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To be cited as: *Chem. Asian J.* 10.1002/asia.201700552

Link to VoR: http://dx.doi.org/10.1002/asia.201700552

A Journal of
ACES
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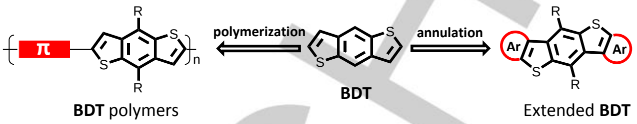
Lateral Extension of Benzodithiophene System: Construction of Heteroacenes Containing Various Chalcogens

Jichang Wei,[a,b,c] Dong Meng,[a,c] Lei Zhang*[b] and Zhaohui Wang[a]

Abstract: A series of novel linear acenes with five fused rings, which contain thiophene, selenophene, and tellurophene as the outmost rings, have been successfully synthesized from well-known benzodithiophene (BDT). It was found that the optical, electrochemical properties and crystal packing motifs could be modulated by changing heteroatoms in the outmost rings.



Scheme 1. Typical Design Strategy to the BDT-based Conjugated Materials for Organic Devices.

The BDT building block has been incorporated into a number of fascinating molecules, including extended linear acenes, as well as two-dimensional conjugated polymers, which have shown significant potentials for applications in electronic devices, such as photovoltaic cells and organic field effect transistors (Scheme 1).[1] This is attributable to the ease of synthesis, particularly with respect to selectively modifying the BDT core on the benzene ring (4-, 8- positions) that have great impact on the material properties.[1,2] Indeed, this functionalization strategy is known to be valuable for tuning the photovoltaic properties of the BDT-based donor-acceptor copolymers, as demonstrated by the successful molecular engineering for improved device performance.[1a,1d,2c]

Another attractive feature of the BDT derivatives is the ability to use well established synthetic chemistry for the lateral fusion of aromatic rings to the thiophene rings in BDT.[3] In general, this pattern of ring fusion, especially five-membered rings containing group 16 elements, such as thiophene, and selenophene, has been found to be a powerful approach for extending the molecular conjugation length, which strongly influences the optical and electronic properties of the materials.[4] It is also indicated by theoretical investigation that the increased conjugation length could be beneficial for improving electronic coupling and reducing reorganization energies in the solid state.[5] The incorporation of the heterocycles into a rigid, tricyclic BDT system should therefore lead to a significantly higher degree of conjugation.[3a,3b,3d] In addition, the use of heteroatom substituent to tune the properties of the materials is very promising as such subtle changes can often result in significant changes in the electronic, optical, and physical properties of the resultant materials. For example, our recent work incorporating heteroatoms (S, Se) into rylene diimides arrays, has demonstrated that the advantageous features of the atomic engineering to fine tune the electronic structures of the materials, which lead to a promising class of non-fullerene electron acceptors for organic solar cells with power conversion efficiencies over 9%.[6] It should be noted that heavier elements (Se, Te) with larger polarizable radius offer certain advantageous properties relative to their lighter analogues (O, S), including a narrow optical band gap, stronger intermolecular interactions, enhanced planarity, and a distinct solid-state structure, which are generally beneficial for improving charge transport.[7]

To fully realize the potential of heterocycles as candidates for promising optoelectronic materials, it is critical to develop efficient procedures for their synthesis as well as their incorporation into more complex, extended π-conjugated systems. Although the synthetic procedures are well established for compounds containing light elements, synthetic access to containing heavy ones, in particular for tellurophene-based molecules, remains great challenges due to the generally high reactivity of carbon−heteroatom bond and weaker orbital overlap when the heteroatom is present.[7,8] Herein, we describe the synthesis of a series of heteroacenes by linear fusion of chalcogenophenes to the BDT cores. The resulting linear acene derivatives constitute five fused rings with thiophene, selenophene, and tellurophene as the outmost rings, respectively. In addition, these heteroatoms, along with the substituents on the benzene, are expected to provide a mean of fine-tuning of the characteristic of the acenes.

Scheme 2 shows the synthesis of linear heteroacene derivatives from the BDT. Our synthetic strategy relies on the intramolecular cyclization of a chalcogenol to an ethynyl group. Compound **6** was prepared using BDT **7** as the starting material according to the literature.[9] A palladium-catalyzed cross coupling reaction between **6** and trimethylsilylacetylene allowed us to produce compound **5** in a 45% yield, which was readily lithiated with butyllithium (*n*-BuLi) and quenched with chalcogen powders (S, Se, Te) and ethanol to generate the chalcogenol intermediates. The resulting chalcogenols subsequently underwent the intramolecular cyclization in situ with the ethynyl groups to form **4** and the deprotection of trimethylsilyl (TMS) groups in present of tetrabutylammonium fluoride (TBAF) gave **3** with high yields. Although **3a** has been synthesized previously by a tandem directed metalation, this approach provides flexibility for embedding different heteroatoms into linear acenes. It should be noted that our initial attempt to prepare **4** via another intramolecular cyclization reaction between the acetylene group and the chalcogenate with Na_2X (X=S, Se) as nucleophile, a general approach which has drawn much attention as a route to

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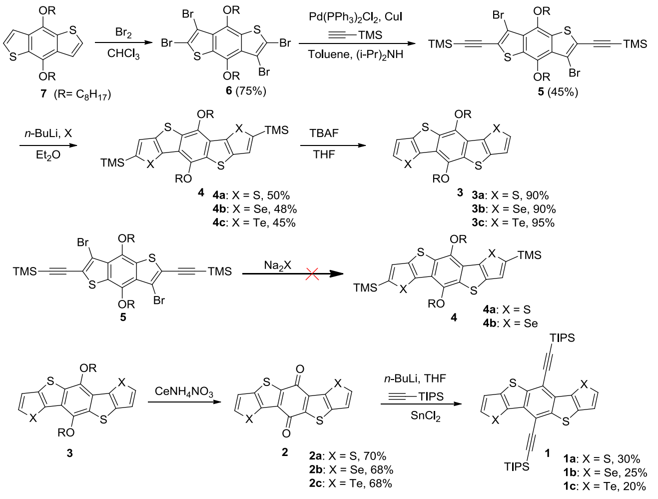
10.1002/asia.201700552

a variety of chalcogenophene fused acenes,[10] led only to a complex mixture and no significant product was isolated.



Scheme 2. Synthesis of Heteroacene Derivatives with Five Fused Rings Containing Various Chalcogens.

When compounds **3** were oxided by ammoniumceric nitrate, quinones **2** were obtained in 60-70% yields. These quinone scaffolds could serve as coupling components for the development of low band-gap, high-crystalline conjugated materials by selectively modification on five-membered ring, and six-membered ring positions. To expand further the versatility of the quinone scaffolds **2**, we considered the triisopropylsilyl (TIPS) ethynyl moiety, which was well known for improvement the solubility and crystallinity.[11] Lithiation of triisopropylsilylacetylene in THF with *n*-BuLi to form its anion and subsequent treatment with quinones **2** gave the relative alcohol derivatives, followed by a reductive aromatization with $SnCl_2$, providing the desired products **1a**, **1b**, and **1c** in 30%, 25%, and 20% yields, respectively. These linear heteroacenes are soluble in common solvents and exhibit excellent tolerant for oxygen, and silica gel, allowing for purification by chromatography. The molecular structures were unambiguously characterized by NMR, mass spectrometry, and x-ray crystallography (see the supporting information).

The UV-vis absorption spectra of **1a**, **1b**, and **1c** were measured in chloroform solution (Figure 1A). The spectra of **1a**, and **1b** are generally similar in shape and exhibit two major absorption bands: a set of absorption band at short wavelength, and a broad longest-wavelength absorption band from 350 to 420 nm, which are characteristic of the acene-like derivatives.[12] However, for **1c**, the spectrum possesses three sets of absorption bands: a prominent band centered at 306 nm, the other band at 340 nm, and another broad absorption band from 370 to 450 nm. As expected, the progressive red-shifts in absorption were found when the heteroatoms within the chalcogenophenes were changed from S to Se to Te with λ_{max} values of 402 to 413 to 423 nm. As a result, the optical band-gaps estimated from absorption edges are 2.96 eV, 2.90 eV, and 2.81 eV for **1a**, **1b**, and **1c**, respectively.

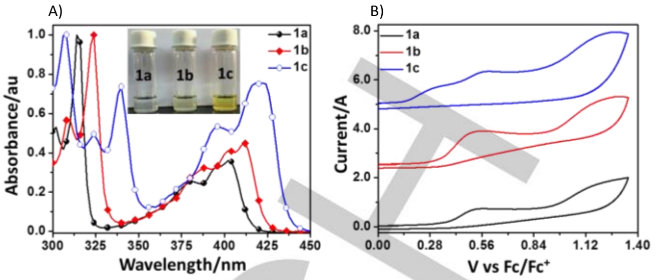


Figure 1. (A) UV-vis spectra of **1a**, **1b** and **1c** in chloroform solution, (B) Electrochemical properties of **1a**, **1b** and **1c** in dichloromethane with tetrabutylammonium hexafluorophosphate (TBAPF6) as the supporting electrolyte.

The cyclic voltammetry (CV) of these compounds exhibits two or three irreversible oxidation peaks and no reduction peak was observed (Fig 1B). According to the onset potential, the highest occupied molecular orbitals (HOMO) were estimated to be -5.16 eV for **1a**, -5.14 eV for **1b**, and -4.95 eV for **1c**. The very similar HOMO values of **1a** and **1b** indicate the replacement of sulfur with selenium has a relatively minor influence of the oxidation potential. While, compared to **1a**, the HOMO level of **1c** is increased to a greater extent due to the lower aromaticity of tellurophene. The lowest unoccupied molecular orbitals (LUMO) were roughly estimated from the optical band gap to be -2.20 eV for **1a**, -2.24 eV for **1b**, and -2.14 eV for **1c**. The comparable LUMO values indicate that the chalcogen atoms in the outmost rings have a negligible influence on the reduction potential, which is in agreement with the study of Takimiya, who suggested that incorporation of heavy chalcogen atoms into annulated acenes led to the HOMO level increased and the LUMO level relatively constant.[12]

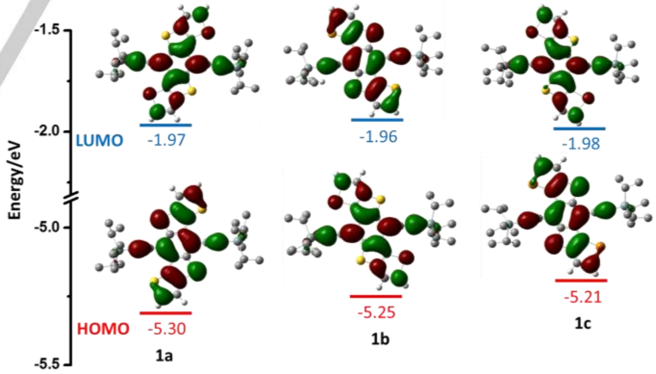


Figure 2. The HOMO, and LUMO levels of **1a**, **1b**, and **1c** calculated by DFT at the B3LYP/6-31(d.p) level (hydrogen atoms omitted for clarity).

To better understand the electronic structures of these three compounds, density functional theory (DFT) calculations were performed in gas phase with Gaussian03 at the B3LYP level. The calculated data are summarized in Table 1, and HOMO/LUMO orbitals of the compounds are shown in Figure 2. It can be seen that these three compounds possess very similar HOMO and LUMO distributions. Their HOMO orbitals are

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distributed over the aromatic cores and $C\equiv C$ bonds. The calculated HOMO levels by DFT are -5.30 eV for 1a, -5.25 eV for 1b, and -5.21 eV for 1c, which are in good consistent with the trend of the experimental values. The calculated LUMO levels are -1.97 eV, -1.96 eV, and -1.98 eV for 1a, 1b and 1c, respectively and the DFT result confirmed the fact that the introduction of heavy heteroatom into the linear acene is beneficial to reducing the bang gap due to the increase of the HOMO level that occurs.

Table 1. Absorption, and electrochemical properties of **1a**, **1b** and **1c**.

Head 1	λ_{max} (nm)	HOMO[a] (theor) [b] (eV)	LUMO[c] (theor) [b] (eV) [c]	E_g[d] (eV)
1a	402	-5.16 (-5.30)	-2.20 (-1.97)	2.96
1b	413	-5.14 (-5.25)	-2.24 (-1.96)	2.90
1c	423	-4.95 (-5.21)	-2.14 (-1.96)	2.81

[a] HOMO values calculated from the onset of the first oxidation peaks; [b] HOMO and LUMO values calculated by DFT; [c] LUMO values estimated from HOMO and optical band gap; [d] Optical band gap calculated from the onset of the absorption peak.

Single crystals of **1a**, **1b** and **1c** were readily grown from hexane and dichloromethane, and their solid-state arrangements were determined by single-crystal X-ray diffraction (Figure 3). These three molecules all have nearly planar frameworks. **1a** exhibits a slipped one-dimensional π-stacking arrangement with an interplanar distance of 3.46 Å. Short C-H···π and Si···H contacts between TIPS groups and acene cores in adjacent stacks are 2.81 Å and 2.89 Å, respectively, and no S···S interactions is observed. The replacement of S with Se yields compound **1b** and induces a significant change in packing motif. **1b** packs in a herringbone-like motif with the TIPS group pointing toward the center of the five membered core of an adjacent molecule. The C-H···π interactions (2.81 Å) between the TIPS groups and acene cores connect adjacent molecules together with an interplanar dihedral angle of 64.63°. However, there is no π-π interaction between acene cores. The C–Se–C angle is 86.69° and the C-Se bond length is 1.863 Å, which are comparable with that of unfused selenophene derivatives.[13] The structure of **1c** presents a striking contrast to that of **1b**. At first glance, the structure appears similar to that of **1b**, but there are four molecules and per dichloromethane (DCM), which are linked together by Cl···Te (3.65 Å), C···Cl (3.34 Å) and C-H···π interactions (2.89 Å). The driving force between **1c** and DCM molecule is likely due to the low electronegativity of tellurium, which leads to the polarized acene core with tellurium positively charged ($Te^{\delta+}$–$C^{\delta-}$), thus favoring the intermolecular interactions. Therefore, DCM molecule appears to act as an adhesive between the adjacent molecules through multiple intermolecular interactions to stabilize the two dimensional crystal network. It appears that the heteroatoms in the outmost rings play a crucial role on the crystal packing, as these chalcogens have different atom size and electronegativity, which impact the electron distribution and the dipole moment on the π-systems.[7] In addition, the **1c** molecules are also linked by C-H···π interactions (2.84 Å) between the TIPS groups and adjacent acene cores with an interplanar dihedral angle of 50.11°. Due to the large size of Te, the C-Te bond length is 2.067 Å and the C–Te–C angle is 80.79° .

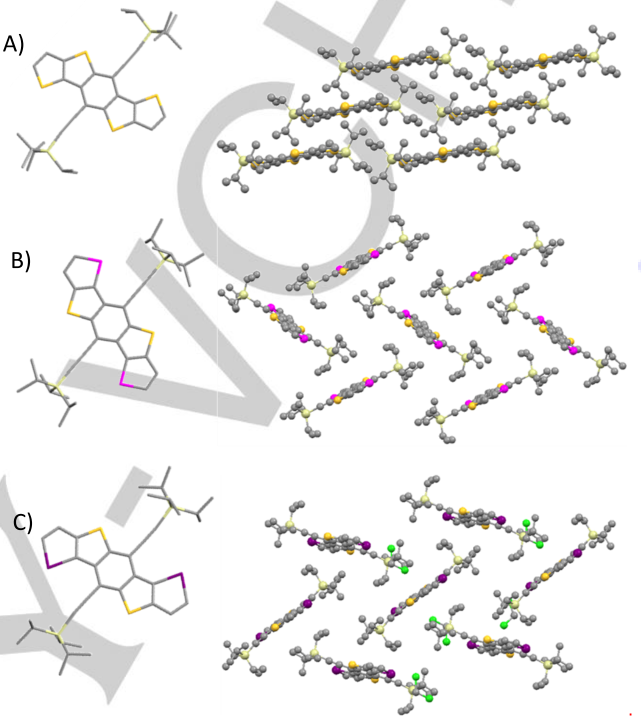

Figure 3. X-ray structures and crystal packing of the heteroacenes: A) **1a**, B) **1b**, and C) **1c**.

In conclusion, we have developed a versatile synthetic route to a novel class of heteroacenes by fusion of thiophene, selenophene, and tellurophene to lateral positions of the BDT. These substituted linear acenes and five-membered quinone scaffolds serve as promising building blocks to synthesize a series of π-conjugated materials. Our investigation indicates that the heavier chalcogen atoms play an important role on the optical, electrochemical properties, and crystal packing motifs. We are currently exploring use of these building blocks for the preparation of new donor-acceptor copolymers, as well as for even larger, expanded π-conjugated heteroacens for organic devices.

Experimental Section

Experimental and characterization details can be found in the Supporting Information.

Acknowledgements

We thank the financial support from the National Natural Science Foundation of China (NSFC) (No., 21428304,

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91427303). L.Z thanks the National Natural Science Foundation of China (21672020).

Keywords: heteroacene • chalcogenophene • linear acene • Benzodithiophene • heterocycle

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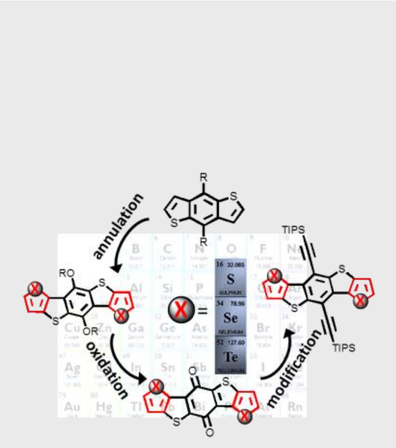

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