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Synthesis and Characterization of [1,2,5]Chalcogenazolo[3,4-f]-benzo[1,2,3]triazole and [1,2,3]Triazolo[3,4-g]quinoxaline Derivatives

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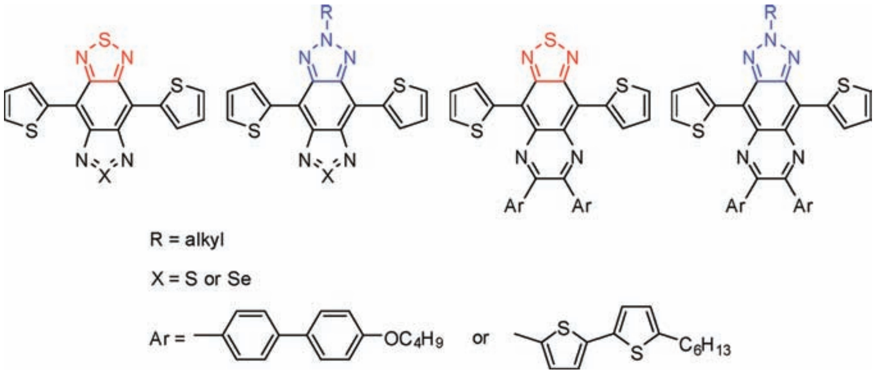
ABSTRACT



The synthesis and characterization is reported of low bandgap [1,2,5]chalcogenazolo[3,4-f]benzo[1,2,3]triazole and [1,2,3]triazolo-[3,4-g]quinoxaline derivatives that display higher solubility and stability then their thiadiazole counterparts, [1,2,5]chalcogenazolo-[3,4-f]benzo[2,1,3]thiadiazole and [1,2,5]thiadiazolo[3,4-g]quinoxaline, respectively.

Recently developed benzo[1,2-c;4,5-c′]bis[1,2,5]thiadiazole (BBT) derivatives have been shown experimentally to be strong electron acceptors with high mobilities and low bandgaps with low LUMO levels.[1−8] Theoretical studies suggest that these properties are a consequence of their strong quinonoid contributions and hypervalent sulfurs.[1−3,5−7,9−11] In the case of benzo-2,1,3-chalcogendiazoles, density functional theory (DFT) B3LYP calculations have shown that the bandgap and LUMO trends are Te < Se < S.[12] Thus, extrapolating from these results, one would expect that the chalcogendiazolo-benzothiadiazoles

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(XBTs) will show the same trend. However, it is well-known that BBT has poor solubility. The fact that heavy main-group elements often display short interatomic contacts that are attributed to secondary bonding interactions,[13] would tend to make the selenium and tellurium analogues of BBT even less soluble. [1,2,5]-Thiadiazolo[3,4-g]quinoxalines (TQs) are also strong electron acceptors and low bandgap materials.[9,14–17] While TQs can be made more soluble via functionalization at the 6 and 7 positions, higher solubility might also be achieved by changing the sulfur in the thiadiazole ring to a nitrogen, as the resulting [1,2,3]triazolo[3,4-g]quinoxaline (TaQ) structure allows a solubilizing group to be attached to the triazole ring and thus increase solubility. Using the same argument, higher solubility could be attained if one changed the thiadiazole ring in XBT to triazole. The resulting chalcogena-diazolobenzotriazoles (XBTa) should be low bandgap and low LUMO materials with good solubility (Figure 1). In this paper, the synthesis and characterization of the new XBTa and TaQ molecules is introduced, and they are compared with their XBT and TQ counterparts.

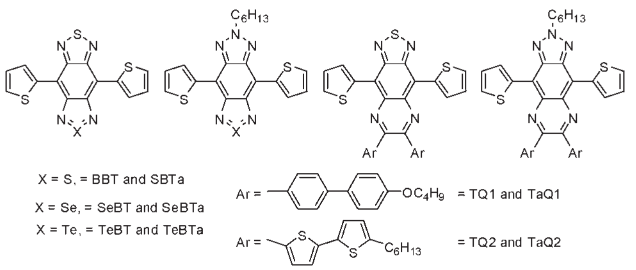
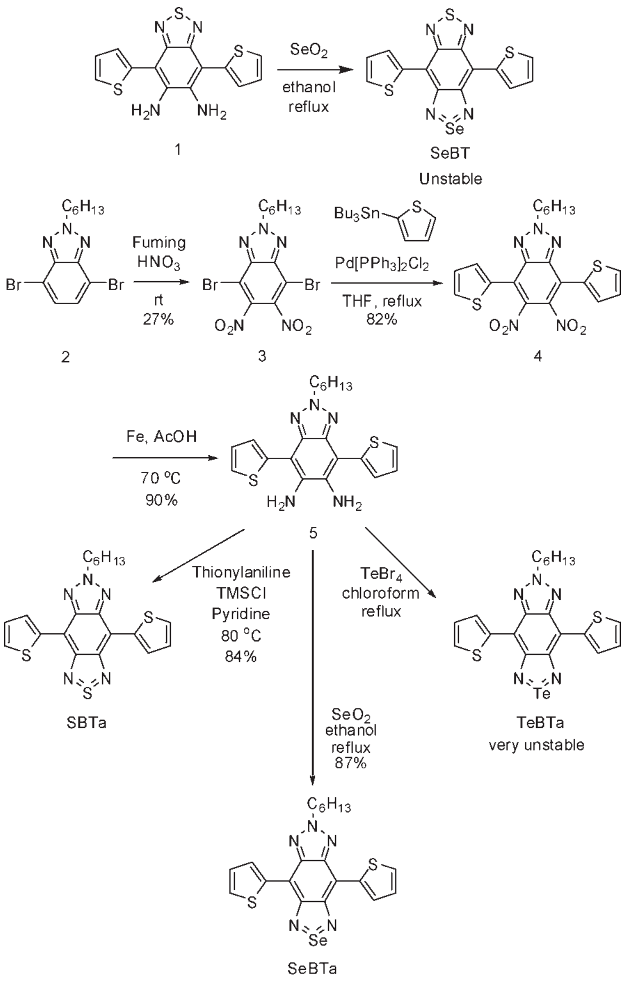


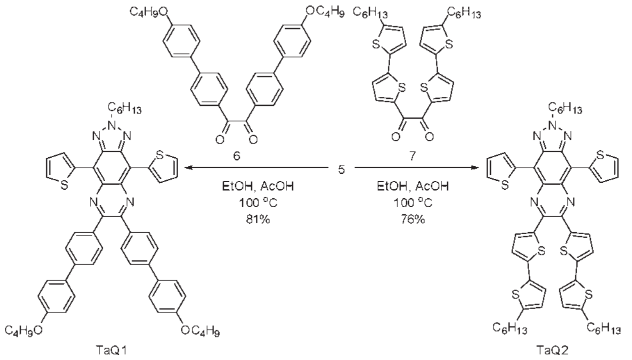
Figure 1. Structures of XBT, XBTa, TQ, and TaQ derivatives.

BBT was synthesized according to our previously reported method.[18] SeBT has not been reported previously in literature, so for comparison purposes, its synthesis was carried out (Scheme 1). Condensation of the known diamine **1** with SeO_2 in refluxing ethanol gives SeBT which, as expected, had very poor solubility and was unstable in air. Cyclic voltammetry and solution UV−vis absorption spectrometry were therefore carried out immediately after purification.

Scheme 1. Synthesis of SeBT, SBTa, SeBTa, and TeBTa



Scheme 2. Synthesis of TaQ1 and TaQ2



In view of the instability and poor solubility of SeBT, TeBT was not prepared as it was expected to be even less stable. The synthesis of **TQ1** and **TQ2** were reported by us recently.[19] The synthesis of **XBTa** and **TaQ** proceeds from **2**, which was prepared according to literature.[11] The subsequent nitration, Stille coupling, reduction, and ring-closure to form SBTa and SeBTa (Scheme 2) were analogous to those used to make BBT and SeBT.[7] It was found that concentrated sulfuric acid with fuming nitric acid was

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too harsh a condition to use for nitration of **2**, but nitration in fuming nitric acid gave **3** in 27% yield. An alternative nitration procedure for benzotriazole was recently reported after completion of the current synthesis of **3**.[20] For **TeBTa**, ring closure was carried using tellurium tetrabromide. The product, whose identity was confirmed only by MALDI-TOF, appears to be soluble in the reaction mixture but was extremely unstable when exposed to air and moisture. No further characterization was attainable. For **TaQ1** and **TaQ2**, condensation with diketones **6** and **7** in ethanol/acetic acid mixture give the desired molecules. The resulting molecules **SBTa**, **SeBTa**, **TaQ1**, and **TaQ2** are highly soluble and stable low bandgap materials.

As can be seen from the UV–visible spectra presented in Figure 2a, the effect of changing the chalcogen from sulfur to selenium in both the **XBT** and **XBTa** series is to red-shift the absorption and reduce the optical bandgaps (E_g, UV) as measured by onset of absorption. By contrast, as can be seen in Figure 2b, the effect of replacing the sulfur in the **BT** and **TQ** series with a nitrogen in **BTa** and **TaQ** is to increase the bandgap slightly. The bandgaps of the new materials still remain below 2 eV.

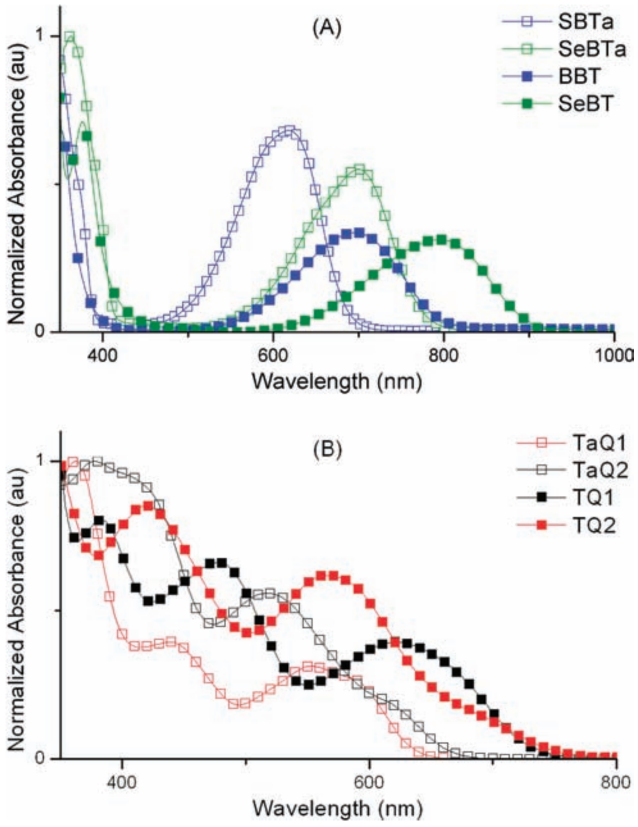

Figure 2. Solution UV–vis absorption spectra of (A) XBTa and XBT series and (B) TaQ and TQ series in dichloromethane.

Table 1. Electrochemical and Photophysical Properties of XBTa, XBT, TaQ, and TQ Series

	HOMO (eV)	LUMO (eV)	$E_{g\,(CV)}$ (eV)	$E_{g\,(UV)}$ (eV)	λ_{max} (nm)[a]
SBTa	−5.15	−3.48	1.67	1.80	337, 618
SeBTa	−5.12	−3.59	1.53	1.60	322, 363, 700
BBT	−5.37	−3.94	1.43	1.49	333, 350, 696
SeBT	−4.92	−3.60	1.32	1.37	344, 377, 797
TaQ1	−5.31	−3.48	1.83	1.95	308, 365, 440, 553, 597s
TaQ2	−5.25	−3.55	1.70	1.86	340, 377, 428s, 516, 626s
TQ1	−5.11	−3.43	1.68	1.70	323, 383, 477, 620
TQ2	−5.08	−3.52	1.56	1.65	331, 418, 567, 650s

[a] s, shoulder.

Electrochemical characterization of **SBTa** and **SeBTa** (Table 1) revealed that replacement of sulfur with selenium slightly increases the HOMO value (HOMO and LUMO values were calculated from onset of oxidation and reduction respectively). The LUMO on the other hand, decreases. The experimental trends for both HOMO and LUMO follow that of benzo-2,1,3- chalcogenadiazoles reported in literature.[12,21] From these trends, we believe the instability of **TeBTa** arises from it having an even higher HOMO above −5 eV.

The decreases in electrochemical bandgap (E_g, CV) from **SBTa→SeBTa** and from **BBT→SeBT** follow the expected trends, but the magnitude of change in HOMO energy for **BBT→SeBT** is larger than for **SBTa→SeBTa**. The changes in LUMO energy show the reverse pattern. These differences are believed to be a consequence of resonance symmetry stabilization of **BBT**, leading to delocalization and thus stabilization of the HOMO and LUMO. The HOMO, LUMO, and bandgap trends of **TaQ1→TaQ2** follow that of **TQ1→TQ2** due to better conjugation between the bithienyls and the core than the biphenyls.

With the exception of symmetrical **BBT**, substitution of sulfur with nitrogen in both **SeBT→SeBTa** and **TQ→TaQ** produces a slightly lower LUMO and a much lower HOMO. These are probably attributable to the higher electron affinity and ionization potential of nitrogen as compared to sulfur. Lower HOMO energies enhance stability of the materials and also have the potential to increase open circuit voltage in organic photovoltaic devices using such materials as donors.[22]

Differential scanning calorimetry (DSC) showed that both **SBTa** and **SeBTa** have low melting temperatures of 134 and 156 °C, respectively. On the other hand, **BBT** and **SeBT** do not melt but decompose. The low melting temperature for the **XBTa** is likely due to the alkyl group on the triazole ring. First, the flexible alkyl group is likely to prevent adjacent molecules on the triazole side coming close to one another. Second, secondary bonding

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interaction on the triazole side is no longer possible, effectively reducing the secondary bonding interaction probability by half. On the other hand, the lack of alkyl groups on **BBT** allows the molecules to come close together, at the same time allowing secondary bonding interactions to occur. Such decrease in intermolecular interactions may also explain why both **SBTa** and **SeBTa** have good solubility whereas **BBT** and **SeBT** do not. **TaQ1** and **TaQ2** also show lower melting temperatures (168 and 117 °C, respectively) than **TQ1** and **TQ2** (242 and 152 °C, respectively) and also much higher solubility.

In conclusion, the triazole analogues of chalcogenadiazolo-benzothiadiazoles and thiadiazolo-quinoxalines have been synthesized and characterized. These triazole analogues have much higher solubilities than the parent compounds, and lower HOMO energies were also achieved, which enhances their stability. While their bandgaps are higher as a result, they remain low bandgap materials. These qualities of higher solubility and stability are generally beneficial in the field of solution processable organic electronics, suggesting that materials containing these units may show promising properties for such applications.

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Supporting Information Available. Detailed descriptions of experimental procedures, plus mass spectra and NMR spectra for all newly synthesized compounds. CV and DSC data for the final products. This material is available free of charge via the Internet at http://pubs.acs.org.