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# Selenophene-based Heteroacenes: Synthesis, Structures, and Physicochemical Behaviors

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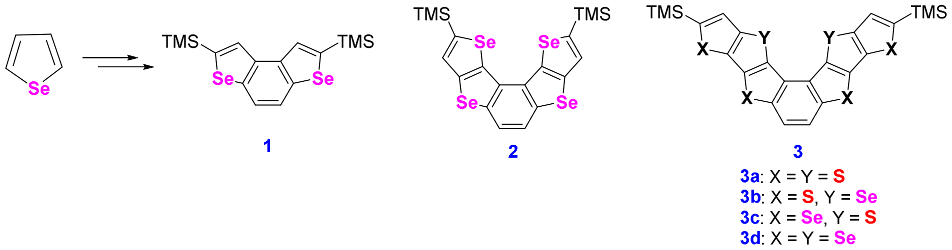


## Abstract

Based on three new building blocks, dithieno[3,2-*b*:2′,3′-*d*]selenophene (*tt*-**DTS**), diseleno[3,2-*b*:2′,3′-*d*]thiophene (*tt*-**DST**) and diseleno[3,2-*b*:2′,3′-*d*]selenophene (*tt*-**DSS**), four thiophene- and selenophene-based heteroacenes (**3a**-**d**) up to seven fused rings were designed and synthesized. Another two selenophene-based heteroacenes (**1** and **2**) with three and five fused rings were prepared. The molecular structures of **1**, **2**, **3a** and **3c** were confirmed by single-crystal analysis. The results showed that molecular structures, spectroscopy features and cyclic voltammetry behaviors could be modulated by changing the heteroatoms from sulfur to selenium for **3a-d** or changing the numbers of selenophene rings for **1**, **2** and **3d**.

## Introduction

Heteroacenes based on thiophene have been widely studied in the field of organic functional materials because of their extended conjugation, rigid planarity and their significant potential for applications in electronic devices.[1] Selenophene, bearing a heavy element selenium (Se) with a large polarizable radius, possesses advantageous properties compared with its lighter analog, namely, thiophene; moreover, with narrow optical band gap, strong intermolecular interactions, and well-aligned solid-state structure shows excellent charge-transport properties.[2,3]

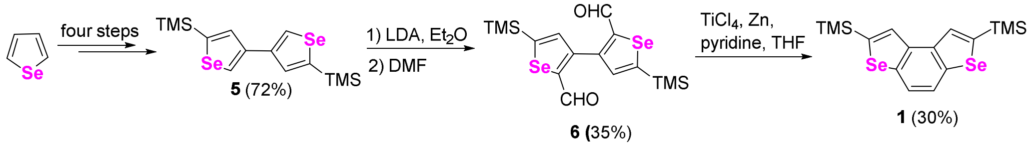
In atomic engineering, a promising method, a subtle change in molecular structure can significantly change the electronic, optical, and physical properties of a material.[4,5] Replacing sulfur with selenium might be a suitable method for fine-tuning the structure and property of thiophene-based heteroacene. In our recent research work, the inner helix climbs, turns in-plane, and the UV-vis absorption spectroscopy feature of benzohetero[7]helicene can be modulated by changing the number of sulfur and selenium atoms.[6] Although different synthesis methods have been established for thiophene-based heteroacenes,[1d,7] the synthesis access to selenophene-based heteroacenes remains high challenge, because of the generally high reactivity of the C–Se bond and the weak orbital overlap when selenium atom is involved.[4] Selenophene-based heteroacenes reported, usually have been prepared by intramolecular cyclization of Se to an ethynyl group.[8-12] Selenophene-based heteroacenes containing two or three rings have been synthesized through the intramolecular cyclization of substituted alkynes and 2,2′-biselenophene,[8] and including four[9], five[10] fused rings and selenophene as the outmost rings[4, 9a, 11] have been obtained via the intramolecular cyclization of Se to an ethynyl group. Yamaguchi *et al*. have reported the synthesis of thiophene- and selenophene-based heteroacenes containing seven fused rings through intramolecular triple cyclization of bis(o-haloaryl)diacetylenes and their single-crystal field-effect transistors properties.[12]

In the present work, intramolecular cyclization of dicarbanions and oxidative photocyclization have been applied to prepare thiophene- and selenophene-based heteroacenes. Three new building blocks, namely, *tt*-**DTS**, *tt*-**DST** and *tt*-**DSS**, and four kinds of thiophene- and selenophene-based heteroacenes up to seven fused rings, namely, **3a**-**d** and selenophene-based heteroacenes with three and five fused rings, namely, **1** and **2** are designed and synthesized. The crystal structures, spectroscopy features, and cyclic voltammetry behavior of the synthesized thiophene- and selenophene-based heteroacenes are studied. In addition, the energy levels and electron cloud distribution of the highest occupied molecular orbitals (HOMO) and the lowest unoccupied molecular orbitals (LUMO) orbitals are predicted.

## Results and Discussion

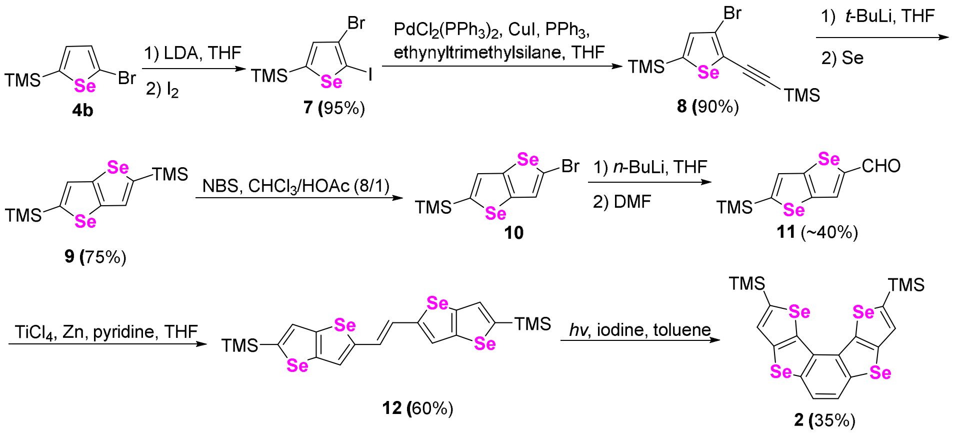
### Synthesis of (TMS)$_2$-*tt*-DTS, (TMS)$_2$-*tt*-DST, (TMS)$_2$-*tt*-DSS, 1, 2 and 3a-d

The synthetic route to **1** is shown in Scheme 1. 5,5′-bis(trimethylsilanyl)-3,3′-diselenophene (**5**) was prepared from selenophene through our previously reported methods.[6b] Following the deprotonate at the α positions in **5** with LDA, DMF was added to produce dialdehyde **6**. After intramolecular McMurry reaction of **6** using $TiCl_4$/Zn/pyridine, a new kind of selenophene-based heteroacene, namely, compound **1** was obtained. The total yield of **1** is 7.5% from selenophene through six step reactions.



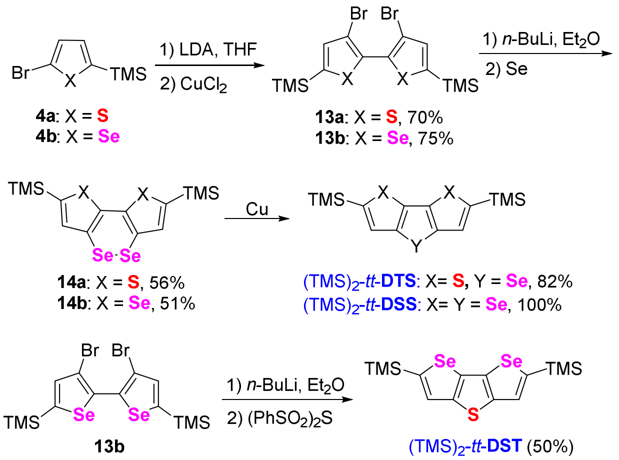
Scheme 1. Synthetic route to **1**

The synthetic route to **2** is shown in Scheme 2. In the synthesis of **2**, 2,5-bis(trimethylsilyl)seleno[3,2-*b*]selenophene (**9**) is the key intermediate and oxidative photocyclization in the final synthetic step is the crucial step. After the highly efficient bromine dance reaction of **4b** by using LDA in THF at -78 $^{o}$C, $I_2$ was added to prepare dihalogenation derivative **7**. Compound **8** was obtained in yield of 90% through the Sonogashira coupling reaction of **7** and ethynyltrimethylsilane. After the intramolecular cyclization in the presence selenium of dicarbanion from the Br/Li exchange on **8** with *t*-BuLi, **9** was obtained in 75% yield. Bromo-substituted derivatives **10** could be generated by treating **9** with NBS in a mixture solvent (HOAc-CHCl$_3$, v/v = 1/8).[6,7c] Through the same preparation methods as **6** and **1**, aldehyde **11** and substituted ethylene **12** were synthesized in yields of about 40% and 60%, respectively. After the oxidative photocyclization of **12** in the presence of iodine in dry toluene through irradiation of 450 W Hg medium pressure lamp for 40 minutes, 5,5'-bis(trimethylsilanyl)benzo[1,2-*b*:3,4-*b*']bis(seleno[3,2-*b*]- selenophene) **(2)** was obtained in yields of 35%. The total yield of **2** is about 4.0% from **4b** through seven step reactions.



Scheme 2. Synthetic route to **2**

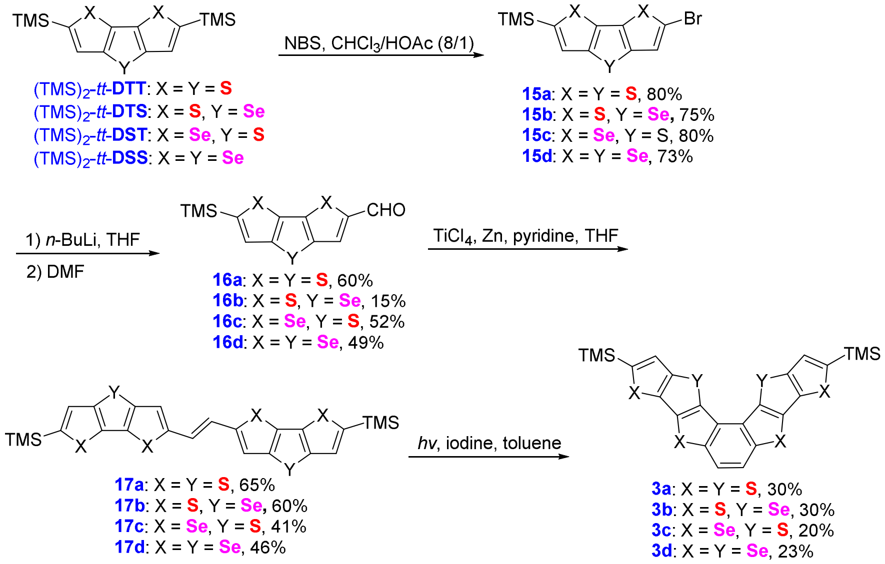
Scheme 3 shows the synthetic route of three novel thiophene- and selenophene-based building blocks, namely, *tt*-**DTS**, *tt*-**DST** and *tt*-**DSS**. Compounds **13a and 13b** were prepared according to the literature methods.[6b,8d-f] The strategy for synthesis of $(TMS)_2$-*tt*-**DTS**, $(TMS)_2$-*tt*-**DST** and $(TMS)_2$-*tt*-**DSS** is the intramolecular cyclization of the dicarbanion generated from **13a** and **13b** in the presence of selenium and $(PhSO_2)_2S$, respectively. After the double Br/Li exchange on **13a** and **13b** with *n*-BuLi, the cyclization with selenium generated [1,2]diseleninecyclohexadienes[6b] derivatives (**14a**, **14b**), instead of $(TMS)_2$-*tt*-**DTS** and $(TMS)_2$-*tt*-**DSS** with yield of 46% and 51%, respectively. The structure of **14a** and **14b** were confirmed by NMR and HRMS analyses. Compounds **14a** and **14b** were successfully converted into $(TMS)_2$-*tt*-**DTS** and $(TMS)_2$-*tt*-**DSS** by heating **14a** and **14b** with Cu nanopowder at 145 $^{o}$C for 30 minutes without any solvent. $(TMS)_2$-*tt*-**DST** was obtained with yield of 50% through cyclization of the dicarbanion from **13b** with $(PhSO_2)_2S$. The total yields of $(TMS)_2$-*tt*-**DTS**, $(TMS)_2$-*tt*-**DST** and $(TMS)_2$-*tt*-**DSS** are 3.2%, 3.8% and 3.8%, starting from **4a**, **4b** and **4b**, respectively.



Scheme 3. Synthetic route to $(TMS)_2$-*tt*-**DTS,** $(TMS)_2$-*tt*-**DST** and $(TMS)_2$-*tt*-**DSS**

The synthetic route of **3** (**3a**-**d**) is shown in Scheme 4. Compounds **3a**-**d** were synthesized from $(TMS)_2$-*tt*-**DTT**,[7c] $(TMS)_2$-*tt*-**DTS,** $(TMS)_2$-*tt*-**DST** and $(TMS)_2$-*tt*-**DSS**, respectively, through four steps: bromination, formylation, McMurry reaction, and photocyclization, and the total yields are 9%, 0.6%, 3%, and 4%, respectively. The oxidative photocyclization in the presence of iodine in dry toluene through irradiation of 450 W Hg medium pressure lamp is the crucial step in the synthesis of **3**.

2-Bromo-substituted derivatives **15a**-**d** were prepared with the similar method for making **10**. Starting from $(TMS)_2$-*tt*-**DTT**,[7c] $(TMS)_2$-*tt*-**DTS**, $(TMS)_2$-*tt*-**DST**, and $(TMS)_2$-*tt*-**DSS**, the yields are 80%, 75%, 80%, and 73%, respectively. Aldehydes **16a**-**d** were obtained according to the similar preparation procedure to **6** and **11**, by quenching of the carbanions of **15a**-**d** from the Li/Br exchange with DMF, the yields are 60%, 15%, 52%, and 49%, respectively. After the intermolecular McMurry reactions of **16a**-**d** using $TiCl_4$/Zn/pyridine, compounds **17a**-**d** were synthesized with yields of 65%, 60%, 41%, and 46%, respectively. After the oxidative photocyclization of **17a**-**d**, four kinds of thiophene- and selenophene-based heteroacenes, namely, **3a**-**d** were obtained in yields of 30%, 30%, 20%, and 23%, respectively.



Scheme 4. Synthetic route to **3**

## Crystallographic Analyses for 9, 1, 2, 3a and 3c

The molecular structures of **9**, **1**, **2**, **3a** and **3c** were confirmed by single-crystal analysis (Figure 1). Compound **9** belongs to the monoclinic, space group $P_12_1/n_1$. In **9**, two selenophene rings are almost completely coplanar (Figure 1a and b) and dihedral angle of two selenophene rings is 0.000(143)°. Compound **1** belongs to the monoclinic, space group $I_12/a_1$. In **1**, all the three rings are completely coplanar (Fig. 1c and d) and the torsion angle of C2–C3–C8–C9 is 1.629(785)°. With the formation of benzene ring from **12**, compound **2** was compressed with [5]helicene structure (Fig. 2a and b). Compound **2** belongs to the monoclinic, space group $P_12_1/c_1$. With the formation of benzene ring from **17a** and **17c**, **3a** and **3c** were compressed into [5]helicene-like structures containing seven fused rings (Figure 1g-j). Compound **3a** belongs to the orthorhombic, space group $P2_12_12_1$, and **3c** belongs to the monoclinic, space group C2/c. Five rings (ring-B to ring-F) in the middle of **3a** and **3c** form a [5]helicene-like structure with slight twisting. Compounds **2**, **3a** and **3c** were compared in terms of the dihedral angle between ring-B and ring-F, the sum of the three distortion angles derived from Se1, C4, C5, C10, C11, Se4 for **2**, S5, C13, C12, C7, C6, S2 for **3a** and S2, C13, C12, C7, C6, S1 for **3c**, the inner six atoms of from ring-B to ring-F helix climbs, and the distance of two terminal heteroatoms (for **3a** and **3c**); which increased with the increase of the numbers for selenium atoms (Table 1).

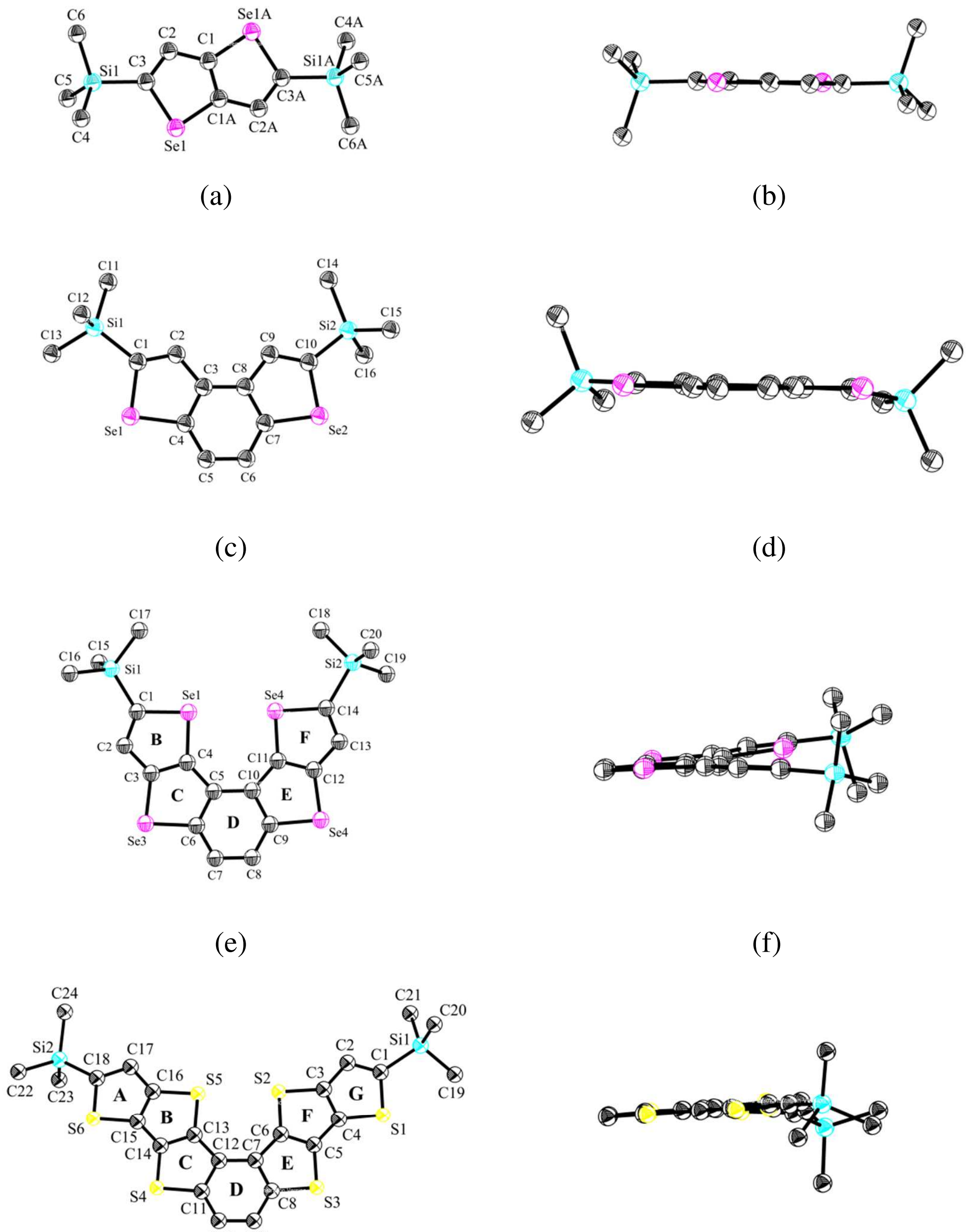
Table 1. Dihedral angles[a] (°), Distortion angles[b] (°), Helix climbs[c] (Å) and Distance[d] (Å).

| Compound | Dihedral angles | Distortion angles | Helix climbs | Distance |
|---|---|---|---|---|
| **3a** | 5.641(240) | 7.878(1821-1942) | 0.2490(28-29) | 11.2867(39) |
| **3c** | 10.583(169) | 13.276(1114-1185) | 0.4530(16-17) | 11.4741(12) |
| **2** | 11.711(131) | 15.510(7850-8220) | 0.4626(6) | --- |

[a] dihedral angle between ring-B and ring-F; [b] defined by the sum of the three distortion angles derived from Se1, C4, C5, C10, C11, Se4 for **2**, S5, C13, C12, C7, C6, S2 for **3a** and S2, C13, C12, C7, C6, S1 for **3c**; [c] the inner six atoms of from ring-B to ring-F helix climbs; [d] defined by the distance of two terminal heteroatoms (for **3a** and **3c**).

Compounds **3a** and **3c** possess a slightly distorted molecular geometry, leading to a herringbone arrangement in their crystals (Figure S94, 95). In the crystal packings of **3a** and **3c**, each **3a** molecule interacts with seven adjacent molecules through intermolecular interactions (S6-H21B (2.99 Å), S2-H23B (2.87 Å), C5-S3 (3.43 Å) and C4-S3 (3.46 Å), Figure S94), and each **3c** molecule interacts with six adjacent molecules through intermolecular interactions (S1-H22B (2.98 Å), Se1-H21B (3.04

Å), Se1-H21A (3.05 Å), C14-Se3 (3.43 Å), C15-Se3 (3.45 Å) and C10-Se4 (3.52 Å), Figure S95). Such multiple interactions are normally considered to be beneficial for their applications in organic electronic devices.[2]

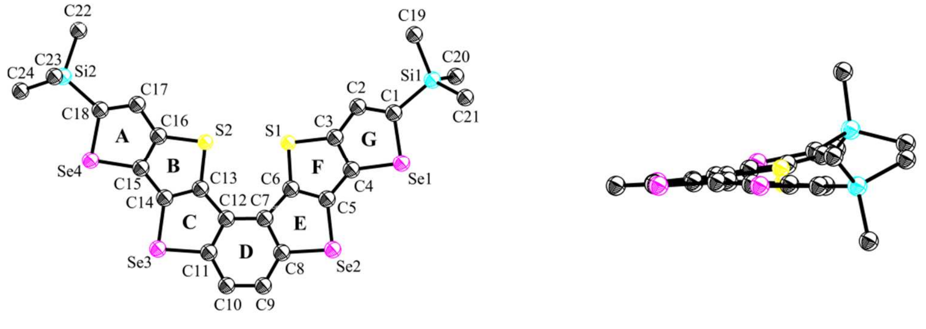


(a) (b)

(c) (d)

(e) (f)

(g) (h)



(i) (j)

Figure 1. The crystal structures (ball and stick) for **9**, **1**, **2**, **3a** and **3c**. (a) Top view for **9**; (b) side view for **9**; (c) Top view for **1**; (d) side view for **1**; (e) Top view for **2**; (f) side view for **2**; (g) Top view for **3a**; (h) side view for **3a**; (i) top view for **3c**; (j) side view for **3c**. All hydrogen atoms are omitted for clarity.

## Spectroscopy features and Electrochemical Properties

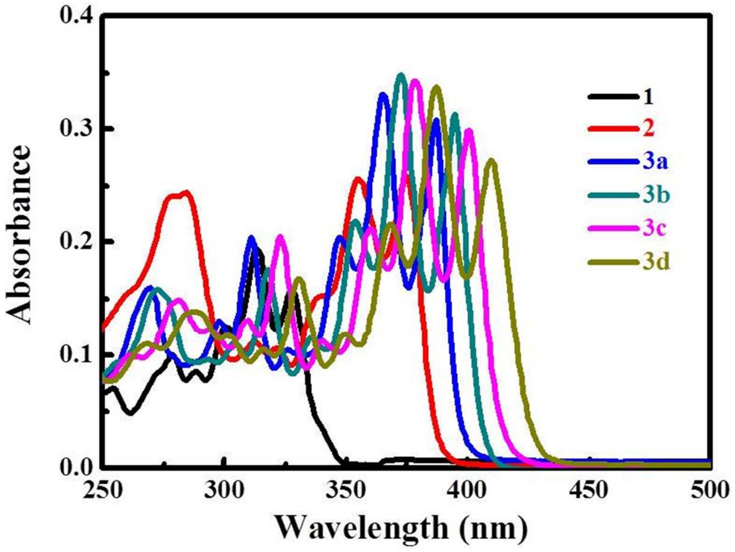


Figure 2. UV-vis absorption spectra of **1**, **2** and **3a-d** in $CH_2Cl_2$ ([C] = $1\times10^{-5}$ M).

Spectroscopy features and cyclic voltammetry behaviors of **1**, **2** and **3a-d** were studied. The UV-vis absorption spectra of **3a-d** are generally similar in shape and exhibit two major absorption bands within 250–355 nm (Band-I) and 335–440 nm (Band-II) (Figure 2). The effect of gradually changing the heteroatoms from sulfur to selenium is evident in the UV-vis absorption profiles. The progressive red-shifts in absorption spectra were found with the increasing of selenium atoms, with $\lambda_{max}$ values peaked at 365 to 373 to 379 to 387 nm from **3a** to **3d**, respectively. Compounds **1**, **2** and **3d** exhibit the maximum absorption peaks significantly red-shifted from 313 to 355 and 387 nm, respectively, with increasing of the number of selenophene (Figure 2). As a result, the optical band-gaps estimated from the absorption edges gradually narrowed down from **1** to **3d** (Table S3). Six sulfur atoms were replaced gradually by selenium atoms from **3a** to **3d**, the fluorescence intensity (Figure S85, 86), fluorescence quantum yield ($\Phi_F$, Figure S87, Table S1), and fluorescence lifetime rapidly decreased (Table S3). The decrease could be due to the fast intersystem crossing from the excited singlet state to the triplet state based on the stronger spin-orbit coupling arising from the heavy atom effect.[13] In 2-methyl tetrahydrofuran at 77 K, the fluorescence emission intensities of **3a**-**d** increased compared with the cases at room temperature, resulting in their fine structures. This phenomenon could be due to the disappearance of non-radiative deactivation processes from molecular vibrations and single bond rotation at 77 K (Figure S85).[14]

The cyclic voltammetry (CV) results of **1** and **2** show irreversible oxidation waves at $E_1^o = +1.55$ V for **1** and $E_1^o = +1.37$ V for **2**. Compounds **3a**-**d** show two reversible waves at $E_1^o = +1.31$ V and $E_2^o = +1.68$ V for **3a**, $E_1^o = +1.27$ V and $E_2^o = +1.60$ V for **3b**, $E_1^o = +1.25$ V and $E_2^o = +1.57$ V for **3c**, and $E_1^o = +1.22$ V and $E_2^o = +1.53$ V for **3d** (vs Fc/Fc$^+$, Figure S88). For compounds **1**, **2** and **3a**-**d**, the HOMO levels gradually increased, the LUMO levels gradually decreased, and the optical band gaps gradually narrowed down (Table S3). The influence of the replacement of sulfur with selenium of heteroacenes with seven fused rings (**3a**-**d**) is smaller than the change of the number for selenophene rings (**1**, **2** and **3d**). However, quantum chemistry calculation was then conducted using Gaussian 09[S1] to predict the energy levels (Table S3) and electron cloud distribution of the HOMO and LUMO orbitals for the six compounds. As presented in Figure 3, **1**, **2**, **3a**-**d** possess very similar HOMO and LUMO distributions, and their HOMO and LUMO orbitals are distributed over the aromatic cores. The calculated HOMO and LUMO levels are consistent with the experimental values (Table S3).

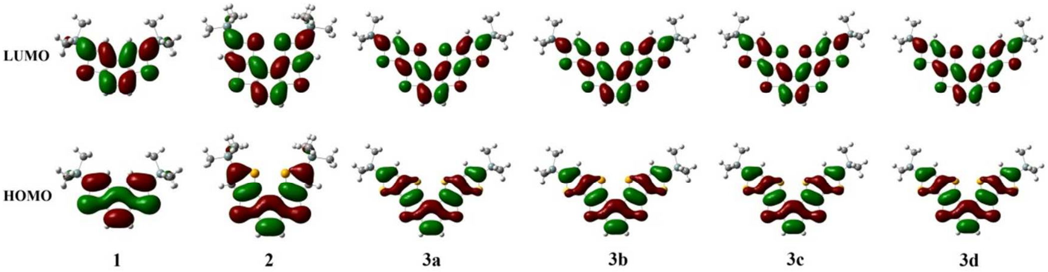


Figure 3. Visualized of HOMO and LUMO distributions (b3lyp/6-31g*) for **1**, **2**, **3a**-**d**.

In summary, three new building blocks, namely, *tt*-**DSS**, *tt*-**DST** and *tt*-**DTS**, were developed, which can be used not only to build thiophene- and selenophene-based heteroacenes but also to prepare new types of organic functional materials based on selenophene.[1e,15] On the one hand, four kinds of thiophene- and selenophene-based heteroacenes, namely, **3a**-**d** were successfully prepared using these building blocks. On the other hand, selenophene-based heteroacenes with three, five and seven fused rings, namely, **1**, **2** and **3d** were also synthesized from selenophene. Their crystal packings exhibit multiple short contacts, such as S···H, S···C, Se···H, and Se···C interactions, which may benefit the OFET properties.[1e,2] The UV-vis absorption peaks gradually red-shifted and the optical band-gaps gradually narrowed down with increasing the number of fused aromatic rings or replacing individual atoms from S to Se. This study provides a strategy for fine-tuning the molecular structure and its physicochemical behavior by replacing individual atoms or changing the numbers of aromatic ring of heteroacenes. This work definitely exhibits the intrinsic nature of fused heteroacenes and benefits both thiophene chemistry and 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.[16] 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. **4a**,[6,8e-f] **4b**,[6] building block of $(TMS)_2$-*tt*-**DTT** and **15a**[7c] were prepared according to the literature methods. All starting materials and reagents were commercially available.

$^1$H NMR and $^{13}$C{$^1$H}NMR spectra were recorded on 300 or 400 MHz NMR instrument using $CDCl_3$ as solvents. IR spectra were obtained using an FT-IR instrument. HRMS analysis was carried out on a mass spectrometer equipped with DART-Positive, MALDI_DHB and MALDI-FT_DHB. Melting point determination was taken on a Melt-Temp apparatus and was uncorrected. The X-ray crystallographic analyses were performed using crystals of compounds **9**, **1**, **2**, **3a** and **3c** with sizes of 0.39 × 0.25 × 0.22, 0.45 × 0.08 × 0.06, 0.30 × 0.19 × 0.14, 0.13 × 0.1 × 0.03 and 0.1 × 0.05 × 0.03 $mm^3$, respectively. The intensity data were collected with the ω scan mode (296 K) on a diffractometer with CCD detector using Cu Kα radiation ($\lambda$ = 1.54184 Å). The data were corrected for Lorentz and polarization effects, and absorption corrections were performed using SADABS program.[17] The crystal structures were solved using the SHELXTL program and refined using full-matrix least-squares.[18] Further details are in the deposited CIF files. Slow evaporation of solutions of **9**, **1**, **2**, **3a** and **3c** in $CHCl_3$-$CH_3OH$ (3:2 for **9**, **1**, **2** and **3a**, 3:1, v/v) were employed for growing single crystals. The fluorescence quantum yields ($\Phi_F$) of **3a-d** are characterized in dichloromethane with quinine sulfate in 0.1 N $H_2SO_4$ as the control.

### Synthesis of 5,5′-bis(trimethylsilanyl)-3,3′-biselenophene-2,2′-dicarbaldehyde (6)

*n*-BuLi (2.30 mL, 2.49 M in hexane, 5.71 mmol, 2.20 equiv) was added dropwise to diisopropylamine (0.81 mL, 5.71 mmol, 2.20 equiv) in dry ethyl ether (10 mL) at 0 °C. After 0.5 h at 0 °C, the prepared LDA solution was transferred by syringe into a solution of **5** (1.05 g, 2.60 mmol) in dry ethyl ether (40 mL) at -78 °C. After 2 h at -78 °C, DMF (0.60 mL, 7.60 mmol, 3.00 equiv) was added at -78 °C and kept 1 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 NaCl (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 °C) HEX/$CH_2Cl_2$ (v/v = 2/1) as eluent to yield **6**

(0.42 g, 35%) as a brown solid, mp: 165-166 °C. $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$ (ppm) 9.59 (s, 2H), 7.64 (s, 2H), 0.38 (s, 18H). $^{13}$C{$^1$H}NMR ($CDCl_3$, 75 MHz): $\delta$ 183.6, 160.8, 150.9, 146.3, 140.0, -0.1. MS (DART-Positive Ion Mode): m/z ) 461.0(83) [M$^+$]. HRMS (DART-FTICR) *m/z*: [M + H]$^+$ Calcd for $C_{16}H_{22}O_2Se_2Si_2$ 462.9562; Found 462.9559. IR (KBr): 3060, 2950, 1650, 1251, 954, 843 cm$^{-1}$.

### Synthesis of 2,7′-bis(trimethylsilanyl)benzo[1,2-*b*:4,3-*b′*]bis(selenophene) (1)

$TiCl_4$ (0.22 mL, 1.96 mmol, 5.00 equiv) was carefully added into dry THF (20 mL) at 0 °C. After keeping at 0 °C for 20 min, zinc dust (0.26 g, 3.92 mmol, 10.00 equiv) was added, and then the mixture was refluxed at 100 °C for 2 h. After that, pyridine (0.16 mL, 1.96 mmol, 5.00 equiv) was added and the mixture was refluxed for another 1 h. After cooling to ambient temperature, a solution of **6** (0.18 g, 0.39 mmol) in dry THF (10 mL) was added and the reaction mixture was refluxed at 100 °C for 18 h. The reaction was quenched with water at 0 °C, then extracted with $CH_2Cl_2$ (3 × 30 mL) and washed with saturated NaCl (25 mL) and $H_2O$ (2 × 25 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 **1** (0.05 g, 30%) as a yellow solid, mp: 152-154 °C. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ (ppm) 8.18 (s, 2H), 7.81 (s, 2H), 0.41 (s, 18H). $^{13}$C{$^1$H}NMR ($CDCl_3$, 100 MHz): $\delta$ 148.0, 141.9, 140.1, 132.4, 121.4, 0.2. MS (DART-Positive Ion Mode): m/z ) 430.0(100) [M$^+$ + 1]. HRMS (DART-FTICR) *m/z*: [M]$^+$ Calcd for $C_{16}H_{22}Se_2Si_2$ 429.9590; Found 429.9586. IR (KBr): 3061, 2950, 1390, 1251, 954, 843 cm$^{-1}$.

### Synthesis of 4-bromo-5-iodo-2-(trimethylsilanyl)selenophene (7)

*n*-BuLi (10.10 mL, 2.50 M in hexane, 25.34 mmol, 1.30 equiv) was added dropwise to diisopropylamine (4.10 mL, 29.24 mmol, 1.50 equiv) in THF (20 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 **4b** (5.50 g, 19.50 mmol) in THF (50 mL) at -78 $^{o}$C. After 6 h at -78 $^{o}$C, iodine (7.42 g, 29.24 mmol, 1.50 equiv) was added to quench the reaction. The reaction mixture was extracted with $CH_2Cl_2$ (3 × 15 mL) and washed with saturated $Na_2S_2O_3$ (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 $^{o}$C) as eluent to yield **7** (7.56 g, 95%) as a orange liquid. $^{1}$H NMR ($CDCl_3$, 300 MHz): $\delta$ (ppm) 7.24 (s, 1H), 0.29 (s, 9H). $^{13}$C{$^{1}$H}NMR ($CDCl_3$, 75 MHz): $\delta$ 155.9, 138.7, 123.1, 81.4, -0.1. MS (MALDI-FT_DHB): m/z 407.8(30) [M$^{+}$]. HRMS (MALDI-FT_DHB-FTICR) *m*/*z*: [M]$^{+}$ Calcd for $C_7H_{10}BrISeSi$ 407.7945; Found 407.7936. IR (KBr): 3042, 2958, 2857, 963, 1251, 843 cm$^{-1}$.

### Synthesis of 4-bromo-5-(trimethylsilyl)ethynyl-2-(trimethylsilanyl)selenophene (8)

To a degassed THF (10 mL) solution of compound **7** (3.60 g, 8.82 mmol) ethynyltrimethylsilane (1.20 mL, 9.26 mmol, 1.05 equiv), $PdCl_2(PPh_3)_2$ (1.72 g, 2.45 mmol, 0.03 equiv), CuI (0.47 g, 2.45 mmol, 0.03 equiv) and $PPh_3$ (0.07 g, 2.45 mmol, 0.03 equiv) were added. The resulting mixture was stirred for 10 h at 40 $^{o}$C, diluted with water (50 mL), extracted with $CH_2Cl_2$ (3×20 mL), 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 $^{o}$C) as eluent to yield **8** (3.00 g, 90%) as a pale yellow liquid. $^1$H NMR ($CDCl_3$, 300 MHz) $\delta$ (ppm) 7.32 (s, 1H), 0.29 (s, 9H)，0.26 (s, 9H). $^{13}$C{$^1$H}NMR ($CDCl_3$, 75 MHz): $\delta$ 151.4, 138.4, 127.4, 118.1, 106.2, 97.8, -0.1, -0.2. MS (MALDI-FT_DHB): m/z ) 378.9(50) [M$^+$]. HRMS (MALDI-FT_DHB-FTICR) *m*/*z*: [M + H]$^+$ Calcd for $C_{12}H_{19}BrSeSi_2$ 378.9447; Found 378.9449. IR (KBr): 3051, 2959, 2893, 1260, 954, 843 cm$^{-1}$.

**Synthesis of 2,5-bis(trimethylsilyl)seleno[3,2-*b*]selenophene (9)**

*t*-BuLi (22.00 mL, 1.18 M in *n*-pentane, 25.90 mmol, 2.05 equiv) was added dropwise into a solution of **8** (4.78 g, 12.63 mmol) in $Et_2O$ (100 mL) at -78 °C, then the reaction mixture was kept for 2 h. Dry Se (metals basis) (2.00 g, 25.30 mmol, 2.00 equiv) was added at -78 °C, the reaction mixture was kept at -78 °C for 1 h, then warmed up slowly to ambient temperature overnight. The reaction mixture was quenched with methanol at -78 °C, 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 **9** (3.59 g, 75%) as a pale yellow solid, mp: 127-128 $^o$C. $^1$H NMR ($CDCl_3$, 300 MHz) $\delta$ (ppm) 7.66 (s, 2H), 0.34 (s, 18H). $^{13}$C{$^1$H}NMR ($CDCl_3$, 75 MHz): $\delta$ 150.3, 147.0, 131.0, 0.1. MS (MALDI-FT_DHB): m/z ) 379.9(100) [M$^+$]. HRMS (MALDI-FT_DHB-FTICR) *m*/*z*: [M]$^+$ Calcd for $C_{12}H_{20}Se_2Si_2$ 379.9434; Found 379.9426. IR (KBr): 3042, 2958, 2883, 963, 843 cm$^{-1}$.

**Synthesis of 5-bromo-2-(trimethylsilanyl)seleno[3,2-*b*]selenophene (10)**

The compound of **9** (0.80 g, 2.11 mmol) was dissolved in $CHCl_3$ (20 mL), NBS (0.45 g, 2.54 mmol, 1.20 equiv) was dissolved in 16 mL HOAc-$CHCl_3$ (v/v = 1/8) 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 **10**. However, we could not obtained the pure **10** from the reaction mixture due to the too similar polarities from **9**, **10** and 2,5-dibromoselenopheno[3,2-*b*]selenophene in the mixture. $^1H$ NMR of crude product of **10**, $^1H$ NMR ($CDCl_3$, 300 MHz) $\delta$ (ppm) 7.56 (s, 1H), 7.51 (s, 1H), 0.34 (s, 9H).

### Synthesis of 5-(trimethylsilanyl)seleno[3,2-*b*]selenophene-2-carbaldehyde (11)

*n*-BuLi (0.91 mL, 2.40 M in hexane, 2.18 mmol, 1.05 equiv) was added dropwise to **10** (0.80 g, 2.08 mmol) in THF (40 mL) at -78 °C. After 2 h at -78 °C, DMF (0.32 mL, 4.15 mmoL, 2.00 equiv) was added at -78 °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 °C) HEX/$CH_2Cl_2$ (v/v = 2/1) as eluent to yield **11** (0.28 g, 40%) as a brown solid, mp: 59-60 °C. $^1H$ NMR ($CDCl_3$, 400 MHz) $\delta$ (ppm) 9.87 (s, 1H), 8.19 (s, 1H), 7.74 (s, 1H), 0.38 (s, 9H). $^{13}C\{^1H\}$NMR ($CDCl_3$, 100 MHz): $\delta$ 184.7, 158.2, 149.3, 148.8, 144.0, 134.9, 131.5, -0.1. MS (MALDI-FT_DHB): m/z 336.9(100) [$M^+$ + 1]. HRMS (MALDI-FT_DHB-FTICR) *m/z*: $[M + H]^+$ Calcd for $C_{10}H_{12}OSe_2Si$ 336.9061; Found 336.9056. IR (KBr): 3061, 2959, 1668, 954, 833 $cm^{-1}$.

### Synthesis of 1,2-bis(5-(trimethylsilanyl)seleno[3,2-*b*]selenophene-2-yl)ethene (12)

$TiCl_4$ (0.43 mL, 3.89 mmol, 5.00 equiv) was carefully added into dry THF (30 mL) at 0 °C. After keeping at 0 °C for 20 min, zinc dust (0.51 g, 7.78 mmol, 10.00 equiv) was added, and then the mixture was refluxed at 100 °C for 2 h. After that, pyridine (0.31 mL, 3.89 mmol, 5.00 equiv) was added and the mixture was refluxed for another 1 h. After cooling to ambient temperature, a solution of **11** (0.26 g, 0.78 mmol) in dry THF (15 mL) was added and the reaction mixture was refluxed at 100 °C for 18 h. The reaction was quenched with water at 0 °C, then extracted with $CH_2Cl_2$ (3 × 30 mL) and washed with saturated $NaHCO_3$ (25 mL) and $H_2O$ (2 × 25 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 **12** (0.15 g, 60%) as a yellow solid (a mixture of cis and trans isomers), mp: 239-240 °C. $^1H$ NMR ($CDCl_3$, 400 MHz) $\delta$ (ppm) 7.60 (s), 7.56 (s), 7.52 (s), 7.38 (s), 6.99 (s), 6.71 (s), 0.35 (s), 0.34 (s). The ratio of integral areas of the peaks at 6.99 and 6.71 ppm is 1.02:1.24. $^{13}C\{^1H\}$NMR ($C_2D_2Cl_4$, 353K, 100 MHz): $\delta$ 150.8, 148.5, 145.1, 140.2, 131.1, 125.2, 124.3, 0.0. MS (MALDI-FT_DHB): m/z ) 640.8(80) [$M^+$ + 1]. HRMS (MALDI-FT_DHB-FTICR) *m/z*: $[M + H]^+$ Calcd for $C_{20}H_{24}se_4Si_2$ 640.8150; Found 640.8145. IR (KBr): 3061, 2959, 1668, 954, 833 $cm^{-1}$.

### Synthesis of 4,4'-bis(trimethylsilanyl)benzo[1,2-*b*:3,4-*b*']bis(seleno[3,2-*b*] selenophene)[6] (2)

To a solution of **12** (0.02 g, 0.03 mmol) in dry toluene (25 mL) and iodine (0.02 g, 0.09 mmol, 3.00 equiv) were added. The reaction solution was irradiated with a 450

W unfiltered Hg medium pressure lamp for 40 minutes. 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) HEX/$CH_2Cl_2$ (v/v = 3:1) as developer to yield **2** (0.007 g, 35%) as a light red solid, mp: 276-277 $^{o}$C. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ (ppm) 7.82 (s, 2H), 7.81 (s, 2H), 0.46 (s, 18H). $^{13}$C{$^1$H}NMR ($CDCl_3$, 100 MHz): $\delta$ 150.9, 141.5, 140.5, 139.4, 133.0, 131.3, 123.2, 0.3. MS (MALDI-FT_DHB): m/z ) 638.8(80) [$M^+$ + 1]. HRMS (MALDI-FT_DHB-FTICR) *m/z*: $[M]^+$ Calcd for $C_{20}H_{22}Se_4Si_2$ 637.7921; Found 637.7910. IR (KBr): 3042, 2950, 1474, 963, 843 cm$^{-1}$.

### Synthesis of 3,3′-dibromo-5,5′-bis(trimethylsilanyl)-2,2′-dithienophene (13a)

*n*-BuLi (21.00 mL, 2.50 M in hexane, 52.90 mmol, 1.50 equiv) was added dropwise to diisopropylamine (7.50 mL, 52.90 mmol, 1.50 equiv) in THF (20 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 **4a** (8.30 g, 35.30 mmol) in THF (200 mL) at -78 $^{o}$C. After keeping at -78 $^{o}$C for 6 h, dry $CuCl_2$ (7.12 g, 52.90 mmol, 1.50 equiv) was added. The reaction mixture was kept at -78 $^{o}$C for 2 h, -55 $^{o}$C for 2 h, then warmed up slowly to ambient temperature overnight. The reaction mixture was quenched with methanol at -78 $^{o}$C, extracted with $CH_2Cl_2$ (3 × 35 mL) and then washed with saturated NaCl (40 mL) and $H_2O$ (2 × 40 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 $^{o}$C) as eluent to yield **13a** (5.79 g, 70%) as a light yellow solid. $^1$H NMR

(CDCl$_3$, 400 MHz): $\delta$ (ppm) 7.46 (s, 2H), 0.33 (s, 18H) (this data is agreement with the analyses reported in the literature).[8e]

Synthesis of 3,3′-dibromo-5,5′-di(trimethylsilanyl)-2,2′-diselenophene **(13b)** was synthesized according to the compound **13a** procedure. **13b**: light yellow solid in yield of 75% (0.90 g). $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ (ppm) 7.46 (s, 2H), 0.33 (s, 18H) (this data is agreement with the analyses reported in the literature).[8e]

### Synthesis of 2,7-bis(trimethylsilanyl)-dithieno[3,2-*c*:2′,3′-*e*][1,2]diseleninecyclohexadienes (14a)

*n*-BuLi (5.40 mL, 2.50 M in hexane, 13.45 mmol, 2.10 equiv) was added dropwise into a solution of **13a** (3.00 g, 2.13 mmol) in Et$_2$O (100 mL) at -78 °C, then the reaction mixture was kept for 2 h. Dry Se (metals basis) (2.53 g, 32.00 mmol, 5.00 equiv) was added at -78 °C, the reaction mixture was kept at -78 °C for 2 h, -55 °C for 2 h, then warmed up slowly to ambient temperature overnight. The reaction mixture was quenched with methanol at -78 °C, extracted with CH$_2$Cl$_2$ (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 **14a** (1.67 g, 56%) as a red solid, mp: 148-149 °C. $^1$H NMR (CDCl$_3$, 300 MHz): $\delta$ (ppm) 7.12 (s, 2H), 0.33 (s, 18H). $^{13}$C{$^1$H}NMR (CDCl$_3$, 75 MHz): $\delta$ 140.9, 140.2, 134.8, 117.9, -0.3. MS (DART-Positive): m/z ) 467.8 (100) [M$^+$]. HRMS (MALDI-TOF) *m*/*z*: [M]$^+$ Calcd for $C_{14}H_{20}Se_2S_2Si_2$ 467.8875; Found 467.8875. IR (KBr): 3051, 2958, 2884, 1669, 1251, 991, 852 cm$^{-1}$.

2,7-Bis(trimethylsilanyl)-diseleno[3,2-*c*:2′,3′-*e*][1,2]diseleninecyclohexadienes (**14b**) was synthesized according to the compound **14a** procedure. **14b**: red solid in yield of 51% (0.77 g), mp: 138-139 $^{o}$C. $^{1}$H NMR ($CDCl_3$, 400 MHz): $\delta$ (ppm) 7.43 (s, 2H), 0.32 (s, 18H). $^{13}C\{^{1}H\}$NMR ($CDCl_3$, 100 MHz): $\delta$ 149.1, 146.3, 137.6, 118.0, 0.0. MS (MALDI-FT_DHB): m/z 561.78(100) [$M^+$]. HRMS (MALDI-FT_DHB-FTICR) *m/z*: $[M + H]^+$ Calcd for $C_{14}H_{21}Se_4Si_2$ 564.7837; Found 564.7835. IR (KBr): 3033, 2963, 1275, 983, 830 cm$^{-1}$.

**Synthesis of 2,6-bis(trimethylsilanyl)selenopheno[3,2-*b*:4,5-*b*']dithiophene ((TMS)$_2$-*tt*-DTS)**

The compound **14a** (1.30 g, 2.79 mmol) and Cu nanopowder(0.89 g, 13.93 mmol, 5.00 equiv) were heated to 145 $^{o}$C without use of any solvent for 0.5 h. The residue was purified by column chromatography on silica gel with petrol ether (60-90 $^{o}$C) as eluent to yield (TMS)$_2$-*tt*-**DTS** (0.89 g, 82%) as a yellow solid. Mp: 118-119 $^{o}$C. $^{1}$H NMR ($CDCl_3$, 300 MHz): $\delta$ (ppm) 7.39 (s, 2H), 0.36 (s, 18H). $^{13}C\{^{1}H\}$NMR ($CDCl_3$, 75 MHz): $\delta$ 141.8, 141.2, 136.8, 129.7, -0.1. MS (DART-Positive): m/z ) 388.0 (100) [$M^+ + 1$]. HRMS (MALDI-TOF) *m/z*: $[M]^+$ Calcd for $C_{14}H_{20}SeS_2Si_2$ 387.9710; Found 387.9720. IR (KBr): 3061, 2958, 2902, 1640, 1251, 991, 843 cm$^{-1}$.

2,6-Bis(trimethylsilanyl)-diseleno[3,2-*b*:2′,3'-*d*]selenophene ((TMS)$_2$-*tt*-**DSS**) was synthesized according to the compound (TMS)$_2$-*tt*-**DTS** procedure. (TMS)$_2$-*tt*-**DSS**: yellow solid in yield of 100% (0.43 g), mp: 132-133 $^{o}$C. $^{1}$H NMR ($CDCl_3$, 400 MHz): $\delta$ (ppm) 7.66 (s, 2H), 0.36 (s, 18H). $^{13}C\{^{1}H\}$NMR ($CDCl_3$, 100 MHz): $\delta$ 149.1, 142.8, 139.8, 132.0, 0.2. MS (MALDI-FT_DHB): m/z ) 466.71(96)[$M^+$-15]. 481.86 (100) [$M^+$]. HRMS (MALDI-FT_DHB-FTICR) *m/z*: [M +

H]$^+$ Calcd for $C_{14}H_{21}Se_3Si_2$ 484.8672; Found 484.8668. IR (KBr): 3036, 2963, 1260, 937, 845 cm$^{-1}$.

### Synthesis of 2,6-bis(trimethylsilanyl)-diselenopheno[3,2-*b*:2′,3'-*d*]thiophene ((TMS)$_2$-*tt*-DST)

*n*-BuLi (0.70 mL, 2.4 M in hexane, 1.68 mmol, 2.10 equiv) was added dropwise into a solution of **13b** (0.45 g, 0.80 mmol) in $Et_2O$ (30 mL) at -78 °C, then the reaction mixture was kept for 2 h. $(PhSO_2)_2S$ (0.26 g, 0.82 mmol, 1.02 equiv) was added at -78 °C, the reaction mixture was kept at -78 °C for 2 h, -55 °C for 2 h, then warmed up slowly to ambient temperature overnight. The reaction mixture was quenched with methanol at -78 °C, extracted with $CH_2Cl_2$ (3 × 15 mL) and then washed with water (3× 15 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 (TMS)$_2$-*tt*-**DST** (0.17 g, 49%) as a light red solid. Mp: 108-109 °C. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ (ppm) 7.63 (s, 2H), 0.36 (s, 18H). $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$): $\delta$ 149.3, 145.1, 138.1, 129.2, 0.1. MS (DART- Positive): m/z) 435.92(100) [M$^+$]. HRMS (DART-FTICR) *m/z*: [M + H]$^+$ Calcd for $C_{14}H_{21}SSe_2Si_2$ 436.9228; Found 436.9229. IR (KBr): 3040, 2947, 1275, 983, 845 cm$^{-1}$.

### Synthesis of 6-bromo-2-(trimethylsilanyl)dithieno[3,2-*b*:2′,3′-*d*]thiophene (15a)

(TMS)$_2$-*tt*-**DTT** (0.44 g, 1.29 mmol) was dissolved in $CHCl_3$ (20 mL), NBS (0.24 g, 1.36 mmol, 1.05 equiv) was dissolved in 16 mL HOAc-$CHCl_3$ (v/v = 1/8) 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 **15a** (0.36 g, 80%) as a yellow solid. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ (ppm) 7.35 (s, 1H), 7.27 (s, 1H), 0.37(s, 9H) (this data is agreement with the analyses reported in the literature).[7c]

6-Bromo-2-(trimethylsilanyl)selenopheno[3,2-b:4,5-b']dithiophen (**15b**) was synthesized according to the compound **15a** procedure. **15b**: yellow solid in yield of 75% (0.61 g), mp: 171-172 °C. $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$ (ppm) 7.39 (s, 1H), 7.29 (s, 1H), 0.36 (s, 9H). $^{13}$C{$^1$H}NMR ($CDCl_3$, 75 MHz): $\delta$ 142.2, 140.3, 137.8, 136.8, 132.6, 129.3, 126.2, 111.5, -0.2. MS (DART-Positive): m/z ) 393.9 (100) [$M^+$]. HRMS (MALDI-TOF) *m/z*: $[M]^+$ Calcd for $C_{11}H_{11}BrS_2SeSi$ 393.8420; Found 393.8426. IR (KBr): 3098, 2958, 1632, 1251, 991, 843 $cm^{-1}$.

6-Bromo-2-(trimethylsilanyl)diselenopheno[3,2-*b*:2′,3′-*d*]thiophene (**15c**) was synthesized according to the compound **15a** procedure. **15c**: yellow solid in yield of 80% (0.27 g), mp: 97-98 °C. $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$ (ppm) 7.63 (s, 1H), 7.49 (s, 1H), 0.36 (s, 9H). $^{13}$C{$^1$H}NMR ($CDCl_3$, 75 MHz): $\delta$ 149.5, 143.8, 140.8, 137.8, 129.2, 128.8, 126.2, 113.7, 0.1. MS (MALDI-FT_DHB): m/z ) 442.8 (22) [$M^+ + 1$]. HRMS (MALDI-FT_DHB-FTICR) *m/z*: $[M + H]^+$ Calcd for $C_{11}H_{12}BrSSe_2Si$ 442.7938; Found 442.7934. IR (KBr): 3073, 2948, 1266, 995, 854 $cm^{-1}$.

6-Bromo-2-(trimethylsilanyl)diselenopheno[3,2-*b*:2′,3′-*d*]selenophene (**15d**) was synthesized according to the compound **15a** procedure. **15d**: yellow solid in yield of 73% (0.08 g), mp: 81-89 °C. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ (ppm) 7.66 (s, 1H), 7 .50 (s, 1H), 0.36 (s, 9H). $^{13}$C{$^1$H}NMR ($CDCl_3$, 100 MHz): $\delta$ 149.3, 142.0, 139.4, 138.9, 136.7, 131.5, 129.0, 113.6, 0.1. MS (MALDI-FT_DHB): m/z ) 488.7 (32) [$M^+ + 1$]. HRMS (MALDI-FT_DHB-FTICR) *m/z*: $[M + H]^+$ Calcd for $C_{11}H_{12}BrSe_3Si$ 490.7382; Found 490.7379. IR (KBr): 3040, 2960, 1253, 960, 854 $cm^{-1}$.

## Synthesis of 6-trimethylsilanyl-dithieno[3,2-*b*:2′,3'-*d*]thiophene-2-carbaldehyde (16a)

*n*-BuLi (0.84 mL, 2.40 M in hexane, 2.03 mmol, 1.05 equiv) was added dropwise to **15a** (0.67 g, 1.93 mmol) in THF (30 mL) at -78 °C. After 2 h at -78 °C, DMF (0.30 mL, 3.86 mmoL, 2.00 equiv) was added at -78 °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 °C) HEX/$CH_2Cl_2$ (v/v = 2/1) as eluent to yield **16a** (0.34 g, 60%) as a brown solid. Mp: 146-147 °C. $^1H$ NMR ($CDCl_3$, 400 MHz): $\delta$ (ppm) 9.95 (s, 1H), 7.95 (s, 1H), 7.41 (s, 1H), 0.39 (s, 9H). $^{13}C\{^1H\}$NMR ($CDCl_3$, 100 MHz): $\delta$ 182.8, 147.8, 147.5, 143.6, 141.8, 137.5, 135.4, 130.5, 126.7, -0.3. MS (DART-Positive): m/z ) 297.0 (100) [$M^+ + 1$]. HRMS (DART-FTICR) *m/z*: $[M + H]^+$ Calcd for $C_{12}H_{13}OS_3Si$ 296.9893; Found 296.9890. IR (KBr): 3072, 2958, 2819, 1650, 1232, 982, 842 $cm^{-1}$.

6-Trimethylsilanyl-selenopheno[3,2-*b*:4,5-*b*']dithiophene-2-carbaldehyde (**16b**) was synthesized according to the compound **16a** procedure. **16b**: brown solid in yield of 15% (0.08 g), mp: 149-151 °C. $^1H$ NMR ($CDCl_3$, 300 MHz): $\delta$ (ppm) 9.96 (s, 1H), 7.98 (s, 1H), 7.45 (s, 1H), 0.39 (s, 9H). $^{13}C\{^1H\}$NMR ($CDCl_3$, 75 MHz): $\delta$ 182.6, 146.8, 145.4, 143.2, 139.5, 139.2, 136.7, 133.3, 129.6, -0.3. MS (DART-Positive): m/z ) 344.9 (100) [$M^+$ + 1]. HRMS (DART-FTICR) *m/z*: $[M+H]^+$ Calcd for $C_{12}H_{13}OS_2{}^{74}SeSi$ 338.9396; Found 338.9397. IR (KBr): 3061, 2958, 2810, 1659, 991, 843 $cm^{-1}$.

6-Trimethylsilanyl-diselenopheno[3,2-*b*:2′,3'-*d*]thiophene-2-carbaldehyde (**16c**) was synthesized according to the compound **16a** procedure. **16c**: brown solid in yield of 52% (0.15 g); Mp: 160-163 °C. $^1H$ NMR ($CDCl_3$, 300 MHz): $\delta$ (ppm) 9.84 (s, 1H), 8.20 (s, 1H), 7.69 (s, 1H), 0.38 (s, 9H). $^{13}C\{^1H\}$NMR ($CDCl_3$, 75 MHz): $\delta$ 184.1, 154.5, 149.1, 148.2, 142.4, 140.8, 138.2, 133.5, 128.9, 0.0. MS (MALDI-FT_DHB): m/z ) 392.9(100) [$M^+$+1]. HRMS (MALDI-FT_DHB-FTICR) *m/z*: $[M+H]^+$ Calcd for $C_{12}H_{13}OSSe_2Si$ 392.8782; Found 392.8782. IR(KBr): 3066, 2960, 1642, 1219, 960, 831 $cm^{-1}$.

6-Trimethylsilanyl-diselenopheno[3,2-*b*:2′,3'-*d*]selenophene-2-carbaldehyde (**16d**) was synthesized according to the compound **16a** procedure. **16d**: brown solid in yield of 49% (0.11 g), Mp: 166-168 °C. $^1H$ NMR ($CDCl_3$, 300 MHz): $\delta$ (ppm) 9.84 (s, 1H), 8.21 (s, 1H), 7.72 (s, 1H), 0.38 (s, 9H). $^{13}C\{^1H\}$NMR ($CDCl_3$, 75 MHz): $\delta$ 183.9, 154.0, 148.0, 147.3, 143.0, 140.3, 139.8, 136.2, 131.7, 0.0. MS (MALDI-FT_DHB): m/z ) 440.8 (88) [$M^+$+ 1]. HRMS (MALDI-FT_DHB-FTICR) *m/z*: $[M + H]^+$ Calcd for $C_{12}H_{13}OSe_3Si$ 440.8226; Found 440.8228. IR (KBr): 3068, 2948, 1666, 1243, 960, 831 $cm^{-1}$.

**Synthesis of 1,2-bis(6-trimethylsilanyl-dithieno[3,2-*b*:2′,3'-*d*]thiophene-2-yl)ethene (17a)**

$TiCl_4$ (0.66 mL, 6.07 mmol, 5.00 equiv) was carefully added into dry THF (30 mL) at 0 °C. After keeping at 0 °C for 20 min, zinc dust (0.79 g, 12.14 mmol, 10.00 equiv) was added, and then the mixture was refluxed at 100 °C for 2 h. After that, pyridine (0.49 mL, 6.07 mmol, 5.00 equiv) was added and the mixture was refluxed for another 1 h. After cooling to ambient temperature, a solution of **16a** (0.36 g, 1.21 mmol) in dry THF (15 mL) was added and the reaction mixture was refluxed at 100 °C for 18 h. The reaction was quenched with water at 0 °C, then extracted with $CH_2Cl_2$ (3 × 30 mL) and washed with saturated $NaHCO_3$ (25 mL) and $H_2O$ (2 × 25 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 **17a** (0.22 g, 65%) as a orange solid. Mp: >300 °C. $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$ (ppm) 7.36 (s, 2H), 7.21(s, 2H), 7.08 (s, 2H), 0.38 (s, 18H). $^{13}$C{$^1$H}NMR ($CDCl_3$, 100 MHz): $\delta$ 143.7, 143.4, 143.0, 142.4, 135.8, 129.4, 126.7, 121.8, 119.8, -0.3. MS (DART Positive Ion Mode): m/z ) 561.0(100) [$M^+$ + 1]. HRMS (DART-FT-ICR) *m/z*: $[M + H]^+$ Calcd for $C_{24}H_{25}S_6Si_2$ 560.9814; Found 560.9814. IR (KBr): 3065, 2951, 1390, 1251, 991, 833 $cm^{-1}$.

1,2-Bis(6-trimethylsilanyl-selenopheno[3,2-*b*:4,5-*b*']dithiophen-2-yl)ethene (**17b**) was synthesized according to the compound **17a** procedure. **17b**: orange solid in yield of 60% (0.12 g), mp: >300 °C. $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$ (ppm) 7.40 (s, 2H), 7.25 (s, 2H), 7.08 (s, 2H), 0.38 (s, 18H). $^{13}$C{$^1$H}NMR ($CDCl_3$, 100 MHz): $\delta$ 142.8, 142.4, 141.3, 139.9, 137.4, 130.8, 129.6, 122.9, 121.6, -0.2. MS (DART-Positive): m/z 655.8 (100) [$M^+$]. HRMS (MALDI-TOF) *m/z*: $[M]^+$ Calcd for $C_{24}H_{24}S_4Se_2$Si2 655.8630; Found 655.8610. IR (KBr): 3070, 2958, 1623, 1251, 991, 843 $cm^{-1}$.

1,2-Bis(6-trimethylsilanyl-diselenopheno[3,2-*b*:2′,3'-*d*]thiophene-2-yl)ethene (**17c**) was synthesized according to the compound **17a** procedure. **17c**: orange solid in yield of 41% (0.04 g, a mixture of cis and trans isomers), mp: >300 °C. $^{13}$C NMR spectra were not recorded due to its poor solubility at 353K. $^{1}$H NMR ($CDCl_3$, 400 MHz) for a mixture of cis and trans isomers of **17c**. $\delta$ (ppm) 7.64 (s), 7.63 (s), 7.50 (s), 7.37 (s), 6.99 (s), 6.75 (s), 0.37 (s), 0.35(s). The ratio of integral areas of the peaks at 6.99 and 6.75 ppm is 0.60:1.00. MS (MALDI-FT_DHB): m/z ) 748.8 (90) [$M^+$]. HRMS (MALDI-FT_DHB-FTICR) *m/z*: $[M + H]^+$ Calcd for $C_{24}H_{25}Se_4S_2Si_2$ 752.7592; Found 752.7592. IR (KBr): 3063, 2960, 984, 843 cm$^{-1}$.

1,2-Bis(6-trimethylsilanyl-diselenopheno[3,2-*b*:2′,3'-*d*]selenophene-2-yl)ethene (**17d**) was synthesized according to the compound **17a** procedure. **17d**: orange solid in yield of 46% (0.03 g, a mixture of cis and trans isomers), Mp: >300 °C. $^{1}$H NMR ($CDCl_3$, 400 MHz) for a mixture of cis and trans isomers of **17d**. $\delta$ (ppm) 7.673 (s), 7.668(s), 7.526 (s), 7.399 (s), 6.988 (s), 6.738 (s), 0.369 (s), 0.351 (s). The ratio of integral areas of the peaks at 6.988 and 6.738 ppm is 1.00:0.93. $^{13}C\{^{1}H\}$NMR ($C_2D_2Cl_4$, 353K, 100 MHz): $\delta$ 149.8, 147.4, 143.1, 141.3, 139.9, 133.6, 131.7, 125.3, 124.8, 0.0. MS (MALDI-FT_DHB): m/z ) 844.7 (100) [$M^+$ + 1]. HRMS (MALDI-FT_DHB-FTICR) *m/z*: $[M + H]^+$ Calcd for $C_{24}H_{25}Se_6Si_2$ 848.6481; Found 848.6484. IR(KBr): 3050, 2948, 972, 843 cm$^{-1}$.

### Synthesis of 4,4'-bis(trimethylsilanyl)benzo[1,2-*b*:3,4-*b*']bis(dithieno[3,2-*b*:2′,3'-*d*] thiophene) (3a)[6]

To a solution of **17a** (0.010 g, 0.018 mmol) in dry toluene (25 mL), iodine (0.014 g, 0.050 mmol, 3.00 equiv) was added. The reaction solution was irradiated with a

450 W unfiltered Hg medium pressure lamp for 40 minutes. 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) HEX/$CH_2Cl_2$ (v/v = 3:1) as developer to yield **3a** (0.003 g, 30%) as a light yellow solid, mp: >300 $^{o}$C. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ (ppm) 7.83(s, 2H), 7.51 (s, 2H), 0.42 (S, 18H), $^{13}$C{$^1$H}NMR (100MHz, $CDCl_3$): $\delta$ 144.3, 144.2, 139.3, 136.0, 135.9, 129.9, 127.2, 126.6, 120.0, -0.1. MS (DART-Positive Ion Mode): m/z ) 559.0 (96) [$M^+$ + 1]. HRMS (DART-FTICR) *m/z*: $[M + H]^+$ Calcd for $C_{24}H_{23}S_6Si_2$ 558.9657; Found 558.9656. IR (KBr): 3065, 2958, 1399, 1334, 1251, 991, 842 cm$^{-1}$.

4,4'-Bis(trimethylsilanyl)benzo[1,2-*b*:3,4-*b*']bis(selenopheno[3,2-*b*:4,5-*b*']dithiophene) (**3b**)[6] was synthesized according to the compound **3a** procedure. **3b**: light yellow solid in yield of 30% (0.005 g), mp: >300 $^{o}$C. $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$ (ppm) 7.83 (s, 2H), 7.53 (s, 2H), 0.42 (s, 18H). $^{13}$C{$^1$H}NMR ($CDCl_3$, 100 MHz): $\delta$ 143.8, 142.0, 139.0, 137.3, 133.5, 131.2, 130.0, 129.3, 119.9, -0.1. MS (DART-Positive): m/z ) 653.8 (100) [$M^+$]. HRMS (MALDI-TOF) *m/z*: $[M]^+$ Calcd for $C_{24}H_{22}S_4Se_2Si_2$ 653.8474; Found 653.8495. IR (KBr): 3061, 2968, 1632, 1251, 991, 843 cm$^{-1}$.

4,4'-Bis(trimethylsilanyl)benzo[1,2-*b*:3,4-*b*']bis(diseleno[3,2-*b*:2′,3'-*d*]thiophene) (**3c**)[6] was synthesized according to the compound **3a** procedure. **3c**: light yellow solid in yield of 20% (0.0024 g), mp: 292-294 $^{o}$C. $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$ (ppm) 7.81 (s, 2H), 7.78 (s, 2H) , 0.41 (s, 18H). $^{13}$C{$^1$H}NMR ($CDCl_3$, 100 MHz): $\delta$ 151.31, 145.23, 141.08, 137.93, 137.90, 131.23, 130.83, 128.83, 123.04, 0.18. MS

(DART-Positive): m/z ) 749.7(100) [M$^+$ + 1]. HRMS (DART-FTICR) *m*/*z*: [M + H]$^+$ Calcd for $C_{24}H_{23}S_2Se_4Si_2$ 750.7435; Found 750.7435. IR (KBr): 3070, 2964, 2922, 2853, 1098, 803 cm$^{-1}$.

4,4'-Bis(trimethylsilanyl)benzo[1,2-*b*:3,4-*b*']bis(diseleno[3,2-*b*:2′,3'-*d*]selenophene) (**3d**)[6] was synthesized according to the compound **3a** procedure. **3d**: light yellow solid in yield of 23% (0.003 g), mp: 295-297 °C. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ (ppm) 7.81 (s, 2H), 7.79 (s, 2H), 0.41 (s, 18H). $^{13}$C{$^1$H}NMR (CDCl$_3$, 100 MHz): $\delta$ 151.4, 143.5, 141.1, 139.8, 135.9, 133.6, 132.9, 131.4, 122.9, 0.2. MS (DART-Positive): m/z ) 840.6 (84) [M$^+$]. HRMS (DART-FTICR) *m*/*z*: [M + H]$^+$ Calcd for $C_{24}H_{23}Se_6Si_2$ 846.6324; Found 846.6328. IR (KBr): 3053, 2959, 2921, 2852, 1095, 804 cm$^{-1}$.

**Supporting Information Available:** NMR and HRMS spectra, fluorescence spectra, and computational data, crystallographic CIF files of **9**, **1**, **2**, **3a** and **3c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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