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Diseleno[2,3-b:3#,2#-d]selenophene(DSS) and Diseleno[2,3-b:3#,2#-d]thiophene(DST): Building Blocks for the Construction of [7]Helicenes

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J. Org. Chem., **Just Accepted Manuscript** • DOI: 10.1021/acs.joc.7b01362 • Publication Date (Web): 27 Sep 2017

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1155 Sixteenth Street N.W., Washington, DC 20036

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Diseleno[2,3-*b*:3′,2′-*d*]selenophene(DSS) and Diseleno[2,3-*b*:3′,2′-*d*] thiophene(DST): Building Blocks for the Construction of [7]Helicenes

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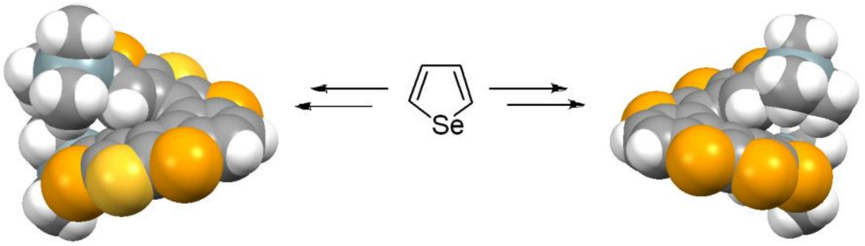


rac-**1** *rac*-**2**

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 series of thiahelicenes such as [5]-, [7]-, [9]-, [11]thiahelicenes.[3b,4] Wang *et al.* have reported 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 analog 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 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 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.

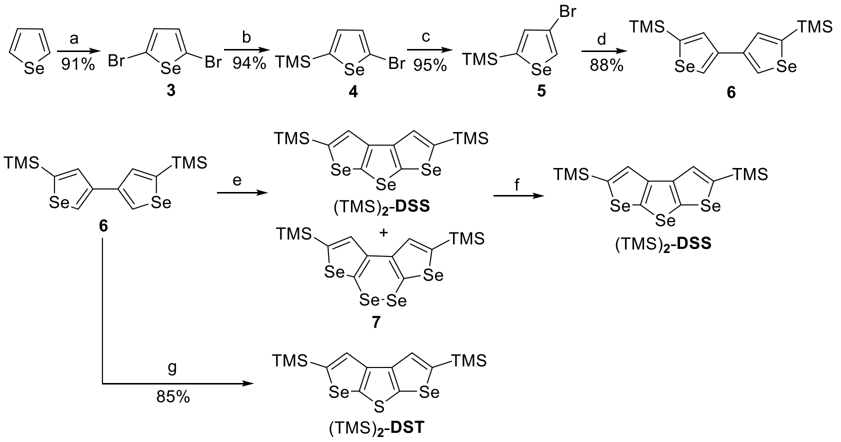
Synthesis of $(TMS)_2$-DSS, $(TMS)_2$-DST, *rac*-1, and *rac*-2

The synthetic route of $(TMS)_2$-**DSS** and $(TMS)_2$-**DST** is shown in Scheme 1. Through bromination, trimehtylsilanyl(TMS-) protection, bromine dance, $CuCl_2$ oxidative coupling, and cyclization with selenium and bis(phenylsulfonyl)sulfide ($(PhSO_2)_2S$), $(TMS)_2$-**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 literature method.[9] Following Br/Li exchange of **3** with *n*-BuLi, chlorotrimethylsilane was added to produce 5-bromo-2-trimethylsilanylselenophene(**4**) with 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 $CuCl_2$ to afford 5,5′-di(trimethylsilanyl)-3,3′-diselenophene(**6**) with 88% yield. *n*-BuLi was introduced to deproton in **6** to give dilithiated **6**. One side, 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 $(TMS)_2$-**DSS** and **7** mixture is problematic owing to their similar solubility and polarity. However, **7** can be successfully converted into $(TMS)_2$-**DSS** by heating mixture of **7** and Cu nanopowder at 140-150 ^{o}C for several minutes without solvent.

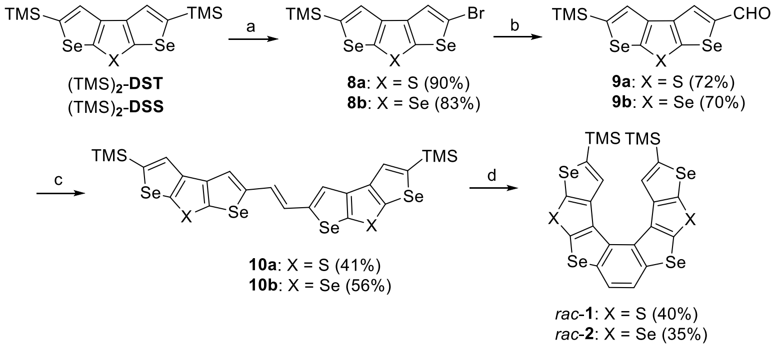
The preparation yield of $(TMS)_2$-**DSS** from **6** is about 75%. For another, $(TMS)_2$-**DST** can be prepared through reaction of dilithiated **6** and $(PhSO_2)_2S$ with 85% yield.

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 mixture solvent(HOAc-$CHCl_3$),[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-trimethylsilanyl-diseleno[2,3-*b*:3′,2′-*d*]selenophene-2-carbaldehyde(**9b**). After intermolecular McMurry reaction of **9a** and **9b** using $TiCl_4$/Zn/pyridine, bis(2-trimethylsilanyl-diseleno[2,3-*b*:3′,2′-*d*]thiophene-5-yl)ethane(**10a**) and bis(2-trimethylsilanyl-diseleno[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 in creating *rac*-**1** and *rac*-**2** with yields of 6.5% and 6.1%, respectively, are shown as follows.



Scheme 1. Synthetic route to $(TMS)_2$-**DSS** and $(TMS)_2$-**DST**[a]

[a]Reagents and conditions: (a) NBS(2.2 equiv), $CHCl_3$, r.t.; (b) (i) *n*-BuLi(1.0 equiv), Et_2O, -78 ^oC/2 h; (ii) TMSCl(1.5 equiv), -78 ^oC/0.5 h; (c) (i) LDA(1.3 equiv), THF, -78 ^oC/6 h; (d) (i) *n*-BuLi(1.0 equiv), Et_2O, -78 ^oC/2 h; (ii) $CuCl_2$(2.0 equiv), -55 ^oC/2 h to r.t.; (e) (i) *n*-BuLi(2.1 equiv), Et_2O, 0 ^oC/2 h; (ii) Se(5.0 equiv), -55 ^oC/2 h to r.t.; (f) Cu(5.0 equiv), 145 ^oC/0.5 h; (g) (i) *n*-BuLi(2.1 equiv), Et_2O, 0 ^oC/2 h; (ii) $(PhSO_2)_2S$(1.02 equiv), -78 ^oC/2 h.



Scheme 2. Synthetic route to *rac*-**1** and *rac*-**2**[a]

[a]Reagents and conditions: (a) NBS(1.05 equiv), $CHCl_3$/HOAc(8/1), 0 ^oC/2 h; (b) (i) *n*-BuLi(1.05 equiv), Et_2O, -78 ^oC/2 h; (ii) DMF(2.0 equiv), -78 ^oC/1 h; (c) $TiCl_4$(5.0

equiv), Zn(10.0 equiv), pyridine(5.0 equiv), THF; (d) *hv*, iodine(0.5 equiv), toluene.

Crystallographic analysis for (TMS)$_2$-DSS, *rac*-1, and *rac*-2

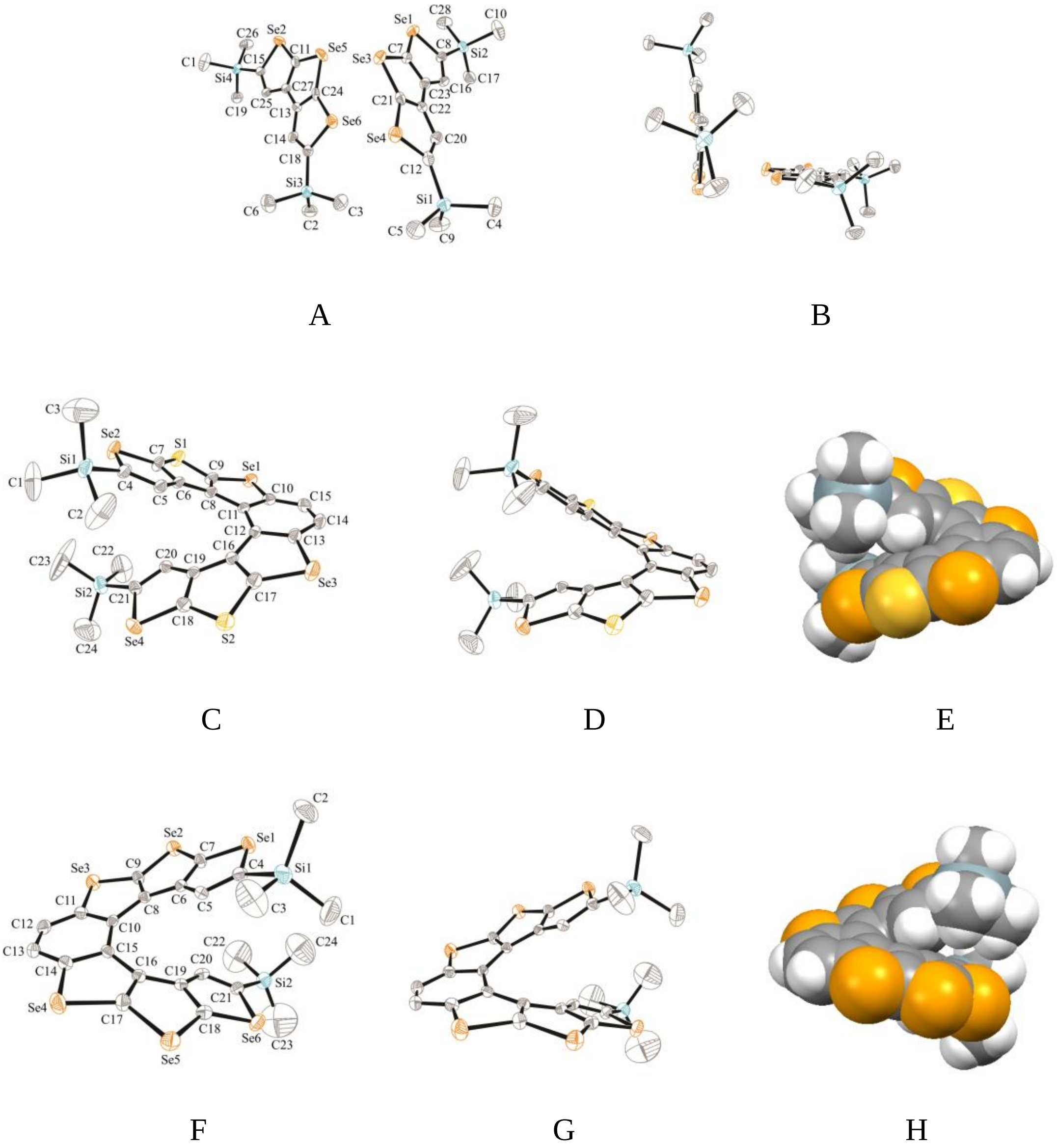


Figure 1. Molecular structures for (TMS)$_2$-**DSS**, *rac*-**1**, and *rac*-**2** and space fill mode for *rac*-**1** and *rac*-**2**. (A) Molecular structure for (TMS)$_2$-**DSS**, (B) side view for (TMS)$_2$-**DSS**, (C) molecular structure for *rac*-**1**, (D) side view for *rac*-**1**, (E) space fill mode for *rac*-**1**, (F) molecular structure for *rac*-**2**, (G) side view for *rac*-**2**, and (H)

space fill mode for *rac*-**2**. Carbon, selenium, sulfur, and silicon atoms are depicted with thermal ellipsoids set at 30% probability level, and all hydrogen atoms are omitted for clarity.

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(Figures 1A, 1B). The C25-C27-C13-C14 and C20-C22-C23-C16 torsion angles are 5.4^o and 4.3^o, respectively. The interplanar angle of two $(TMS)_2$-**DSS** molecules is 84.8^o. With the formation of benzene ring from **10a**, *rac*-**1** is compressed with helical structure(Figures 1C, 1D, 1E). 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^o and 12.3^o. With 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^o, which are 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^o) being smaller than that of C-S-C (90.1^o) 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(Figures 1F, 1G, 1H). The distance between H5A–H20A is 3.15 Å, which is larger than that of in *rac*-**1**. The interplanar angle between terminal selenophene rings is 49.0^{o}, which is smaller than that of in *rac*-**1**. The angles between the least-squares planes of neighboring rings are between 7.5^{o} and 10.8^{o}. With 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^{o}, which are larger than that of 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^{o}. 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[5b] to *rac*-**1** and *rac*-**2**, the inner helix climb and turn in-plane gradually become larger. The result shows that modification of the inner helix climb and turn in-plane of benzohetero[7]helicene, including thiophene and selenophene, can be achieved by changing the number of thiophenes and selenophenes.

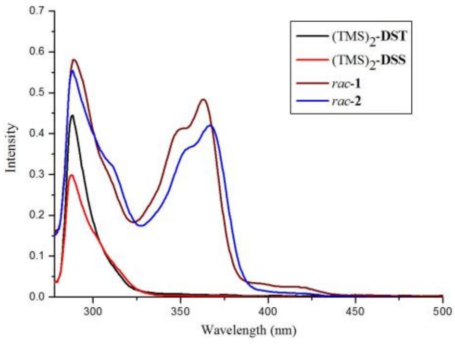


Figure 2. UV-vis absorption spectra of (TMS)$_2$-**DST**, (TMS)$_2$-**DSS**, *rac*-**1**, and *rac*-**2** in dichloromethane at room temperature([C] = 1×10^{-5} M).

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 bis(trimethylsilanyl)benzohexathia-[7]helicene (absorption peaks at 264, 332, and 347 nm).[5b] *Rac*-**1** and *rac*-**2** are significantly red-shifted than bis(trimethylsilanyl)benzohexathia[7]helicene and show two major absorption bands at 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 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 the 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→LUMO+10, HOMO−1→LUMO+5, and HOMO→LUMO+3. The absorption peaks of 349 and 363 nm in Band-II are characterized mainly by the contributions of HOMO−1→LUMO and HOMO→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 maximum absorption peak at 288 nm and 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→LUMO+2 and HOMO→LUMO+3, respectively. Absorption peaks in Band-II are characterized mainly by the contributions of HOMO→LUMO and HOMO−1→LUMO, respectively. 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 than bis(trimethylsilanyl)benzohexathia[7]helicene.[5b]

In addition, we have evaluated the transitions 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 Figure S36, 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 twofold 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 climb and turn in-plane gradually become 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, 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 stop-cock were employed. All starting materials and reagents were commercially available.

^{1}H NMR and ^{13}C NMR spectra were recorded on 300 or 400 MHz NMR instrument using $CDCl_3$ 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 the size 0.43 × 0.16 × 0.14, 0.41 × 0.12 × 0.09, 0.34 × 0.25 × 0.06 mm, respectively. The intensity data were collected with the ω scan mode (296 K) on diffractometer with CCD detector using Mo K_α radiation (λ = 0.71073Å). The data were corrected for Lorentz and polarisation 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 CIFs. Slow evaporation of solutions of $(TMS)_2$-**DSS**, *rac*-**1** and *rac*-**2** in $CHCl_3$-CH_3OH (1:3, 2:3, 1:1, v/v) was employed, respectively 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) at the b3lyp/6-31g* level.

Synthesis of 2,5-dibromoselenophene (3)

Selenophene (1.76 g, 13.4 mmol) was dissolved in $CHCl_3$ (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 H_2O at room temperature, extracted with CH_2Cl_2 (3 × 15 mL) and then washed with saturated $Na_2S_2O_3$ (20 mL) and water (2 × 20 mL). After drying over $MgSO_4$, the solvent was removed under vacuum. The residue was purified by column chromatography on silica gel with petrol ether (60-90 ^{o}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. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 7.00$ (s, 2H) (this data is 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), *n*-BuLi (2.9 mL, 2.3 M in hexane, 6.7 mmol, 1.0 equiv) was added dropwise at -78 ^{o}C. After keeping at -78 ^{o}C for 2 h, TMSCl (1.3 mL, 10.2 mmol, 1.5 equiv) was added at -78 ^{o}C, then the reaction mixture was kept at -78 ℃ for 0.5 h, then warmed up slowly to ambient temperature overnight. The reaction mixture was quenched with H_2O at -78 ^{o}C, extracted with CH_2Cl_2 (3 × 20 mL) and then washed with H_2O (3× 25 mL). After drying over $MgSO_4$, the solvent was removed under vacuum. The residue was purified by column chromatography on silica gel with petrol ether (60-90 ^{o}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. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 7.28 (d, J = 3.6 Hz, 1H), 7.21 (d, J = 3.6 Hz, 1H), 0.29(s, 9H) (this data is 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 ^{o}C. After 0.5 h at 0 ^{o}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 ^{o}C. After 6 h at -78 ^{o}C, methanol was added to quench the reaction. The reaction mixture was extracted with CH_2Cl_2 (3 ×15 mL) and washed with saturated NaCl (20 mL) and H_2O (2 × 20 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 ^oC) 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. ^1H NMR ($CDCl_3$, 400 MHz): δ 8.10 (s, 1 H), 7.41 (s, 1H), 0.31 (s, 9 H) (this data is agreement with the analyses reported in the literature).[15]

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), *n*-BuLi (1.2 mL, 2.5 M in hexane, 3.0 mmol, 1.0 equiv) was added dropwise at -78 ^oC. After keeping at -78 ^oC for 2 h, dry $CuCl_2$ (0.8310 g, 6.2 mmol, 2.0 equiv) was added. The reaction mixture was kept at -55 ^oC for 2 h, then warmed up slowly to ambient temperature overnight. The reaction mixture was quenched with methanol at -78 ^oC, extracted with CH_2Cl_2 (3 × 15 mL) and then washed with H_2O (3× 20 mL). After drying over $MgSO_4$, the solvent was removed under vacuum. The residue was purified by column chromatography on silica gel with petrol ether (60-90 ^oC) as eluent to yield **6** (0.5500 g, 88%) as a light yellow solid. Mp: 68-69 ^oC. From another reaction on the 3.3088 g scale of **5**, 2.1660 g (91%) of **6** was obtained. ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm) 8.28 (s, 2H), 7.76 (s, 2H), 0.35(s, 18H), ^{13}C NMR($CDCl_3$, 100 MHz): δ 148.63, 142.35, 136.51, 129.87, 0.29. HRMS (DART-Positive) *m*/*z*: $[M+H]^+$ calcd for $C_{14}H_{23}Se_2Si_2$ 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 Et_2O (30 mL) at 0 ^oC, then the reaction mixture was kept for 2 h. $(PhSO_2)_2S$ (0.2851 g, 0.9 mmol, 1.02 equiv) was added at -78 ^oC, the reaction mixture was kept at -78 ^oC for 2 h, then warmed up slowly to ambient temperature overnight. The reaction mixture was quenched with methanol at -78 ^oC, extracted with CH_2Cl_2 (3 × 15 mL) and then washed with water (3 × 10 mL). After drying over $MgSO_4$, the solvent was removed under vacuum. The residue was purified by column chromatography on silica gel with petrol ether (60-90 ^oC) as eluent to yield (TMS)$_2$-**DST** (0.3284 g, 85%). Mp: 76-78 ^oC. From another reaction on the 1.70 g scale of **6**, 1.49 g (82%) of (TMS)$_2$-**DST** was obtained. ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm) 7.76 (s, 2H), 0.36(s, 18H), ^{13}C NMR($CDCl_3$, 75 MHz): δ 150.61, 143.69, 143.54, 127.76, 0.24. HRMS (DART-Positive) *m*/*z*: $[M+H]^+$ calcd for $C_{14}H_{21}SSe_2Si_2$ 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 Et_2O (30 mL) at 0 ^oC, 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 ^oC, the reaction mixture was kept at -55 ^oC for 2 h, then warmed up slowly to ambient temperature overnight. The reaction mixture was quenched with methanol at -78 ^oC, extracted with CH_2Cl_2 (3 × 25 mL) and then washed with water (3 × 30 mL). After drying over $MgSO_4$, 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 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, 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. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 7.79 (s, 2H), 0.36(s, 18H), ^{13}C NMR($CDCl_3$, 100 MHz): δ 152.15, 145.61, 141.29, 129.24, 0.27. HRMS (DART-Positive) *m*/*z*: $[M+H]^+$ calcd for $C_{14}H_{21}Se_3Si_2$ 484.8672; found 484.8670, and *m*/*z*: $[M+NH_3]^+$ calcd for $C_{14}H_{23}Se_3Si_2N$ 500.8859; found 500.8621. IR(KBr): 3040, 2950, 2897 cm^{-1}

Synthesis of 2-bromo-5-(trimethylsilanyl)diseleno[2,3-*b*:3′,2′-*d*]thiophene (selenophene) (8a, 8b)

$(TMS)_2$-**DST** (0.3284 g, 0.76 mmol) was dissolved in $CHCl_3$ (20 mL), NBS (0.1420 g, 0.80 mmol, 1.05 equiv) was dissolved in 16 mL HOAc-$CHCl_3$ (v/v = 1/3) and added dropwise under good stirring at 0 °C. After stirring for 2 h, the reaction mixture was quenched with H_2O and extracted with CH_2Cl_2 (3 × 10 mL), then washed with saturated $NaHCO_3$ (20 mL) and water (2 × 20 mL). The organic layer was dried over anhydrous $MgSO_4$. After the solvent was removed under vacuum, the residue was washed with 3 × 5 mL hexane to yield **8a** (0.3001 g, 90%) as a reddish brown oil. ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm) 7.68 (s, 1H), 7.63 (s, 1H), 0.37(s, 9H), ^{13}C NMR($CDCl_3$, 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 $C_{11}H_{12}BrSSe_2Si$

442.7938; found 442.7933. IR(KBr): 3037, 2952, 2854 cm^{-1}.

8b: reddish brown oil in yield of 83% (0.0930 g), ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm) 7.71 (s, 1H), 7.65 (s, 1H), 0.36(s, 9H), ^{13}C NMR ($CDCl_3$, 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 $C_{11}H_{12}BrSe_3Si$ 490.7382; found 490.7378. IR(KBr): 2945, 2852 cm^{-1}.

Synthesis of 5-trimethylsilanyl-diseleno[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 ^{o}C. After 2 h at -78 ^{o}C, DMF (0.1 mL, 1.44 mmol, 2.0 equiv) was added at -78 ^{o}C and kept 0.5 h, then the reaction mixture warmed up slowly to ambient temperature overnight. The reaction mixture was quenched with H_2O, extracted with CH_2Cl_2 (3 × 15 mL). The organic layer was washed with saturated $NaHCO_3$ (20 mL) and water (2 × 20 mL), and then dried over $MgSO_4$. The residue was purified by column chromatography on silica gel with petrol ether (60-90 ^{o}C)/CH_2Cl_2(v/v = 2/1) as eluent to yield **9a** (0.2017 g, 72%) as a brown solid. Mp: 126-128 ℃. ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm) 9.84 (s, 1H), 8.28 (s, 1H), 7.79 (s, 1H), 0.38 (s, 9H). ^{13}C NMR($CDCl_3$, 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 $C_{12}H_{13}OSSe_2Si$ 392.8782; found 392.8779. IR(KBr): 2950, 2843, 1661 cm^{-1}.

9b: brown solid in yield of 60% (0.1351 g), Mp: 143-145 ^{o}C. ^{1}H NMR ($CDCl_3$, 300 MHz) *δ* (ppm) 9.82 (s, 1H), 8.28 (s, 1H), 7.82 (s, 1H), 0.38 (s, 9H). ^{13}C

NMR(CDCl$_3$, 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 $C_{12}H_{13}OSe_3Si$ 440.8226; found 440.8227. IR(KBr): 2966, 2902, 1646 cm^{-1}.

Synthesis of bis(2-trimethylsilanyl-diseleno[2,3-*b*:3′,2′-*d*]thiophene(selenophene)-5-yl)ethane (10a, 10b)

TiCl$_4$ (0.14 mL, 1.28 mmol, 5.0 equiv) was carefully added into dry THF (10 mL) at 0 ^{o}C. After keeping at 0 ^{o}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 ^{o}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 cooling 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 ^{o}C for 18 h. The reaction was quenched with water at 0 ^{o}C, then extracted with CH_2Cl_2 (3 × 15 mL) and washed with saturated $NaHCO_3$ (15 mL) and H_2O (2 × 15 mL), and then dried over $MgSO_4$. After removing the solvent in vacuum, the residue was washed with Et_2O (3 × 5 mL) to yield **10a** (0.0397 g, 41%) as a orange solid. Mp: 231-234 ^{o}C. ^{1}H NMR (CDCl$_3$, 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), 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. ^{13}C NMR (CDCl$_3$, 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 $C_{24}H_{25}S_2Se_4Si_2$ 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 ^{o}C. ^{1}H NMR (300 MHz, CDCl$_3$): *δ* (ppm) 7.74 (s, 2H), 7.51 (s, 2H), 6.98 (s, 2H), 0.37 (s, 18H) ^{13}C

NMR ($CDCl_3$, 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 $C_{24}H_{25}Se_6Si_2$ 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), iodine (0.0119 mg, 0.047 mmol, 3.0 equiv) and 2-methyloxirane (0.1 mL) was added. The reaction solution was irradiated with a 450 W unfiltered Hg medium pressure lamp. The reaction was monitored by TLC every 15 minutes, and irradiation was stopped when the **10a** was consumed up. The reaction was quenched with saturated $Na_2S_3O_3$ (10 mL). The reaction mixture was extracted with CH_2Cl_2 (3 × 10 mL) and washed with H_2O (3 × 10 mL), and then dried over $MgSO_4$. After removing the solvent in vacuum, the crude product was purified by PTLC with petrol ether (60-90 ^{o}C) /CH_2Cl_2 (v/v = 3:1) as developer to yield *rac*-**1** (0.0045 g, 39%) as a light yellow solid. Mp: 269-271 ^{o}C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm) 7.70 (s, 2H), 7.28 (s, 2H) , 0.04 (s, 18H). ^{13}C NMR ($CDCl_3$, 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 ^{o}C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm) 7.72 (s, 2H), 7.31 (s, 2H), 0.03 (s, 18H). ^{13}C NMR ($CDCl_3$, 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 $C_{24}H_{23}Se_6Si_2$ 846.6324; found 846.6323. IR(KBr): 3080, 3042, 2920, 2859 cm^{-1}.

Acknowledgment We gratefully acknowledge Mr. Pengtao Ma and Mr. Yuquan Feng for their assistance in the crystal measurements and discussion. This work is financially supported by the NSFC (51503056, U1304207, and 21672054), the Innovation Scientists and Technicians Troop Construction Projects of Henan Province (C20150011), and the Foundation for Distinguished Young Scientists of Henan University (YQPY20140056).

Supporting Information Available: Characterization data of all compounds; crystallographic CIF files of $(TMS)_2$-**DSS**, *rac*-**1**, and *rac*-**2**; 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 are included. This material is available free of charge at http://pubs.acs.org.

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