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Benzothiadiazole-Based D−π-A−π-D Organic Dyes with Tunable Band Gap: Synthesis and Photophysical Properties

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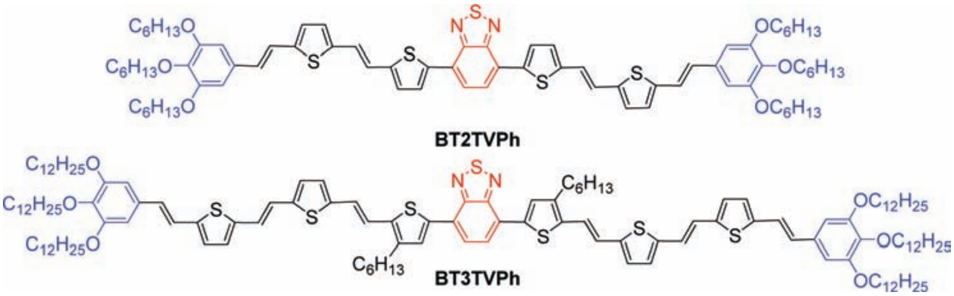
ABSTRACT



A series of symmetrical D−π-A−π-D molecules based on benzothiadiazole and oligo(thienylenevinylene)s were facilely developed. The investigation of their photophysical and electrochemical properties demonstrated that these compounds exhibited broad absorption covering the whole visible range with appropriate energy levels for light-harvesting donors.

π-Conjugated organic molecules as alternatives to conjugated polymers have attracted considerable attention in solution-processable solar cells due to their monodisperse, reproducible preparation, and easy fuctionalization.[1,2] The benzothiadiazole skeleton as a strong acceptor unit is usually empolyed to modulate the HOMO or LOMO energy levels for low band gap features in optoelectronic devices.[3,4]

In this contribution, we present a series of symmetrical linear donor(D)−π-acceptor(A)−π-donor(D) oligomers with benzothiadiazole as acceptor core and oligo(thienylenevinylene)s (OTVs)[5] with different size as donor segments. Such D−π-A−π-D molecular design makes it possible to probe the relationship between the extension of donor chromophores and their corresponding photophysical and electrochemical properties. It is desirable to modulate their absorption bands to cover the whole visible region, which

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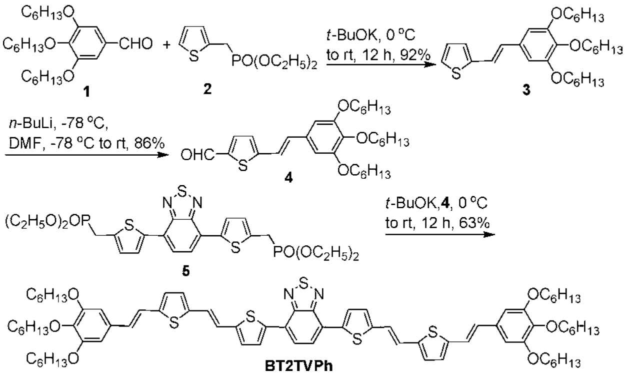
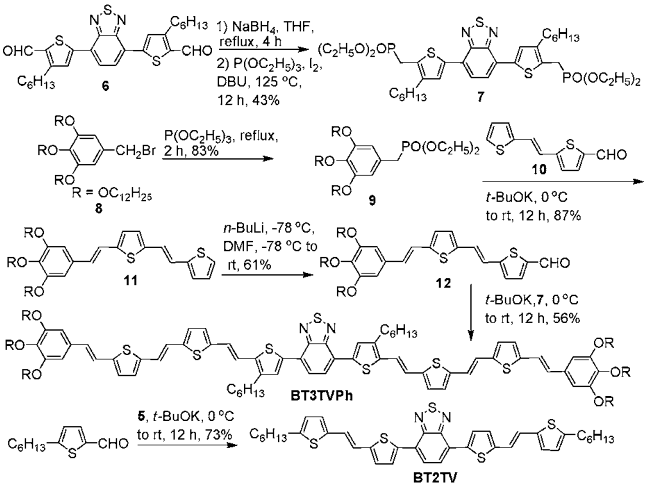
might bring insight into the synthesis of good donor candidates for solution-processable solar cells. Furthermore, long aliphatic chain at both ends of the D−π-A−π-D rodlike structures may help induce liquid crystal properties and better molecular packing.

Scheme 1. Synthesis of **BT2TVPh**



Scheme 1 illustrates the synthetic approaches to donor−acceptor−donor chromophores **BT2TVPh**. A Wittig−Horner reaction between 3,4,5-tris(hexyloxy)benzaldehyde **1**[6] and diethyl 2-thienylmethylphosphonate **2**[5a] afford **3** in 92% yield. Treatment of **3** with *n*-BuLi followed by anhydrous DMF facilely gave the monoaldehyde **4** in 86% yield. **BT2TVPh** with all *trans* double bonds was obtained Wittig−Horner reaction of diphosphonate **5**[7] and monoaldehyde **4** at room temperature in 63% yield.

Scheme 2. Synthesis of **BT3TVPh** and **BT2TV**



As shown in Scheme 2, to improve the solubility and processability of **BT3TVPh**, multiple alkyl groups were introduced at the acceptor core and the donor terminal alkoxy groups were elongated.[8] Reduction of dialdehyde **6**[9] with NaBH$_4$ gave a diol, and then the crude diol was treated triethylphosphate, iodide, and DBU to afford the diphosphonate **7** in overall 43% yield. Phosphonate **9** was prepared from treating 3,4,5-tridodecyloxybenzyl bromide **8**[10] with triethylphosphate in 83% yield.[11] **11** with extending thienyl vinylene segment was obtained from **9** and monoaldehyde **10**[12] through a Wittig−Horner reaction, which is converted to extended monoaldehyde **12** using *n*-BuLi and anhydrous DMF in 53% yield with two steps. Finally, a two-fold Wittig−Horner reaction of **12** and **7** generated **BT3TVPh** in 56% yield. To better understand the photophysical properties of these D−A−D molecules, **BT2TV** as model compound was afforded from treating **5** with 5-hexylthiophene-2-carbaldehyde[13] in 73% yield.

All new compounds showed good solubility in common organic solvents at room temperature. As hoped, the solubility of **BT3TVPh** proved to be much higher than that of the

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Table 1. Photophysical and Electrochemical Properties of these D−π-A−π-D Molecules in Solutions and in Thin Films

compd	λ_{max} abs[a], nm (log ε)	λ_{max} em[a], nm	λ_{max} abs[b], nm	λ_{max} em[b], nm	Φ_{PL}, %	$E_{ox(onset)}$[d], V	$E_{red(onset)}$[d], V	E_{HOMO}, eV	E_{LUMO}, eV	$E_{g(cv)}$, eV	$E_{g(opt)}$, eV
BT2TV	387 (4.84)	623	415	692	21[c]	0.65	−1.60	−5.36	−3.11	2.25	2.01
	539 (4.78)		552								
BT2TVPh	419 (5.87)	656	430		1[e]	0.48	−1.30	−5.19	−3.41	1.78	1.87
	559 (5.04)		573								
BT3TVPh	460 (5.19)	678	462		0.1	0.44	−1.15	−5.15	−3.56	1.59	1.62
	580 (5.17)		595								

[a] In cyclohexane solution (5 × 10^{-6} M). [b] In thin films. [c] In cyclohexane solution and rhodamine B (Φ_{PL}= 0.65 in ethanol) as the standard. [d] Reference electrode: Ag/AgNO$_3$. [e] In cyclohexane solution and **BT2TV** as standard.

other two compounds in common organic solvents. Their structures and purity were fully characterized and verified by ^{1}H, COSY, and ^{13}C NMR, elemental analysis, and MALDI-TOF MS (see Supporting Information). The *E*-configured double bonds of these new compounds were confirmed from the values of the coupling constant (*J*) between vinyl protons (ca. 16 Hz). Meanwhile, the protons assigned to the benzothiadiazole core shifted upfield with increasing concentration (see Figure S11 in Supporting Information), which was caused by a shielding effect from π−π stacking.

The investigation of the thermal properties of these new compounds indicated that they exhibited good stability with decomposition temperature higher than 350 °C in nitrogen atmosphere. Figure S1 in Supporting Information showed crystalline to liquid crystalline phase transition at about 98 °C for **BT2TV** and 55 °C for **BT3TVPh** and liquid crystalline to isotropic liquid phase transition at 188 °C for **BT2TV** and 125 °C for **BT3TVPh**. **BT2TVPh** exhibited only single melting point transition at about 160 °C.

The photophysical properties of these D−π-A−π-D linear molecules were investigated in dilute solutions and in thin films. Their photophysical data in solutions and in thin films are summarized in Table 1. As shown in Figure 1, all molecules showed two distinct absorption bands in the range of 300−500 and 500−700 nm in cyclohexane dilute solutions. The absorption maximum λ_{max} peaked at 387 and 539 nm for **BT2TV**, 419 and 559 nm for **BT2TVPh**, and 460 and 580 nm for **BT3TVPh**. The peaks at 387−460 nm could be assigned to the π−π* transition, and those at longer wavelengths absorption peaks should result from an intramolecular charge transfer (ICT) between the peripheral donor part and the acceptor core group. The absorption bands exhibited the successive red-shift in agreement with the increase of the effective conjugation length and formation of donor−acceptor type structures upon appending electron-rich alkoxyl phenyl group to the electron-deficient cores.[14] Meanwhile, the molar extinction coefficient also gradually increased from **BT2TV** (0.60 × 10^5 M^{-1} cm^{-1} at 539 nm) to **BT3TVPh** (1.48 × 10^5 M^{-1} cm^{-1} at 580 nm). Such high molar extinction coefficients are favorable for absorbing the solar radiation.

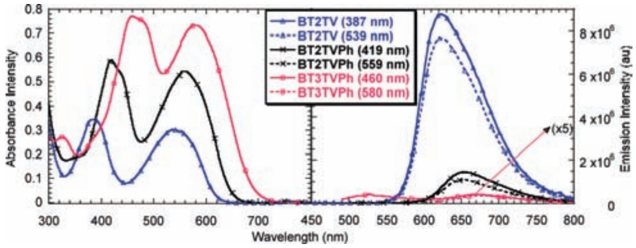

Figure 1. Absorption and PL spectra of three molecules in cyclohexane solution (5 × 10^{-6} M). PL spectra were recorded at different excitation wavelengths shown in every parentheses. Emission spectrum of **BT3TVPh** scaled up (×5).

Figure 1 also shows the photoluminescent (PL) spectra of these D−π-A−π-D molecules in cyclohexane solutions. A emission maximum; λ_{max} peaked at 623 nm for **BT2TV**, 656 nm for **BT2TVPh**, and 678 nm for **BT3TVPh**. The red-shift trend of emission spectra confirmed that **BT3TVPh** had the longest effective conjugation length. Moreover, the fluorescence quantum yields (Φ_{PL}) of these molecules in cyclohexane solution successively decreased from 21% for **BT2TV** to 0.1% for **BT3TVPh** due to extending thienylvinylene segment. Interesting, the emission band of **BT2TV** and **BT2TVPh** both came exclusively from the charge transfer band when excited at short wavelength, which indicated that a highly efficient intramolecular energy transfer processed from the π−π* transition band to charge transfer band. For **BT3TVPh**, residual fluorescence in the short wavelength region was clearly observed due to its relative lowest quantum efficiency of **BT3TVPh**.

The absorption spectra of our D−π-A−π-D molecules were nearly independent of solvent polarity. However, the emission spectra of these D−π-A−π-D molecules were solvatochromic, which further confirmed the strong intramolecular CT in these compounds (see Supporting Information). Emission maximum λ_{max} of **BT2TVPh** red-shifted from 654 nm in cyclohexane solution to 714 nm in DMF solution along with successively decreased emission intensity because the dipole moment is larger in the excited state than in the ground

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state.[15] Meanwhile, the emission of **BT3TVPh** was absent in THF, indicating the stronger charge-transfer excited state in relatively polar THF.

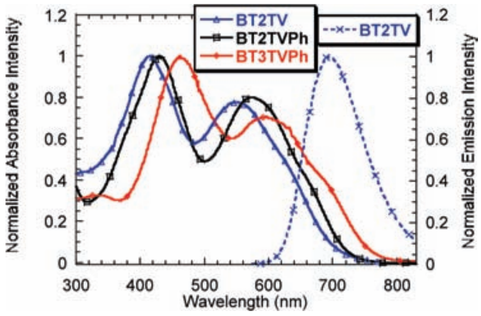

Figure 2. Absorption and PL spectra of these D−A−D molecules in thin films. PL spectra recorded under excitation at the absorption λ_{max} wavelength at room temperature.

Figure 2 shows the absorption and PL spectra of three D−π-A−π-D molecules in the solid state. The thin films used for absorption and emission measurements were obtained by spin coating THF solutions (ca. 10 mg/mL) of our molecules onto quartz plates at 1000 rpm. All compounds exhibited good film forming properties. The absorption spectra covered almost UV−vis region and showed almost same features as those in dilution solution although their absorption λ_{max} obviously red-shifted, especially in longer wavelength range due to the formation of *J*-aggregates.[16]

The results suggested our molecules are suitable for future applications in organic solar cells. Table 1 illustrates the energy band gap of these molecules, which were estimated from the onset of the absorption spectra in thin films. As shown in Figure 2, for **BT2TV**, weak emission with the maximum λ_{max} at 692 nm was observed; however, the emission of **BT2TVPh** and **BT3TVPh** in thin film was totally quenched due to the lower PL quantum yield of those compounds in solution and strong intermolecular interactions in thin films.[17]

As shown in Figure 3 and Table 1, the HOMO and LUMO energy levels of these D−π-A−π-D molecules in thin films were determined by cyclic voltammetry on a Pt electrode. One single-electron quasi-reversible reduction were observed at −1.66/−1.50 V for **BT2TV**, −1.52/−1.33 V for **BT2TVPh**, and −1.40/−1.35 V for **BT3TVPh**. These compounds exhibited irreversible oxidation process. From these onset of oxidative or reductive potentials, estimated the HOMO and LUMO level were −5.36/−3.11 eV for **BT2TV**, −5.19/−3.41 eV for **BT2TVPh**, −5.15/−3.56 eV for **BT3TVPh**. Consequently, the band-gaps and LUMO level were obviously reduced with the increase of the effective conjugation length in our molecules and were in agreement with these obtained from their absorption spectra in thin films. These results indicated that our compounds had promising electrochemical properties as donor materials in organic solar cells.

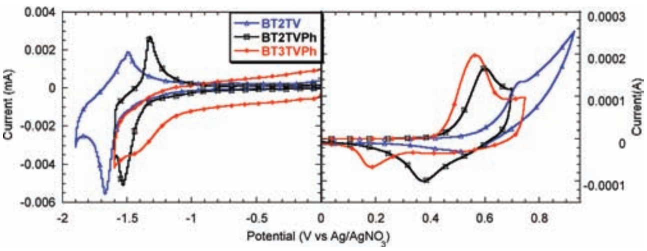

Figure 3. Cyclic voltammagram of D−A−D conjugated oligomers films on Pt electrode in 0.1 M Bu_4NPF_6 in CH_3CN solution with a scan rate of 100 mV/s.

In conclusion, we have facilely developed a new family of linear benzothiadiazole-based D−π-A−π-D organic molecules in good yields. Their absorption and emission features are significantly modulated by changing the length of OTV segments in our molecules. **BT2TVPh** and **BT3TVPh** in thin films show a broader and stronger absorption band in the range of 300 to 800 nm covering the whole visible region. Such D−π-A−π-D synthetic strategy with simple molecular structures and extended absorption bands obviates the difficulty in the preparation of longer OTVs. These photophysical and eletrochemical properties showed that our molecules are good candidates for high-performance solution-processable organic solar cells and organic field-effect transistors. Further experiments to explore their liquid crystal properties and organic solar cells are underway in our laboratory.

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Supporting Information Available: Experimental procedures, ^{1}H and ^{13}C NMR, and MS data for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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