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One-Pot Synthesis of 4, 8-Dibromobenzo[1,2-d;4,5-d′]bistriazole and Synthesis of its Derivatives as New Units for Conjugated Materials

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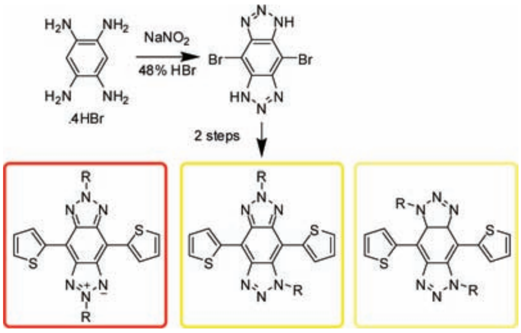
ABSTRACT



The one-pot synthesis of 4,8-dibromobenzo[1,2-d;4,5-d′]bistriazole, followed by alkylation and Stille coupling to yield three different isomeric derivatives with markedly different optoelectronic properties, is reported. These derivatives show potential as new units in organic oligomers and polymers for electronics applications.

Ever since the first conjugated benzotriazole (BTa) materials were synthesized by Tanimoto and Yamamoto in 2004,[1] BTa materials have potential uses in areas such as electrochromics, organic light emitting diodes, and organic photovoltaic devices (OPVs).[2–12] A high power conversion efficiency (PCE) of 7.1% for OPV was achieved recently by Price et al. using a copolymer containing a fluorine-substituted BTa unit,[10] thus showing the desirability of exploring new BTa derivatives for OPV. Toppare and co-workers reported the use of BTa copolymers in electrochromics that show exceptionally enhanced properties.[11] Unlike its isoelectronic relative benzo[1,2-c;4,5-c′]bis[1,2,5]thiadiazole (BBT), which has been extensively explored as a strong electron-accepting unit in organic

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electronic materials,[13−22] the use of benzo[1,2-d:4,5-d′]bistriazole (BBTa) in the same area is practically unknown, and only a few reports on BBTa-based materials are found in literature.[23−29] BBTas have been used as a dibenzyne equivalent for Diels−Alder reactions[25−27] and as ligands for metal coordination framework.[24] [1,2,5]Thiadiazolo[3,4-f]benzo[1,2,3]triazole (SBTa), which is an intermediate between BBT and BBTa in terms of structure, was reported by us recently (Figure 1).[30] To date, the common approach for the synthesis of BBTa starts from 1,3-diamino-4,6-dinitrobenzene 1 (Scheme 1).[26] This multistep synthesis of BBTa may act as a major disincentive for the widespread use of this material, despite its high yield, and we were inspired to seek a shorter route.

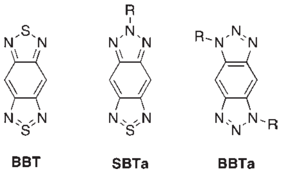
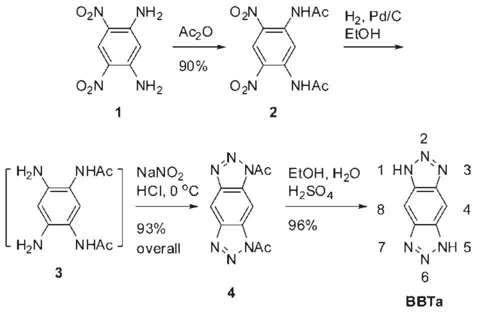


Figure 1. Structures of BBT, SBTa and BBTa.

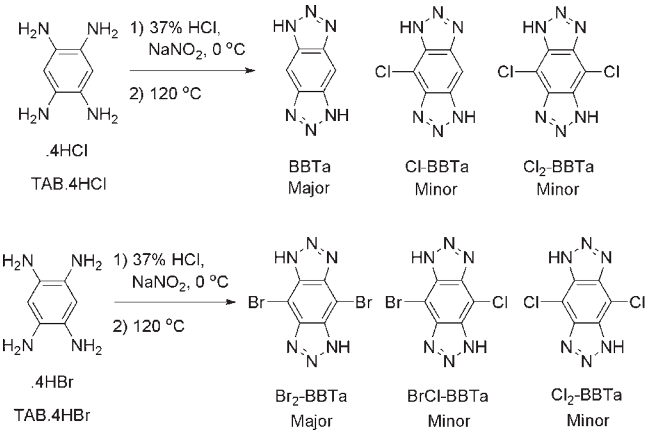
It has been reported that treatment of tetraaminobenzene (TAB) using nitrous acid failed to give the desired BBTa product.[28] We have now found that reacting **TAB.4HBr** in 48% HBr with sodium nitrite gave **Br_2-BBTa** (Scheme 3). We found reacting **TAB.4HBr** with sodium nitrite in 37% HCl gave mixed halogenated products, with brominated products appearing to be the more dominant species by MALDI-TOF analysis (Scheme 2). The hydrochloride **TAB.4HCl** in 37% HCl gave **Cl_2-BBTa**, but also mono and unhalogenated products (Scheme 2). We propose the halogen anion X^- plays a part in halogenation of the **BBTa** as it can be oxidized to X_2 by nitric acid, plausibly arising from aerial oxidation of the nitrous acid under the reaction conditions. Nitrous acid (E^0 +1.00 V) is not able to oxidize HBr or HCl to Br_2 (E^0 +1.07 V) or Cl_2 (E^0 +1.36 V), but it reportedly catalyzes oxidation by nitric acid of HBr to Br_2,[31] which could then halogenate the **BBTa** that was formed. The ratio of the chlorinated versus brominated BBTa products can then be attributed to the greater difficulty of nitric acid to oxidize HCl to Cl_2 due to its more positive reduction potential. An anion dependent reaction was also observed in the synthesis of 4,8-dihalogenated **BBT** from TAB but the mechanism in that case was quite different as it involved nucleophilic rather than electrophilic halogenation.[22]

Scheme 1. Synthesis of BBTa According to Literature



Dialkylation of the crude **Br_2-BBTa** with 11-(bromomethyl)tricosane yielded structural isomers, of which the 2,6-isomer **5a** is quite unexpected, because of the charged nitrogens. The only previously reported example of a 2,6-isomer was synthesized from oxidation of diazo derivatives of TAB using copper sulfate.[32] However, very little characterization of that structure was reported. The structure of the 2,6-isomer derivative was concluded from comparison of the ^1H, ^{13}C NMR and MALDI-TOF of the crude mixture with those of **6a**. The presence of only one type of N−CH_2, the ratio of the proton

Scheme 2. Initial Attempts to Synthesize BBTa[a]



[a] Amount of products were assumed to be proportional to intensity in MALDI-TOF spectra.

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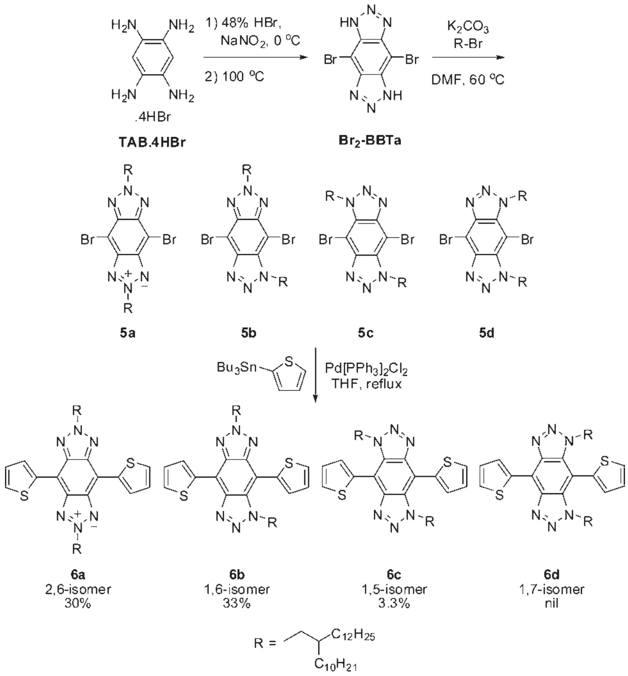
Scheme 3. One-Pot Synthesis of **Br$_2$-BBTa**, Followed by Alkylation and Stille Coupling[a]



[a] Yield indicates overall isolated yield.

integrals, and the simplicity of the ^{13}C NMR spectrum suggested C_2 symmetry in this BBTa derivative.

5b, **5c** and **5d**, were also identified by comparison of the spectra of the mixture with those of the isolated isomers **6** and with those of nonbrominated regioisomers known for other BBTa derivatives, though similar mixtures have not previously been obtained from alkylation procedures.[23] The occurrence of **5a** is probably due to the presence of large bromine atoms hindering alkylation at the 1 and 5 (or 7) positions, thus making positions 2 and 6 more available. Such steric influenced regioselectivity has previously been reported for benzotriazole[23] and triazole[32−35] derivatives. The purification of the alkylated **Br$_2$-BBTa** isomers proved to be difficult. However, it turned out the purification of **6a**, **6b** and **6c**, the products of Stille coupling of the crude mixture, was much easier and these could be obtained pure with an overall yield of 30, 33 and 3.3%, respectively, via column chromatography. Note that these three products were the only ones isolable. Katritzky et al. have reported the ratio of the 1,6-, 1,5- and 1,7-isomers to be 4:63:33 when BBTa-paraformaldehyde-morpholine adduct was allowed to reach an equilibrium in solution.[23] Since in our case the 1,5-isomer **6c** is only obtained in 3.3% yield, the combination of lower formation ratio and high steric hindrance (which can hinder Stille coupling on the dialkyl substituted side) are likely to cause the 1,7-isomer **6d** to be absent. We postulate that bulkier alkyl halide or substituents at the 4 and 8 position of BBTa would result in a higher yield of the 2,6-isomer.

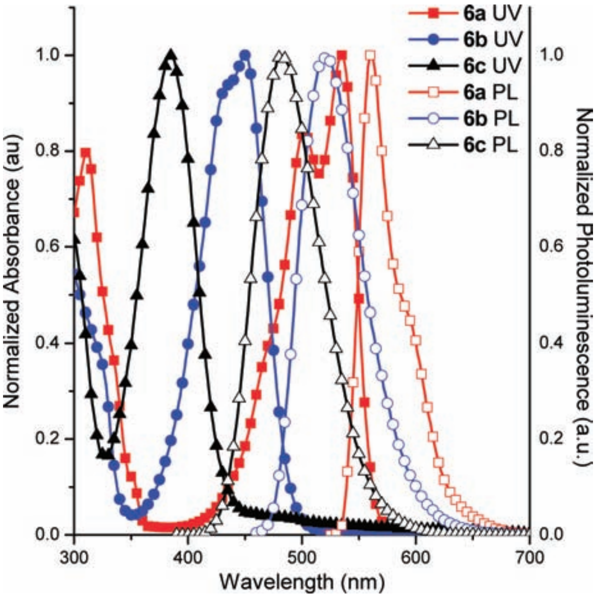


Figure 2. UV−vis and PL of **6a**−**6c** in chloroform.

UV−vis and PL measurements (Figure 2 and Table 1) show a progressive increase in optical bandgap and Stokes shift from **6a** to **6c**. These can be easily explained by the decrease in planarity of the molecules due to steric hindrance between the BBTa core and the thienyl groups when the alkyl groups are at the 1 and 5 positions. Effective conjugation and rigidity of the molecule are reduced and thus bandgap and Stokes shift increase respectively. The decrease in planarity which results in decrease in conjugation is also reflected in the HOMO and LUMO values. The decreasing conjugation from **6a** to **6c** leads to decreasing HOMO and increasing LUMO. Thus the position of the alkyl chains offers a simple way to tune the optoelectronic properties of the molecules, and presumably of oligomers or polymers containing them.

Density Functional Theory (DFT) studies were carried out to compare the frontier orbitals and their energies, as well as bond length and dihedral angles for Th$_2$−BBT, Th$_2$−SBTa and **6a** (Figure 3). The calculated HOMO and LUMO values are in good match with the experimental values obtained for HOMO from CV and the estimated values obtained by combining the measured HOMO values with the optical bandgaps. Comparing the shape of

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Table 1. Characterization of **6a**−**6c**[a]

	HOMO[b]/eV	LUMO[c]/eV	opt. E_g/eV	UV λ_{max} (lg ε)/nm	PL λ_{max}/nm	Stokes shift/nm	T_m/°C
6a	−5.29	−3.08	2.21	311 (4.36), 502 (4.38), 535 (4.46)	560	25	74
6b	−5.59	−3.04	2.55	450 (4.39)	522	72	50
6c	−5.81	−2.91	2.90	384 (4.05)	482	98	58

[a] Electrochemical and photophysical properties were measured in chloroform. [b] Determined from CV. [c] Determined from HOMO and optical bandgap. Melting point was determined by differential scanning calorimetry.

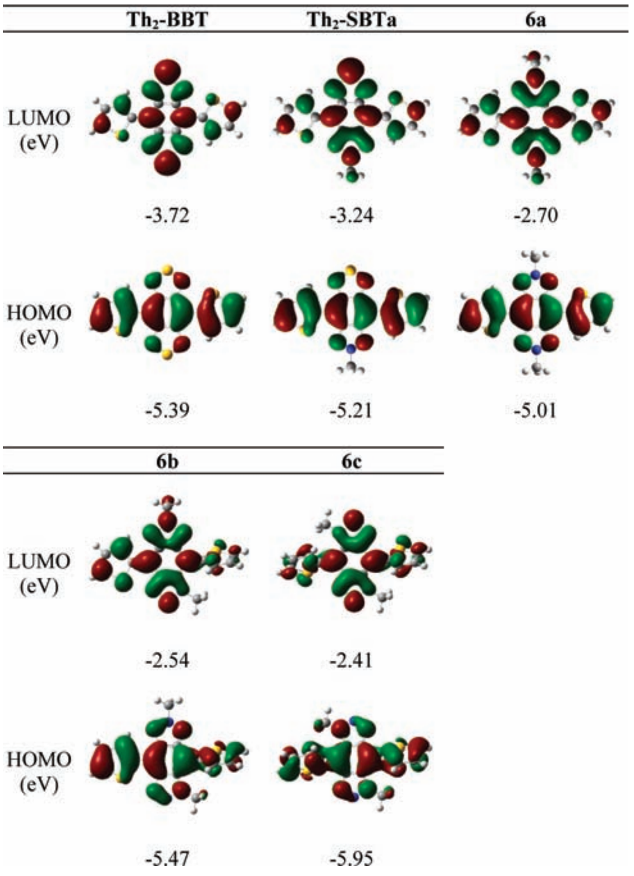

Figure 3. DFT calculation of Th_2-BBT, Th_2-SBTa, **6a**, **6b** and **6c** via geometry optimization using B3LYP 6-31^{+2}(3d,3p) for Th_2-BBT and Th_2-SBTa and 6-31G^{+2}(d,p) for **6a**, **6b** and **6c**. The large alkyl groups were reduced to methyl groups for simplicity.

the HOMO, bond length and dihedral angle between Th_2−BBT (1.44938 Å, 0.000°), Th_2−SBTa (1.44946 Å, 0.005°) and **6a** (1.44976 Å, 0.099°) respectively, there is an indication of quinoid character along the 4 and 8 positions of **6a** (Table 2). The calculated LUMO shows predominant localization in the BBTa core which is also very similar to that seen in Th_2−BBT. However, the lack of hypervalency in BBTa does not permit the stabilization of LUMO which occurs in both BBT and SBTa.

The DFT studies also show that the position of the alkyl groups for **6a**, **6b** and **6c** causes large twists for the thienyls when they are at the 1 and 5 position of the BBTa unit. These twists reduce conjugation which leads to higher LUMO and lower HOMO. These trends are in accordance to the experimental bandgap, Stokes shift, and HOMO and LUMO energies discussed previously.[33]

In conclusion, we have demonstrated the one-pot synthesis of halogenated BBTa and the subsequent alkylation resulting in the formation of the unprecedented 2,6-dialkyl isomer. Though separation of this isomer from the other three isomers proved to be difficult, the dithienyl coupled product **6a** can be easily separated, resulting in a 30% overall yield. The 1,6- (**6b**) and 1,5-isomer (**6c**) can also be isolated with overall yields of 33 and 3.3%, respectively. The yields of these isomers are lower than can be obtained by specific synthesis using literature procedures, but the current route is much shorter and the separation of the isomers is not difficult enabling useful amounts of all three to be obtained quickly for evaluation. Further optimization of the reaction conditions, for example, by changing the nature of the alkyl group, may enable selective enhancement of the yields of the isomers, making this route more useful for synthesis of materials for applications. These new molecules display optical and electronic properties suggesting they could be very useful building blocks for preparing conjugated organic materials with tunable HOMO and LUMO energies, thus enabling optimization of their properties to suit possible applications.

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Supporting Information Available. Detailed description of experimental procedures, plus mass spectra, NMR spectra, DSC and CV plots for 6a, 6b and 6c. Mass spectra of chlorinated BBTa and mixed halides BBTa. This material is available free of charge via the Internet at http://pubs.acs.org.