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A Simple Route toward the Synthesis of Bisbenzothiadiazole Derivatives

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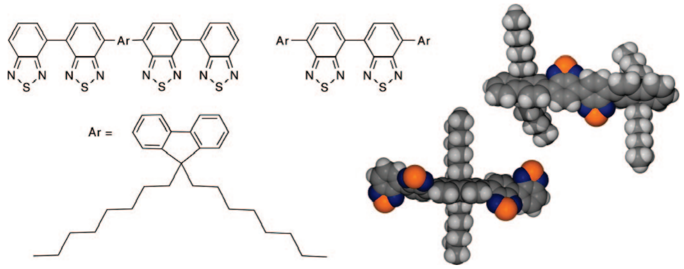
ABSTRACT



A simple and efficient route toward the synthesis of 4,4′-bis(2,1,3-benzothiadiazole) and 7,7′-dibromo-4,4′-bis(2,1,3-benzothiadiazole) has been developed. Oligomers were synthesized with bisbenzothiadiazole units either at the periphery or core, and each oligomer was characterized by X-ray crystallography. Both crystal structures display supramolecular interactions between the conjugated backbones, although the former, bearing two bisbenzothiadiazole units, has extended interactions within layers that engage all of the thiadiazole rings.

2,1,3-Benzothiadiazole-based oligomers and polymers have been widely studied in recent years as active materials in various optoelectronic devices because of the electron-accepting capability of the heterocyclic group and the observed low band gap in polymers containing it.[1−3] Thiadiazole-containing compounds show a tendency to form well-ordered crystal structures due to strong intermolecular interactions across heteroatom contacts and/or $\pi-\pi$ interactions.[4] 2,1,3-Benzothiadiazole derivatives are efficient fluorophores, and polymers containing them have shown promise for use in electroluminescent devices.[5−7] Copolymerization of benzothiadiazole with fluorene, thiophene, or other suitable aromatics can be used as a means to tune the HOMO−LUMO levels in the resulting polymers.[8,9] However, there are relatively few reports on the use of bisbenzothiadiazole based materials, in part due to a lack of an efficient method for their synthesis.[10−12] Here we report a facile method for the synthesis of 4,4′-bis(2,1,3-benzothiadiazole) and its brominated derivative 7,7′-dibromo-4,4′-bis(2,1,3-benzothiadiazole). The latter has been coupled with suitable alkylated fluorene moieties to generate soluble conjugated molecules with bisbenzothiadiazole units both at the core and the periphery.

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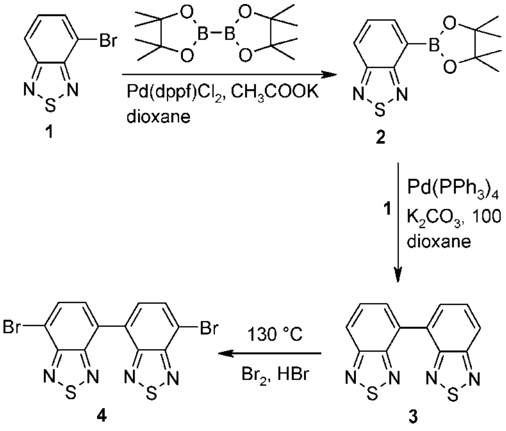
The synthesis of bisbenzothiadiazole **3** is shown in Scheme 1. 4-Bromo-2,1,3-benzothiadiazole **1** was prepared according to literature.[13] This was converted to the corresponding boronate ester **2** in 62% yield using bis(pinacolato)diboron in the presence of Pd(dppf)Cl_2 as a catalyst. Standard Suzuki coupling of **1** and **2** gave bisbenzothiadiazole **3** in 86% isolated yield. This method is far superior to previously reported nickel-based coupling methods in terms of both yield and simplicity of purification.[14] Bisbenzothiadiazole **3** was further brominated with molecular bromine by refluxing it in the presence of aqueous HBr (47%) to afford 7,7′-dibromo-4,4′-bis(2,1,3-benzothiadiazole) **4** in 50% yield.

Compounds **1**, **2**, and **4** are useful reagents for the synthesis of well-defined bisbenzothiadiazole-based oligomers and polymers, in particular the difunctional compound **4**, which holds great potential as a comonomer in the synthesis of low band gap materials. Using the above reagents, two types of oligomers were synthesized: one in which the benzothiadiazole units are introduced at the periphery and a second in which a bisbenzothiadiazole unit constitutes the core.

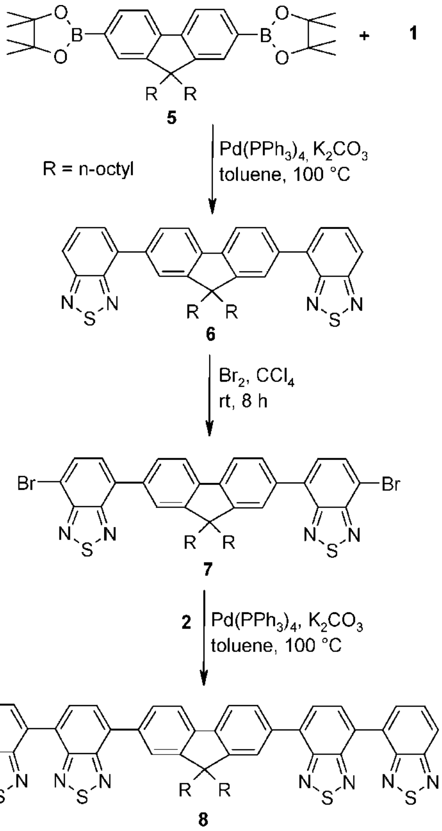
Scheme 1. Synthesis of 7,7′-Dibromo-4,4′-bis(2,1,3-benzothiadiazole) **4**



The synthetic approach toward the synthesis of oligomer **8** with two benzothiadiazole units at either side of a fluorene moiety is shown in Scheme 2. Suzuki coupling of the diboronate ester **5** with **1** gave 2,7-di(2,1,3-benzothiadiazol-4-yl)-9,9-dioctylfluorene **6** in 78% yield. This was brominated with molecular bromine to generate 2,7-di(4-bromo-2,1,3-benzothiadiazol-7-yl)-9,9-dioctyl-fluorene **7** in 71% yield. Coupling of the boronic ester **2** with **7** under standard conditions generated 2,7-di(bisbenzothiadiazolyl)-9,9-dioctylfluorene **8** in 50% yield. This monomer shows good solubility in common organic solvents and can be purified by recrystallization.

The related molecule **10** was synthesized in which alkylated fluorene units are at the periphery of a bisbenzothiadiazole core (Scheme 3). Again, Suzuki coupling of **4** with a 2-boronate ester of fluorene **9** gave 7,7′-di(9,9-dioctylfluoren-2-yl)-4,4′-bis(2,1,3-benzothiadiazole) **10** in 50% yield. This compound also shows very good solubility in common organic solvents. All of the oligomers described above were characterized by ^{1}H and ^{13}C NMR, elemental analysis, mass spectrometry (MALDI-TOF), UV−vis absorption and emission spectroscopies, and in some cases, by X-ray crystallography.

Scheme 2. Synthesis of 2,7-Di(bisbenzothiadiazolyl)-9,9-dioctylfluorene **8**



To investigate their electronic properties, compounds **3**, **6**, **8**, and **10** were characterized by UV−vis spectroscopy. A plot of extinction coefficient versus wavelength for all the above compounds as measured in THF is depicted in Figure 1. Bisbenzothiadiazole has an absorption maximum of 360 nm, whereas 2,1,3-benzothiadiazole absorbs at 306 nm. When fluorene is end-capped at the 2,7-positions with benzothiadiazole (**6**), the absorbance maximum is observed at 393 nm. It should be noted that 9,9-dioctylfluorene absorbs at 314 nm, and thus the introduction of two benzothiadiazole units induces a red shift of 79 nm. When two benzothiadiazole units are introduced at both sides of the fluorene moiety, the wavelength of maximum absorbance now increases to 425 nm. On the other hand, when bisbenzothiadiazole is end-capped with fluorene units on either side, the absorbance maximum is observed at 436 nm. The observed trend is in accordance with what is expected; however, the extent of

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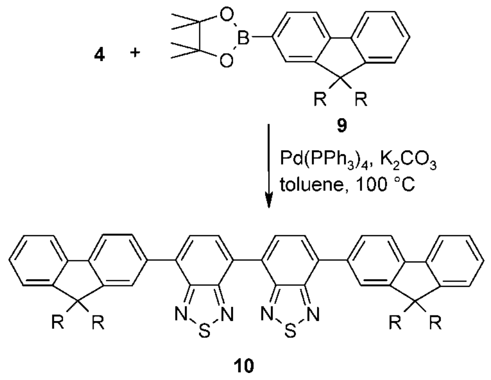
conjugation between neighboring benzothiadiazole units and fluorene units will largely depend on the twist angle. The above data clearly suggest that the corresponding polymers have potential as low band gap materials, an application of these oligomers that is currently being investigated.

Scheme 3. Synthesis of 7,7′-Di(9,9-dioctylfluoren-2-yl)-4,4′-bis(2,1,3-benzothiadiazole) **10**



The photoluminescence spectra for the various oligomers were recorded in THF and are depicted in Figure 1. Bisbenzothiadiazole has an emission maximum at 442 nm. The fluorene-bisbenzothiadiazole based oligomers emit in the green region of the spectrum. When fluorene is end-capped at the 2,7-positions with bisbenzothiadiazole (**8**), the emission maximum is observed at 525 nm. However, when bisbenzothiadiazole is end-capped with fluorene units on either side, the emission maximum is observed at 531 nm. The observed Stokes shifts for compounds **3**, **6**, **8**, and **10** are 82, 105, 100, and 95 nm, respectively, which suggests that there is a large twist between benzothiadiazole units themselves as well as between benzothiadiazole and neighboring aromatic units. This has further been probed by X-ray crystallographic studies, which in addition to confirming atomic connectivity provide insight into molecular conformation and solid state organization.

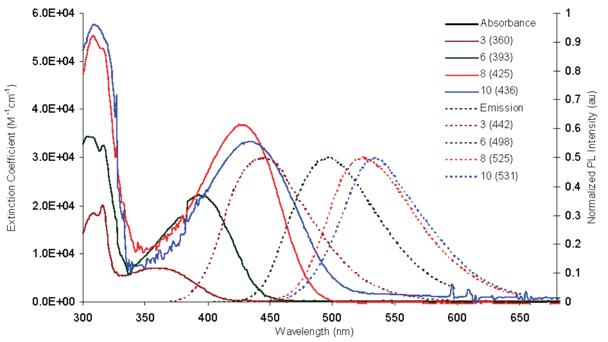


Figure 1. Normalized absorbance and emission spectra (the observed maxima shown in brackets) of the various oligomers in THF.

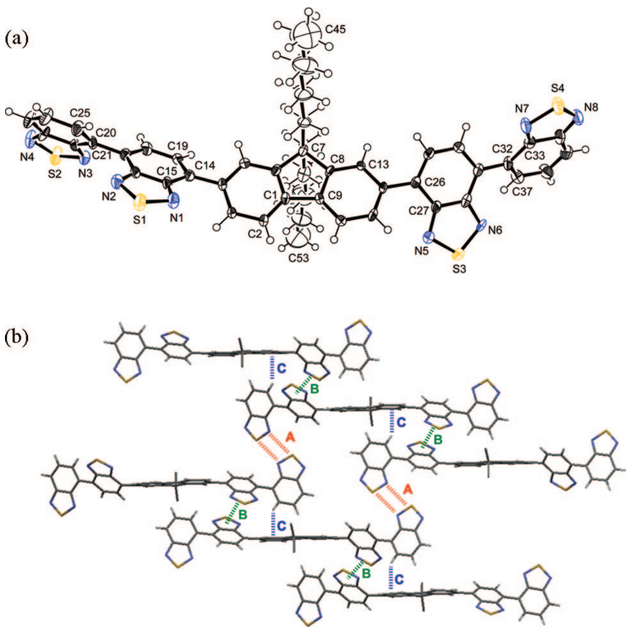


Figure 2. Crystal structure of **8**. (a) ORTEP perspective of one of two molecules in the asymmetric unit. (b) Packing as viewed down the *a*-axis, indicating significant intermolecular interactions (only the first carbons of the octyl chains are shown).

Slow diffusion of methanol into a solution of **8** in dichloromethane yielded single crystals suitable for X-ray diffraction structure analysis (Figure 2). The monomer **8** crystallizes with two molecules in the asymmetric unit, related through a pseudoinversion center and thus having similar geometries. The unsaturated core has a nonplanar conformation, with twist angles of 43.8−54.0° within the bisbenzothiadiazole units (anti to each other), which in turn are 36.16−41.6° with respect to the central fluorene. Three crystal structures containing a 4,4′-bis(2,1,3-benzothiadiazole) have been previously reported, all symmetrically substituted in the 7,7′ positions. 4,4′-Bis(7-(1-pyrrolidinyl)-2,1,3-benzothiadiazole)[12] and 4,4′-bis(7-iodo-2,1,3-benzothiadiazole)[15] each have a nonplanar core with twist angles of 43.4° and 48.4°, respectively; however, the monocation of the first (as a PF$_6$ salt)[12] is close to planar (3.6°/4.6°). The crystal packing of **8** provides an indication of how it may organize within the thin films typically used in optoelectronic devices. Tightly packed sheets of **8**, stacked along the *a*-axis, display significant intermolecular contacts (Figure 2b). Pairs of short S···N contacts (**A**) (3.088−3.237 Å) between each terminal benzothiadiazole and its neighbor give rise to ribbons running along the *c*-axis. These ribbons combine through *π*-stacking (**B**) of inner benzothiadiazole groups, and C−H···arene interactions (**C**) between the electron-poor benzothiadiazole (C−H) and electron-rich fluorene. Close S···N intermolecular contacts in crystals have been previously described and

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attributed to electrostatic interaction between dipoles and/or weak intermolecular bonding involving a partial rehydridization at sulfur with *d*-orbital participation.[4] The octyl chains of **8** lie in the plane of and at the interface between adjoining layers (Figure SI1, Supporting Information).

Crystals of **10** grown by slow diffusion of methanol into a chloroform solution were also subjected to X-ray diffraction analysis. Oliogomer **10** crystallizes in a centrosymmetric space group, in this case with an inversion center lying on the bond between the benzothiadiazoles (Figure 3). A twist angle of 37.7° between the benzothiadiazoles (anti) and of 30.1° between the fluorenyl and bisbenzothiadiazole core results in an overall rotation from end to end of nearly 98°. In contrast to the layers of **8**, the molecules of **10** pack into ordered double columns along the *c*-axis (Figures SI2 and SI3, Supporting Information), surrounded by a sheath of octyl chains with significant disorder. No S···N contacts are observed, but short edge-to-face contacts between S and the neighboring fluorene ring (3.38 Å) (**D**; Figure 3b) and fluorenyl C−Hs and a benzothiadiazole ring (**E**) are expected to contribute the stability of the columns. The lower ratio of benzothiadiazole to octyl chain in **10** (1:2) compared with **8** (2:1) provides fewer opportunities for favorable S···N interactions, resulting in a lower density packing.

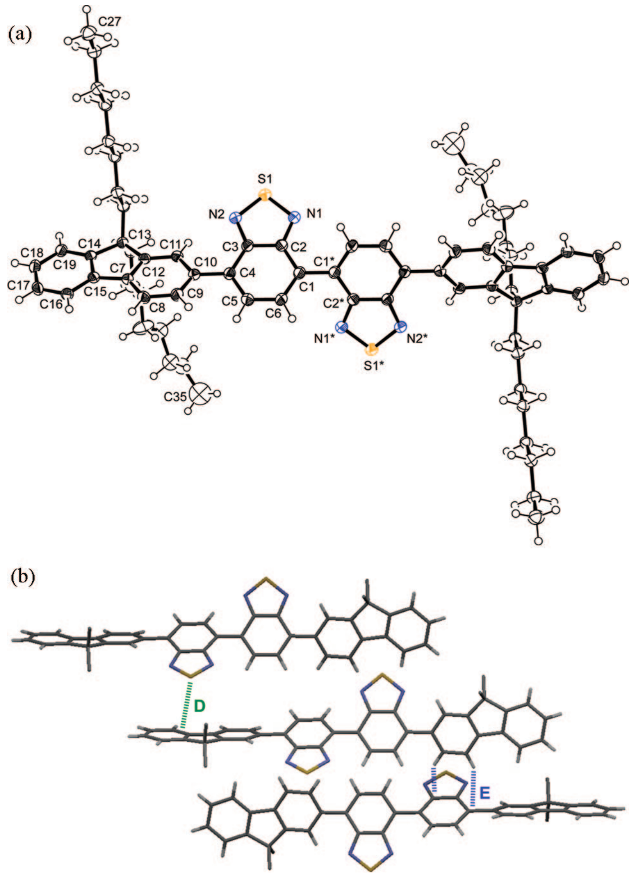

Figure 3. Crystal structure of **10**. (a) ORTEP perspective of the symmetry expanded asymmetric unit. (b) Packing as viewed down the *b*-axis, showing significant intermolecular interactions (only the first carbons of the octyl chains are shown).

In conclusion, a simple and efficient route toward the synthesis of 7,7′-dibromo-4,4′-bis(2,1,3-benzothiadiazole) has been developed. Studies on oligomers containing this unit suggest that its incorporation into polymers could potentially lead to new classes of low band gap materials. Crystallographic studies on the newly synthesized oligomers containing bisbenzothiadiazole and dialkylfluorenyl moieties highlight the types of supramolecular interactions that drive their packing and provides evidence for rationalizing structure−property relationships.

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Supporting Information Available: Synthetic and crystallographic experimental procedures, full spectroscopic data for all new compounds and additional crystal structure packing diagrams, including CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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