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Synthesis and Molecular Properties of Tricyclic Biselenophene-Based Derivatives with Nitrogen, Silicon, Germanium, Vinylidene, and Ethylene Bridges

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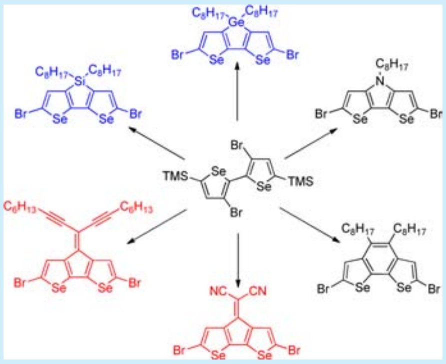
Supporting Information

ABSTRACT: A new class of biselenophene-based materials including an sp^3-silicon-bridged diselenosilole (**DSS**), an sp^3-germanium-bridged diselenogermole (**DSG**), and an sp^3-nitrogen-bridged diselenopyrrole (**DSP**) as well as an sp^2-vinylidene-bridged dicyanodiselenofulvene (**CDSF**), a diacetylenediselenofulvene (**ADSF**), and a dioctylethylene-bridged benzodiselenophene (**BDS**) have been successfully synthesized and characterized. The bridging moieties play an important role in determining the optical and electrochemical properties. The six brominated derivatives are ready to construct various biselenophene-based conjugated materials with tunable properties for organic photovoltaics and field effect transistors.



Thiophene is the most ubiquitous component to comprise enormous optoelectronic materials due to its tunable molecular properties and well-developed synthetic chemistry.[1] Coplanar tricyclic bithiophene-based materials where the 3,3′-positions of the bithiophene are fastened by different bridging atoms have been demonstrated as superior building blocks to construct considerable solution-processable organic materials utilized in a broad spectrum of diverse applications such as organic field-effect transistors (OFETs), polymer solar cells (PSCs), and organic dye-sensitized solar cells (DSSCs). The molecular properties of these tricyclic skeletons could be modulated by changing the bridging moiety embedded in a central aromatic or heterocyclic ring. The carbon-bridged 4*H*-cyclopenta[2,1-*b*:3,4-*b*′]dithiophene (**CPDT**) units have been extensively used to construct successful donor−acceptor copolymers for PSCs,[2] while the nitrogen-bridged dithienopyrrole (**DTP**) units have been employed as the strong electron-releasing donor in the donor−acceptor materials.[3] The silicon-bridged dithienosilole (**DTS**) units with longer carbon−silicon bond lengths have been incorporated into the polymers and small dye molecules, showing a higher degree of crystallinities and thus prominent solar cell performances.[4] More recently, the germanium-bridged dithienogermole (**DTG**) units with improved chemical stability also emerged as promising materials.[5] Selenophene is an analogue of thiophene with selenium replacing the sulfur atom. Selenophene and its polymers have several potential advantages over their thiophene counterparts and received growing attention for the applications in OFETs and PSCs.[6] Theoretical calculations unveil that polyselenophene has the more quinoidal character and less tendency of twisting than polythiophene, resulting in a smaller band gap of 1.6 eV.[7] Furthermore, selenium is more polarizable than sulfur, which might induce an intermolecular Se−Se interaction.[8] These properties are beneficial characteristics for improving light-harvesting ability and charge carrier mobility. Nevertheless, compared to the thiophene analogues, the development of the selenophene-based materials is more scarce because the functional group transformations of selenophene are more challenging and thus have not been well explored. Consequently, the synthesis of tricyclic biselenophene-based derivatives with intriguing molecular properties is highly desirable and worthy of in-depth investigation. Herein, for the first time, we report a new class of tricyclic biselenophene-based materials, including an sp^3-silicon-bridged diseleno[3,2-*b*:2′,3′-*d*]silole (**DSS**), an sp^3-germanium-bridged diseleno[3,2-*b*:2′,3′-*d*]germole (**DSG**), and an sp^3-nitrogen-bridged diseleno[3,2-*b*:2′,3′-*d*]pyrrole (**DSP**). Furthermore, more planar derivatives, an sp^2-vinylidene-bridged dicyanodiselenofulvene (**CDSF**) and diacetylenediselenofulvene (**ADSF**), as well as a dioctylethylene-bridged benzo[2,1-*b*:3,4-*b*′]diselenophene (**BDS**) were also developed. The α-positions of the outer selenophene units in the six materials were brominated to form **Br-BDS**, **Br-DSP**, **Br-DSS**, **Br-DSG**, **Br-CDSF**, and **Br-ADSF** building blocks which are ready for the extension of π-conjugation to prepare a variety of novel polymers as well as small molecules. All the materials in this research are derived from an identical starting material, 3,3′-dibromo-5,5′-bistrimethylsilyl-2,2′-biselenophene compound

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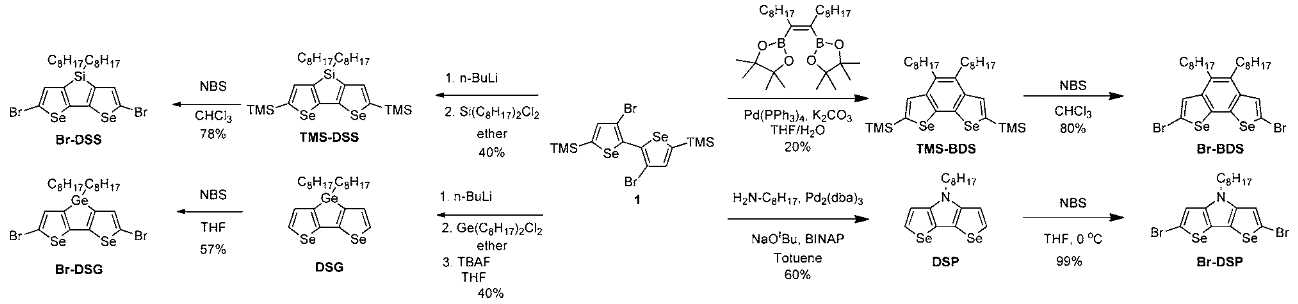
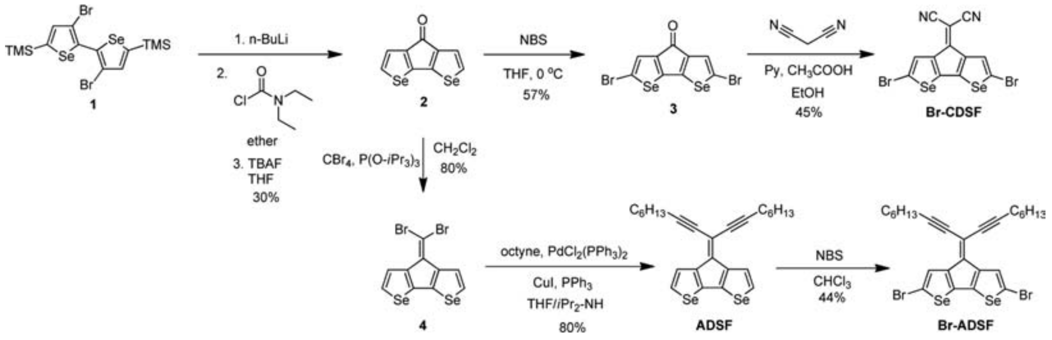
Scheme 1. Synthetic Routes of Br-BDS, Br-DSP, Br-DSS, and Br-DSG



Scheme 2. Synthetic Routes of Br-CDSF and Br-ADSF



1.[9] The synthesis of **Br-BDS, Br-DPS, Br-DSS,** and **Br-DSG** are shown in Scheme 1. The Pd-catalyzed Suzuki cross-coupling of **1** with dioctylbis(pinacolatoboryl)alkene successfully formed a fused dioctylbenzene ring to afford **TMS-BDS**. The bromination of **TMS-BDS** at the 2,7-positions yielded **Br-BDS**.

Similarly, the Pd-catalyzed Buchwald–Hartwig amination of **1** with octylamine resulted in the formation of an embedded *N*-octyl pyrrole ring in the **DSP**. The bromination of **DSP** at the 2,6-positions furnished **Br-DSP** in almost quantitative yield. In addition to the transition-metal catalyzed reactions, compound **1** can also be lithiated with *n*-butyllithium in ether followed by quenching with dichlorodioctylsilane to afford **TMS-DSS** in 40% yield. It is worth mentioning that when THF is used as the solvent, the yield decreased dramatically. The germanium-bridged **TMS-DTG** can be obtained in a similar manner when dichlorodioctylgermane is used as the electrophile. The crude product was desilylated with tetrabutylammonium fluoride (TBAF) to afford **DSG**. The bromination of **TMS-DSS** and **DSG** yielded the **Br-DSS** and **Br-DSG**, respectively. The synthesis of **CDSF** and **ADSF** is depicted in Scheme 2. The synthesis of cyclopenta[2,1-*b*:3,4-*b*′]diselenophene-4-one (**2**) was first reported with less than 5% yield.[10] The lithiation of **1** to react with diethylcarbamoyl chloride in ether followed by desilylation afforded the ketone compound **2**. We found that by changing the solvent from THF to ether, the yield can be increased to 30%. This improvement enables us to complete the synthesis of **CDSF** and **ADSF** with reasonable overall yields. The NBS bromination of **2** at 0 °C generated compound **3** which underwent the Knoevenagel condensation with malononitrile in the presence of acetic acid/pyridine to form a central fulvene unit in the **Br-CDSF**. On the other hand, the Wittig-type reaction of **2** with CBr$_4$/triisopropylphosphite furnished compound **4** containing a 1,1-dibromovinylidene moiety which can successfully carry out the Sonogashira coupling reaction with octyne to form **ADSF** in 80% yield. The bromination of **ADSF** resulted in the final **Br-ADSF**.

The absorption spectra of **Br-BDS, Br-DSP, Br-DSS, Br-DSG, Br-CDSF,** and **Br-ADSF** are shown in Figure 1. The nonfused 5,5′-dibromo-2,2′-biselenophene and 5,5′-dibromo-2,2′-bithiophene were also synthesized as model compounds for comparison. In Figure S1, 5,5′-dibromo-2,2′-biselenophene exhibits a more red-shifted absorption maximum (λ_{max} = 337 nm) and stronger extinction coefficient compared to 5,5′-dibromo-2,2′-bithiophene (λ_{max} = 322 nm) due to selenophene's higher degree of quinoidal character.[7] Although **Br-BDS** and **Br-DSP** have more coplanar structures, they show more blue-shifted maximum absorbances (λ_{max} = 315 and 326 nm, respectively) than that of the nonfused 5,5′-dibromo-2,2′-biselenophene, suggesting that the central benzene and pyrrole rings have higher aromaticity with more confined π-electrons. Besides, the vibronic structures from **Br-BDS** (332 nm, 347 nm) and **Br-DSP** (339 nm) were also observed as a result of the more planar and rigid structures. However, the silicon-bridged **Br-DSS** and germanium-bridged **Br-DSG** show very similar absorption profiles (λ_{max} = 374 and 369 nm, respectively) and much more red-shifted spectra in comparison with the nonfused 5,5′-dibromo-

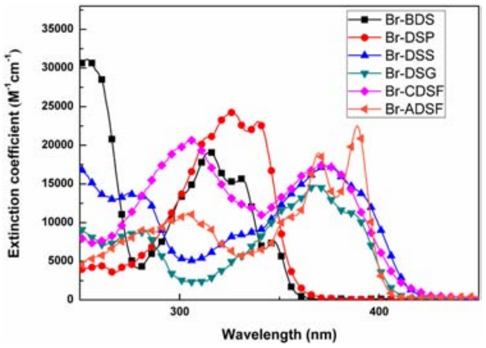


Figure 1. Absorption spectra of **Br-BDS, Br-DSP, Br-DSS, Br-DSG, Br-CDSF,** and **Br-ADSF** measured in chloroform.

2,2′-biselenophene, indicating that the silicon and germanium moieties mainly function as bridges to planarize the tricyclic units, thus enhancing the π-delocalization and effective conjugation length. In addition to a common transition band at shorter wavelengths (λ_{max} = 305 nm), **Br-CDSF** embedding a vertically aligned 6,6-dicyanofulvene unit shows another absorption band at 373 nm which might be ascribed to the charge transfer transition from the horizontal backbone to the electron-withdrawing dicyanovinylidene moiety. Another vinylidene-bridged **Br-ADSF** with a 6,6-diacetylenefulvene motif also shows similar absorption bands with more vibronic structures at longer wavelengths (370 and 389 nm), implying that the dialkynylvinylidene group also has certain electron-withdrawing capability.[11]

The emission spectra of the six materials are shown in Figure 2 using chloroform as the solvent. **Br-BDS** and **Br-DSP** with higher aromaticities and largest optical band gaps exhibit the most blue-shifted emission λ_{max} at 366 and 368 nm, respectively. **Br-DSS** and **Br-DSG** not only have the similar absorption spectra, but also show close emission λ_{max} at 470 and 467 nm that represent the largest Stokes shifts among these materials. Despite that the sp^2-vinylidene-bridged **Br-CDSF** and **Br-ADSF** have very similar optical band gaps with **Br-DSS** and **Br-DSG**, they display more hypsochromic shifts of the λ_{max} emissions at 420 and 424 nm, respectively.

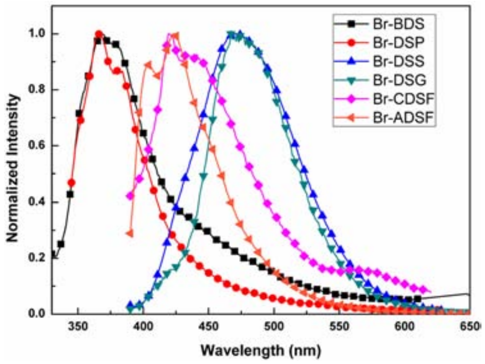


Figure 2. Emission spectra of **Br-BDS**, **Br-DSP**, **Br-DSS**, **Br-DSG**, **Br-CDSF**, and **Br-ADSF** measured in chloroform.

The electrochemical properties of **Br-BDS**, **Br-DSS**, **Br-DSG**, **Br-DSP**, **Br-CDSF**, and **Br-ADSF** were evaluated by cyclic voltammetry and shown in Figure 3. The HOMO energy levels were estimated by the oxidation onset vs ferrocene.[12] **Br-BDS** shows the highest oxidative potential (1.05 V) and thus deepest-lying HOMO level (−5.85 eV) because of the higher aromaticity of the central benzene ring, while **Br-DSP** has the lowest oxidative potential (0.52 V) and highest-lying HOMO level (−5.32 eV) due to the strong electron-donating power of the nitrogen atom. The silole and germole units have been known to have certain electron-accepting ability associated with $\sigma^*-\pi^*$ conjugation.[12] Therefore, **Br-DSS** and **Br-DSG** exhibit rather deep-lying HOMO levels of −5.53 and −5.51 eV, respectively. Since only **Br-CDSF** and **Br-ADSF** exhibit reduction potentials in the CV measurements, the LUMO energy levels of **Br-BDS** (−2.40 eV), **Br-DSP** (−1.85 eV), **Br-DSS** (−2.54 eV), and **Br-DSG** (−2.46 eV) were estimated by subtracting the band gap values from their corresponding HOMO levels.

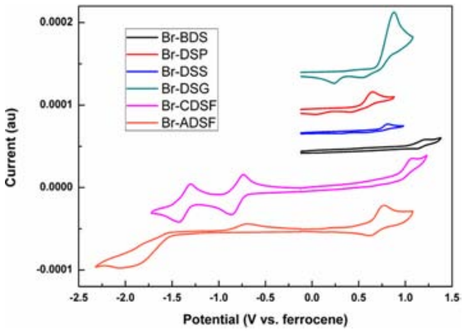


Figure 3. Cyclic voltammograms of **Br-BDS**, **Br-DSP**, **Br-DSS**, **Br-DSG**, **Br-CDSF**, and **Br-ADSF** measured in dichloromethane at a scan rate of 50 mV/s.

Br-CDSF possesses the deep-lying HOMO/LUMO energy levels at −5.74/−4.08 eV due to the strong electron-withdrawing effect of the dicyanovinylidene group. It is envisaged that the **CDSF**-based materials can potentially function as n-type materials with an ambipolar nature. Besides, **Br-ADSF** also exhibits relatively lower-lying HOMO/LUMO energy levels of −5.46/−3.30 eV, again suggesting that the diacetylenevinylidene unit also has certain electron-accepting ability.[13]

To better understand the molecular orbital properties of the materials, quantum−chemical calculations were performed with the Gaussian09 suite employing the B3LYP and TD-B3LYP density functionals in combination with the 6-311G (d,p) basis set. The calculated HOMO/LUMO energies, excitation energies, oscillator strength, and configuration of the excited states are shown in Figure 4 and summarized in Table S1. Although there are some deviations, the trend of the HOMO/LUMO values correlates well with the experimental data. The most probable vertical excitations are calculated to be 322, 330, 394, 387, 300, and 402 nm, respectively, for **Br-BDS**, **Br-DSP**, **Br-DSS**, **Br-DSG**, **Br-CDSF**, and **Br-ADSF**, which are in good agreement with their experimental absorption λ_{max} values (315, 326, 374, 369, 305, and 389 nm, respectively). It should be noted that the electron densities of the LUMO orbitals of **Br-CDSF** and **Br-ADSF** are extended to the dicyanovinylidenyl and diacetylenevinylidenyl moieties, suggesting the existence of the photoinduced charge transfer transitions. The NMR analysis on the chemical shifts of the selenophene's β-proton (H_β) in the six

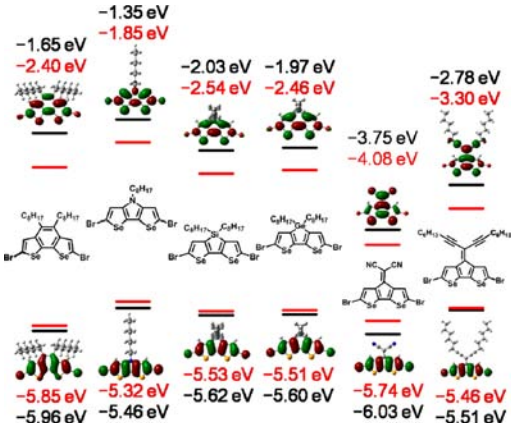


Figure 4. Frontier molecular orbitals of **Br-BDS**, **Br-DSP**, **Br-DSS**, **Br-DSG**, **Br-CDSF**, and **Br-ADSF** calculated with the DFT B3LYP/6-311G (d,p) level; experimental and theoretical HOMO/LUMO values are represented by red and black lines, respectively.

molecules might provide insights into the electronic effects imposed by the neighboring bridging moieties.

The chemical shifts of the H_β in **Br-DSS** and **Br-DSG** are almost identical (7.15 ppm) due to the similar electronegativities of silicon and germanium (1.90 and 2.01), whereas the chemical shift of the H_β in **Br-DSP** (7.29 ppm) is relatively downfield probably due to the higher electronegativity of nitrogen (3.04). With the electron-withdrawing dicyanovinylidene group, **Br-CDSF** exhibits more downfield shifted H_β at 7.69 ppm. The chemical shift of H_β in **Br-ADSF** at 7.85 ppm is the most downfield presumably owing to the ring-current effect of the triple bonds.

In summary, the tricyclic bithiophene-based materials have been extensively demonstrated as an important category of organic semiconductors. Nevertheless, their corresponding biselenophene-based analogues have never been reported. For the first time, we have demonstrated that 3,3′-dibromo-5,5′-bistrimethylsilyl-2,2′-biselenophene can undergo palladium-catalyzed reactions to afford the nitrogen-bridged **DSP** and ethylene-bridged **BDS** materials. Furthermore, this starting material can also be lithiated followed by nucleophilic substitutions to construct the silicon-bridged **DSS** and germanium-bridged **DSG** and lead to the formation of the vinylidene-bridged **CDSF** and **ADSF** derivatives. The six brominated molecules can be used to create a new class of promising p-type or n-type materials which will pave the way for exploring the biselenophene-based materials in various opto-electronic applications.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Detailed synthetic procedures, theoretical calculations, and ^{1}H and ^{13}C NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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