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Thieno[3,2-*b*]pyrrolo Donor Fused with Benzothiadiazolo, Benzoselenadiazolo and Quinoxalino Acceptors: Synthesis, Characterization, and Molecular Properties

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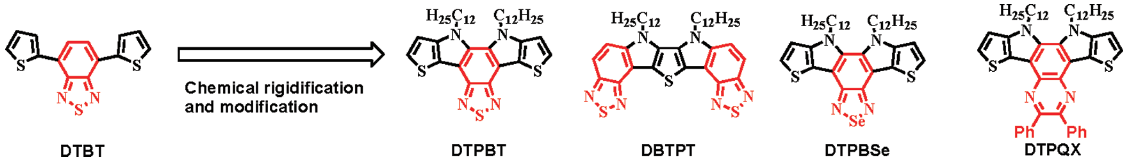
ABSTRACT



Nitrogen-bridged donor–acceptor multifused dithienopyrrolobenzothiadiazole (DTPBT) and dibenzothiadiazolopyrrolothiophene (DBTPT) were successfully synthesized by intramolecular Cadogan annulation. The electron-deficient benzothiadiazole unit in DTPBT can be converted to benzoselenadiazole and quinoxaline moieties through reduction/cyclization to generate dithienopyrrolobenzoselenadiazole (DTPBSe) and dithienopyrroloquinoxaline (DTPQX), respectively. The nitrogen atoms function as the bridges for covalent planarization to induce intermolecular interaction and intramolecular charge transfer.

In recent years, tremendous research effort has been focused toward organic photovoltaics (OPVs) to realize low-cost, lightweight, large-area, and flexible photovoltaic devices.[1] Development of novel conjugated polymers continues to play the most important role in boosting the high efficiency of OPVs.[2] The widely used strategy to produce a low band gap (LBG) polymer is to polymerize an electron-rich donor (D) monomer with an electron-deficient acceptor (A) monomer along the conjugated polymer backbone.[3] In addition to the D-A strategy, forced planarization by covalently fastening adjacent aromatic units in the polymer backbone provides an effective way to reduce the band gap and enhance the intrinsic charge mobility.[4] In this regard, extensive research effort has been focused on the design and synthesis of coplanar electron-rich donors having multifused aromatic or heteroaromatic structures.[5]

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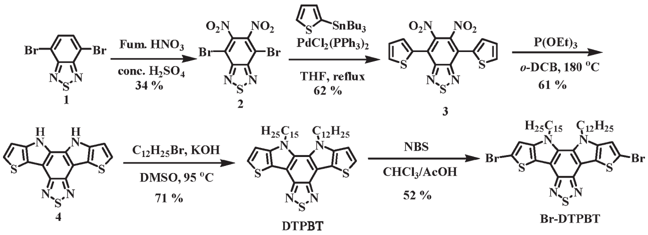
By copolymerization with appropriate acceptors, these fascinating structures have produced a variety of promising D-A polymers that led to high-performance solar cells. We envision that the electronic interactions between the donor and the acceptor units in a D-A copolymer might be greatly enhanced, if the neighboring electron-rich donor and electron-deficient acceptor units along the polymer backbone are covalently locked and conformationally rigidified into a coplanar interfused D-A assembly.[6] To our surprise, however, utilization of a fused D-A polymer for OPVs has not been well exploited presumably due to the lack of a useful synthetic approach to prepare a suitable fused D-A monomer precursor. Among a range of electron-deficient heteroaromatic units, the benzothiadiazole (BT), benzoselenadiazole (BSe), and quinoxaline (QX) units are of particular interest due to their strong electron affinity and simple planar structure.[7] The benzothiadiazole unit (acceptor) coupled with two electron-rich thienyl rings (donor) to form a nonfused D-A-D 4,7-di(thiophen-2-yl)benzothiadiazole (**DTBT**) unit has been the commonly used core structure in D-A polymers for OPVs.[8] Inspired by the skeleton of the **DTBT** unit, we have developed a fused D-A-D dithienopyrrolobenzothiadiazole (**DTPBT**) structure in which the 3-positions of the two outer thiophenes (D) are covalently linked to the 5- and 6-positions of the central benzothiadiazole core (A) by a nitrogen bridge, forming two pyrrole rings embedded in a pentacyclic structure (Scheme 1). Furthermore, a fused A-D-A type structure, dibenzothiadiazolopyrrolothiophene (**DBTPT**) with reversed structural arrangement of BT and thiophene units in **DTPBT**, was also synthesized (Scheme 2). More importantly, the structure of **DTPBT** can serve as a useful precursor to synthesize two other fused D-A-D structures, dithienopyrrolobenzoselenadiazole (**DTPBSe**) and dithienopyrroloquinoxaline (**DTPQX**), with different acceptors. The nitrogen bridges in the pentacyclic units also allow us to introduce aliphatic side chains to promote sufficient solubility of the resultant conjugated polymers.

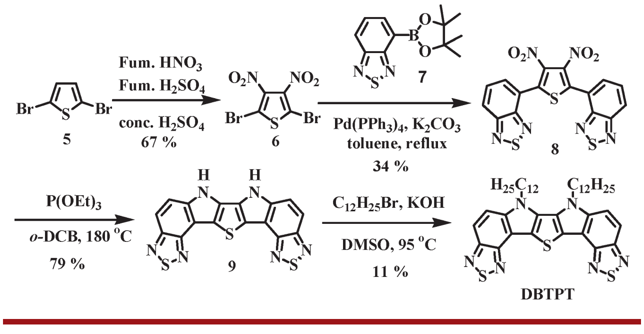
Scheme 1 depicts the synthetic route of **DTPBT**. Nitration of 4,7-dibromobenzothiadiazole **1** afforded the 4,7-dibromo-5,6-dinitrobenzothiadiazole **2** which was then reacted with 2-tributylstannyl thiophene by Stille coupling to yield compound **3**. Double intramolecular Cadogan reductive cyclization of **3** in the presence of triethyl phosphate successfully furnished the fused D-A-D structure **4** in 61% yield.[9] *N*-Alkylation of **4** with an excess amount of 1-bromododecane in the presence of potassium hydroxide resulted in the formation of **DTPBT** in 71% yield. Fortunately, NBS bromination of **DTPBT** regioselectively occurred at the 5-position of the thienyl moieties to yield the brominated monomer **Br-DTPBT** which can be readily polymerized with a variety of conjugated units to prepare polymers containing fused D-A segments.

Scheme 1. Synthesis of Fused D-A-D Pentacylic Structure **DTPBT**



The synthesis of fused A-D-A **DBTPT** is shown in Scheme 2. Suzuki coupling of compound **6** with **7** afforded the compound **8**. Double intramolecular Cadogan annulation of **8** obtained the desired product **9** where the central dipyrrolothiophene moiety was fused with two outer benzothiadiazole units. *N*-Alkylation of **9** resulted in **DBTPT** with two dodecyl side chains in a lower yield of 11% probably due to the less nucleophilic nitrogens as a result of two electron-withdrawing BT units.

Scheme 2. Synthesis of Fused A-D-A **DBTPT**



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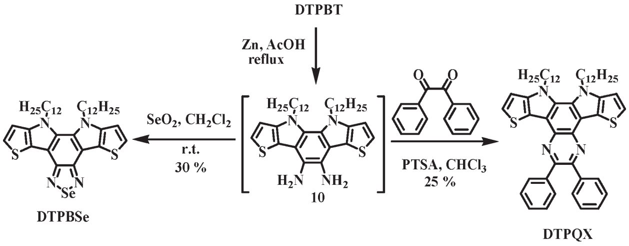
Scheme 3. Synthesis of Fused D-A-D **DTPBSe** and **DTPQX**



The thiadiazole ring in **DTPBT** was reduced by Zn/AcOH to generate corresponding diamine intermediate **10** (Scheme 3). Without any purification, **10** was directly reacted with selenium dioxide to produce **DTPBSe** in 30% yield. Meanwhile, double imine condensation of **10** with benzil led to the formation of **DTPQX** in 25% yield. All the target molecules with aliphatic side chains exhibit good solubility in common organic solvents such as hexane, dichloromethane, acetone, chloroform, and THF. All the compounds were fully characterized by using ^{1}H and ^{13}C NMR and mass spectrometry (see the Supporting Information (SI)).

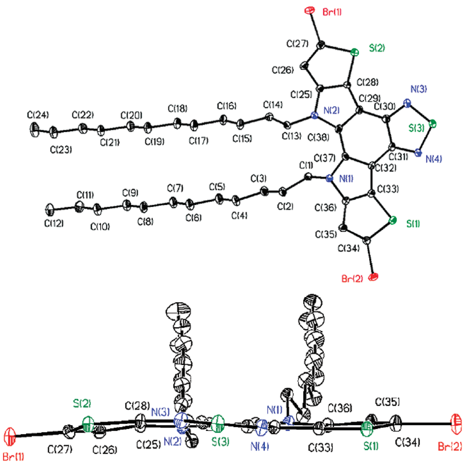


Figure 1. Top view (top) and side view (bottom) of ORTEP drawing of **Br-DTPBT** (50% probability for thermal ellipsoids).

The structure of **Br-DTPBT** was particularly analyzed by single-crystal X-ray crystallography as shown in Figure 1 (side and top views). The dihedral angle between the central phenylene and outer thiophene rings of **Br-DTPBT** is 6.9°, indicating a coplanar π-conjugated framework due to the nitrogen bridges. The crystal packing is also shown in Figure 2. It is found that **Br-DTPBT** molecules are packed as anticofacial dimers with a short intermolecular distance of 3.4 Å, indicating strong $\pi-\pi$ interaction. Note that the aliphatic side chains are also interdigitated in a regular arrangement.

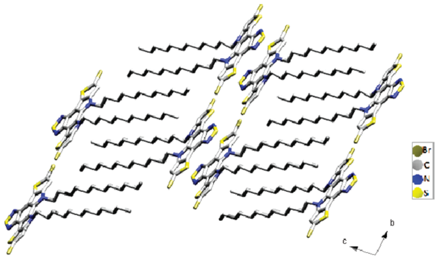


Figure 2. Crystal packing of **Br-DTPBT** along *a*-axis. Hydrogen atoms are removed for clarity.

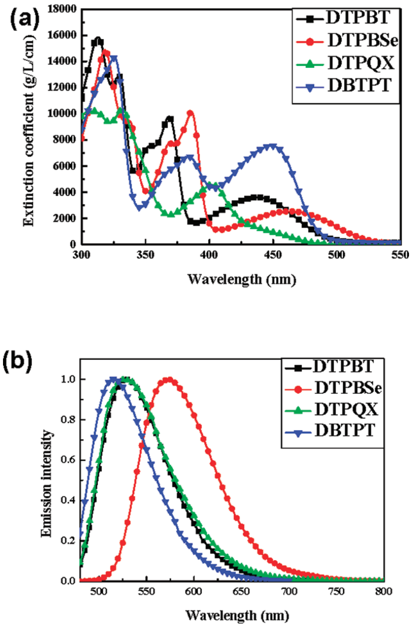


Figure 3. Absorption spectra (a) and emission spectra (b) of all the fused D–A molecules in toluene.

The absorption spectra of these fused molecules in toluene are shown in Figure 3a, and the corresponding data are summarized in Table 1. The nonfused **DTBT** exhibited two characteristic bands in the absorption spectra in toluene (Figure S1). The shorter wavelength absorbance at ~310 nm comes from the $\pi-\pi$ * transition of the pentacyclic units, while the lower energy band at ~450 nm is attributed to the intramolecular charge transfer (ICT) between the thiophene units and the benzothiadiazole segments. **DTPBT** displays well-defined vibronic structures in the $\pi-\pi$* transition bands as a result of its coplanar and rigid conformation. In addition to the two typical bands similar to **DTBT**, an extra band at ~368 nm was observed in the fused **DTPBT** analogue. This band could be ascribed to another charge transfer transition from a short D-π-A structure in **DTPBT**. This indicates that the N-atom not only serves as a bridge but also induces a charge transfer due to the coplanar structure, leading to a greater dipole moment in the excited state. Consistently,

Table 1. Optical and Electrochemical Properties of Fused D-A Materials

Compd	λ_{abs} (nm)	λ_{em} (nm)	Stokes shift (nm)	HOMO [a] (eV)	LUMO [b] (eV)	E_g^{opt} (eV)
DTPBT	313, 368, 437	528	91	−5.36	−2.84	2.52
DTPBSe	318, 369, 463	574	111	−5.31	−2.96	2.35
DTPQX	307, 332, 402	527	125	−5.30	−2.73	2.57
DBTPT	325, 383, 448	514	66	−5.46	−2.91	2.55

[a] The HOMO energy levels were obtained from the equation HOMO = $-(E_{ox}{}^{onset} - E_{(ferrocene)}{}^{onset} + 4.8)$ eV. [b] LUMO levels were obtained from the equation LUMO = HOMO + $E_g{}^{opt}$.

DTBT showed little solvatochromism effect, whereas N-bridged **DTPBT** exhibited a more pronounced bathochromic shift with the increasing solvent polarity. **DTPBSe** and **DTPQX** also showed similar N-induced absorption characteristics. However, compared to **DTPBT**, **DTPBSe** exhibited bathochromic-shifted peaks, whereas **DTPQX** showed a hypsochromic-shifted spectrum, indicating that the accepting strength is in the order **BSe** > **BT** > **QX**. The stronger accepting ability of benzoselenodiazole is associated with the smaller ionization potential and more polarizable character of selenium.[10] In comparison with **DTPBT**, **DBTPT** having reversed arrangement of thiophene and BT units exhibited a very similar absorption profile. However, the lower-energy transition band in **DBTPT** is more red-shifted and intense due to the higher content of the **BT** units. The emission λ_{max} of **DTPBT**, **DTPQX**, and **DBTPT** are in the green-yellow region with λ_{max} at ~514−528 nm, while the λ_{max} of **DTPBSe** is in the orange-red region with λ_{max} at ~574 nm in toluene (Figure 3b). The emission spectra also showed a strong dependence on the polarity of the solvent (Figure S2). All the molecules showed a large Stokes shift between their corresponding absorption and emission spectra. Such a Stokes shift and solvent-dependent emission indicate the effective intramolecular charge transfer in the excited states between the thieno[3,2-*b*]pyrrole units and corresponding acceptor units.

To gain insight into the excited states of **DTPBT**, theoretical calculations have been performed using time-dependent density functional theory (TD-DFT); for technical details, see SI. The recorded absorption spectra of both compounds can be well interpreted using frontier molecular orbitals shown in Figure 4. For **DTPBT**, the three lowest, optically active excited states, roughly characterized as the HOMO→LUMO+1, HOMO−1→LUMO, and HOMO→LUMO transitions, are located by TD-DFT at 312, 349, and 454 nm, respectively, agreeing well with their experimental λ_{max} wavelengths (313, 368, and 437 nm in toluene). A similar calculation of **DBTPT** is also conducted and shown in the SI.

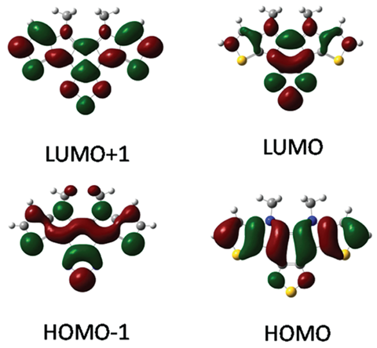


Figure 4. Frontier molecular orbital plots of **DTPBT** calculated with TD-DFT at the B3LYP level.

The electrochemical properties have been evaluated by cyclic voltammetry (Figure S3). The HOMO energy level was estimated to be −5.36, −5.31, −5.30, −5.46 eV, respectively (Table 1). It is envisaged that the low-lying HOMO energy levels will be beneficial for oxidative stability and open-circuit voltages of photovoltaic devices.

The LUMO energy levels are deducted from their HOMO energy levels and optical band gaps. The LUMO energy levels were approximately estimated by subtracting the band gap values from the corresponding HOMO levels

In summary, we have developed two fused donor−acceptor pentacyclic structures **DTPBT** and **DBTPT** by double intramolecular Cadogan cyclization. The benzothiadiazole unit in **DTPBT** can be further modified to benzoselenadiazole and quinoxaline moieties through reduction/cyclization to yield **DTPBSe** and **DTPQX**, respectively. The nitrogen atoms can not only function as the bridge for covalent planarization to induce $\pi-\pi$ interaction but also facilitate intramolecular charge transfer for better light harvesting. Incorporation of these fused D-A frameworks into conjugated polymers are highly promising and currently underway in our laboratory. Those results will be reported in due course.

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Supporting Information Available. Detailed synthesis, absorption and emission spectra, X-ray crystallographic data of **DTPBT**, theoretical calculation of **Br-DTPBT**, CV measurements, and NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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