yl)ethane (10a, 10b). TiCl₄ (0.14 mL, 1.28 mmol, 5.0 equiv) was carefully added into dry THF (10 mL) at 0 °C. After being kept at 0 °C for 20 min, zinc dust (0.1675 g, 2.56 mmol, 10.0 equiv) was added, and then the mixture was refluxed at 100 °C for 2 h. After that, pyridine (0.11 mL, 1.28 mmol, 5.0 equiv) was added, and the mixture was refluxed for another 1 h. After being cooled to ambient temperature, a solution of **9a** (0.1000 g, 0.26 mmol) in dry THF (5 mL) was added, and the reaction mixture was refluxed at 100 °C for 18 h. The reaction was quenched with water at 0 °C, extracted with CH_2Cl_2 (3 × 15 mL), washed with saturated NaHCO₃ (15 mL) and H_2O (2 × 15 mL), and then dried over MgSO₄. After the solvent was removed in vacuum, the residue was washed with Et₂O $(3 \times 5 \text{ mL})$ to yield 10a (0.0397 g, 41%) as an orange solid: mp 231– 234 °C; ¹H NMR (CDCl₃, 300 MHz) (for a mixture of cis and trans isomers of 10a) δ (ppm) 7.71 (s), 7.62 (s), 7.48 (s), 6.97 (s), 6.76 (s),

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0.38 (s), 0.36 (s); the ratio of integral areas of the peaks is 1.5:1:0.5:0.5:1:4.5:9; ¹³C NMR (CDCl₃, 75 MHz) δ 151.28, 151.14, 148.93, 145.04, 144.37, 144.34, 142.76, 142.73, 141.33, 141.28, 140.13, 136.96, 127.67, 127.59, 126.16, 124.85, 123.56, 120.77, 0.23; HRMS (DART-Positive) m/z [M + H]⁺ calcd for C₂₄H₂₅S₂Se₄Si₂ 752.7592; found 752.7591; IR (KBr) 2955, 1648, 920, 833 cm⁻¹.

10b: orange solid in yield of 56% (0.0330 g); mp 258–260 °C; ¹H NMR (300 MHz, CDCl₃) δ (ppm) 7.74 (s, 2H), 7.51 (s, 2H), 6.98 (s, 2H), 0.37 (s, 18H); ¹³C NMR (CDCl₃, 75 MHz) δ 152.69, 150.33, 146.25, 143.39, 140.73, 135.13, 129.07, 124.93, 122.13, 0.26. HRMS (DART-Positive) m/z [M + H]⁺ calcd for C₂₄H₂₅Se₆Si₂ 848.6481; found 848.6477; IR (KBr) 2949, 2848, 1510, 916, 835 cm⁻¹.

Synthesis of 5,5'-Di(trimethylsilanyl)benzo[1,2-b:3,4-b']bis-(diseleno[2,3-b:3',2'-d]thiophene(selenophene)) (rac-1, rac-2). To a solution of 10a (0.0117 g, 0.016 mmol) in dry toluene (25 mL) were added iodine (0.0119 mg, 0.047 mmol, 3.0 equiv) and 2-methyloxirane (0.1 mL). The reaction solution was irradiated with a 450 W unfiltered Hg medium pressure lamp. The reaction was monitored by TLC every 15 min, and irradiation was stopped when the 10a was consumed. The reaction was quenched with saturated $Na_2S_3O_3$ (10 mL). The reaction mixture was extracted with CH_2Cl_2 $(3 \times 10 \text{ mL})$ and washed with H₂O $(3 \times 10 \text{ mL})$ and then dried over MgSO₄. After the solvent was removed in vacuum, the crude product was purified by PTLC with petroleum ether (60-90 °C)/CH2Cl2 (v/v = 3:1) as developer to yield rac-1 (0.0045 g, 39%) as a light yellow solid: mp 269–271 °C; ¹H NMR (CDCl₃, 300 MHz) δ (ppm) 7.70 (s, 2H), 7.28 (s, 2H), 0.04 (s, 18H); ¹³C NMR (CDCl₃, 75 MHz) δ 147.73, 146.39, 142.55, 142.44, 138.75, 138.41, 131.67, 130.00, 121.34, -0.04; HRMS (DART-Positive) $m/z [M + H]^+$ calcd for $C_{24}H_{23}S_2Se_4Si_2$ 750.7435; found 750.7435; IR (KBr) 3085, 3061, 2930 cm⁻¹.

rac-2: light yellow solid in yield of 35% (0.0034 g); mp >300 °C; ¹H NMR (CDCl₃, 300 MHz) δ (ppm) 7.72 (s, 2H), 7.31 (s, 2H), 0.03 (s, 18H); ¹³C NMR (CDCl₃, 75 MHz) δ 148.91, 148.05, 143.46, 140.52, 140.27, 137.87, 132.72, 131.01, 120.90, 0.04; HRMS (DART-Positive) m/z [M + H]⁺ calcd for C₂₄H₂₃Se₆Si₂ 846.6324; found 846.6323; IR (KBr) 3080, 3042, 2920, 2859 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.7b01362.

X-ray data for (TMS)₂-DSS (CIF)

X-ray data for *rac*-1 (CIF)

X-ray data for rac-2 (CIF)

Characterization data of all compounds; predicted UV/ vis spectra, HOMO and LUMO distributions; the calculated frontier orbital energies for *rac*-1 and *rac*-2; and isomerization barriers of *rac*-1-H and *rac*-2-H (PDF)

AUTHOR INFORMATION

Corresponding Authors

*E-mail: chunli79@126.com. *E-mail: hwang@henu.edu.cn.

L-man. mwangtonenu.eeu.e.

ORCID [©]

Chunli Li: 0000-0003-0707-2800

Author Contributions

[†]W.X. and L.W. contributed equally to this work.

Notes

The authors declare no competing financial interest.

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