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Star-Shaped D-π-A Conjugated Molecules: Synthesis and Broad Absorption Bands

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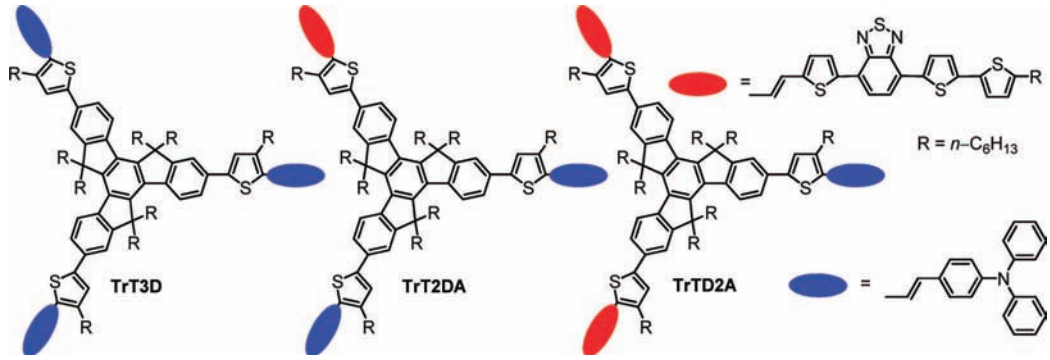
ABSTRACT



Two donor−acceptor hybrid star-shaped D-π-A molecules were facilely developed. The absorption spectra of TrTD2A and TrT2DA, which almost covered the whole visible range, were tuned by changing the ratio of donor and acceptor groups. However, the PL quantum effieciencies of TrTD2A and TrT2DA in solutions were dramatically reduced after the introduction of benzothiadiazole unit as acceptor chromophore.

π-Conjugated small molecules have attracted considerable attention as active materials in solution-processable solar cells due to their high purity and reproducible properties.[1] To improve the power conversion efficiencies of solar cells, it is of critical importance to develop new organic small

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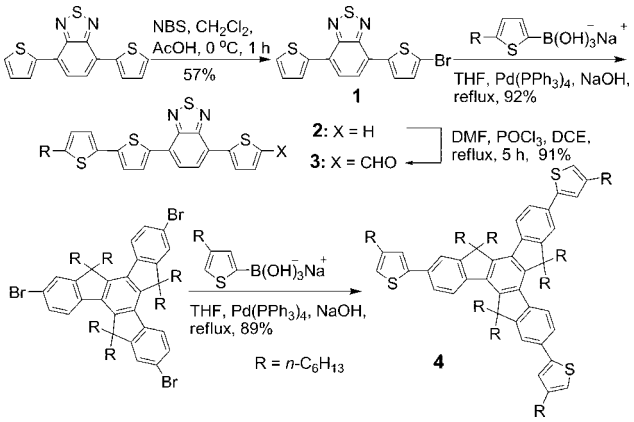
molecules with a higher absorption coefficient and broader absorption features.[2] Herein, we present a series of soluble star-shaped molecules with triphenylamine unit as donor, functionalized benzothiadiazole moiety as acceptor, and truxene as the core. The aim of systematic structural variations on these molecules is to provide insight into understanding the relationship between the structures and properties and to modulate their absorption bands to cover the whole visible region.[3] Such structural modulation might make our star-shaped D-π-A molecules as good candidates for solution-processable solar cells.

Scheme 1 illustrates the synthetic approaches to acceptor segment and core chromophore. 4,7-Bis(2-thienyl)-2,1,3-

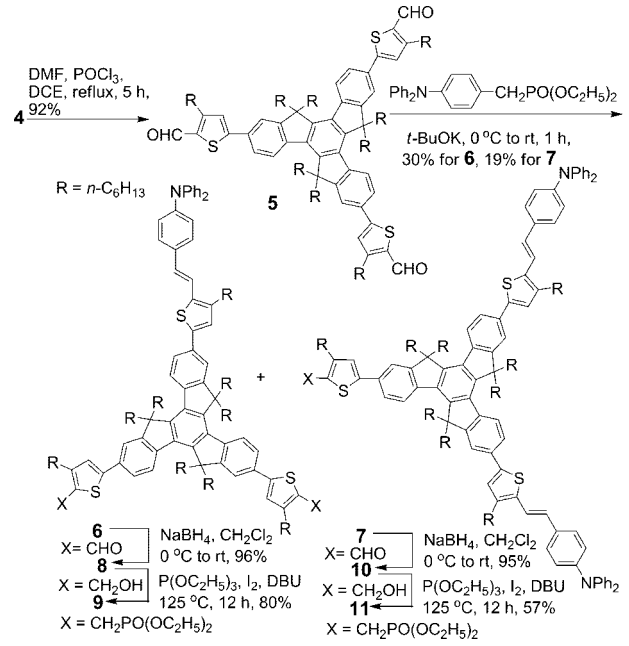
Scheme 1. Synthesis of Core and Acceptor Chromophores



benzothiadiazole[4] was facilely converted to monobrominate **1** with *N*-bromosuccinimide (NBS) in 57% yield.[5] A Suzuki coupling reaction between sodium 4-hexyl-2-thienylboronate[6] and **1** followed by a Vilsmeier reaction[7] afforded **3** in 84% overall yield. Core **4** was prepared by a Suzuki coupling reaction between tribromohexahexyltruxene and sodium 4-hexyl-2-thienylboronate[6] in 89% yield.[8]

Scheme 2 outlines the synthesis of some precursors. The key component for the synthesis of **TrTD2A** and **TrT2DA**

Scheme 2. Synthesis of Partially Functionalized Truxenes



is the AB_2 building block, which bears two or one active aromatic aldehyde groups with other branches functionalized by triphenylamine donor units. A Wittig−Horner coupling reaction between diethyl 4-(diphenylamino)benzyl phosphonate[9] and trialdhehyde **5** obtained from a Vilsmeier reaction of **4** afforded dialdehyde **6** (30% yield) and monoaldehyde **7** (19% yield).[10] Reduction of **6** with $NaBH_4$ gave alcohol **8** in 96% yield, which was treated in triethyl phosphate with iodine and DBU to afford phosphonate **9** in 80% yield.[11] Through the same procedures, **11** was obtained from **7** in 54% overall yield.

Scheme 3 illustrates the synthetic approach to our target molecules. The Wittig−Horner coupling between aldehyde and phosphonate afforded **TrT2DA** (66%), **TrTD2A** (63%), and **TrT3D** (81%), respectively. All new compounds showed good solubility in common organic solvents at room temperature. Their structures and purity were fully characterized and verified by ^{1}H and ^{13}C NMR, elemental analysis, and MALDI-TOF MS or ESI MS (see the Supporting Information). The *E*-configured double bonds of our new compounds were confirmed from the values of the coupling constant (*J*) between vinyl protons (ca. 16 Hz).

The photophysical properties of these D-π-A star-shaped molecules were investigated both in dilute solutions and in thin films. Table 1 summarizes their photophysical data in solutions and in thin films. As shown in Figure 1, **TrT3D** showed an absorption band corresponding to a $\pi-\pi^*$

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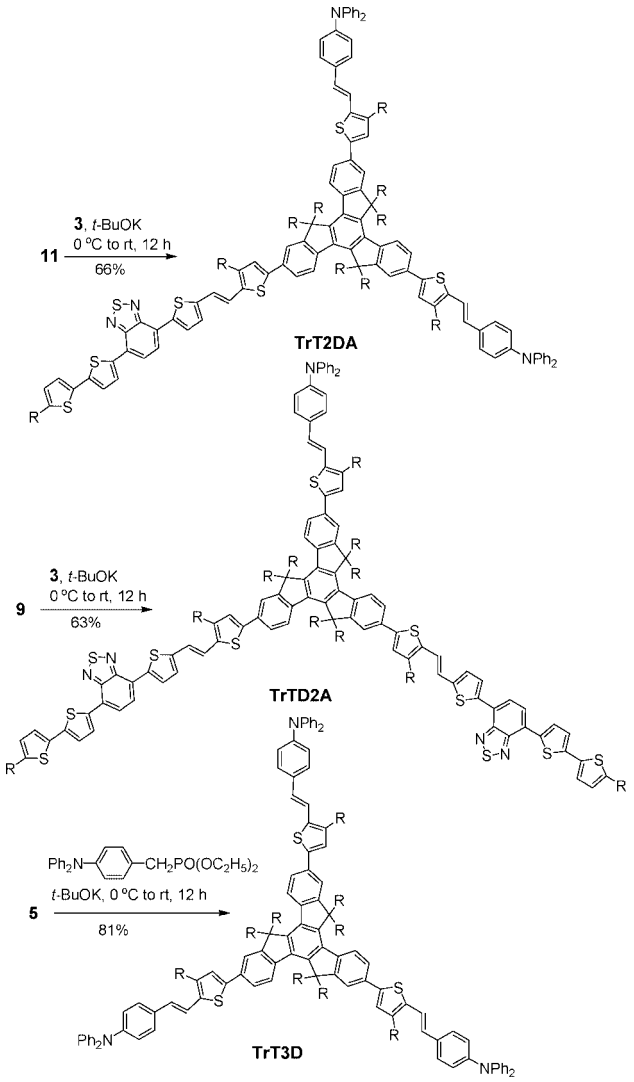
Scheme 3. Synthesis of **TrT2DA**, **TrTD2A**, and **TrT3D**



transition with λ_{max} at 425 nm. **TrT2DA** and **TrTD2A** exhibited similar absorption features, and two bands with λ_{max} at 425 and 542 nm were observed after the introduction of acceptor groups. The absorption band at 542 nm was assigned to those of benzothiadiazole unit as acceptor branch

Table 1. Photophysical Properties of Star-Shaped Molecules in Solutions and in Thin Films

compd	λ_{max} abs[a] (nm) (log ε)	λ_{max} emis[a] (nm)	λ_{max} abs[b] (nm)	λ_{max} emis[b] (nm)	Φ_{PL} (%)
TrT3D	425 (5.34)	484	433	531	71[c]
TrT2DA	425 (5.31)	619	433	684	1.5[d]
	542 (4.78)		550		
TrTD2A	427 (5.28)	623	433	700	1[d]
	542 (5.12)		560		

[a] In cyclohexane solution (10^{-6} M). [b] In thin films. [c] In cyclohexane solution and coumarin 152 (Φ_{PL} = 0.21 in ethanol) as the standard. [d] In cyclohexane solution and rhodamine B (Φ_{PL} = 0.65 in ethanol) as the standard.

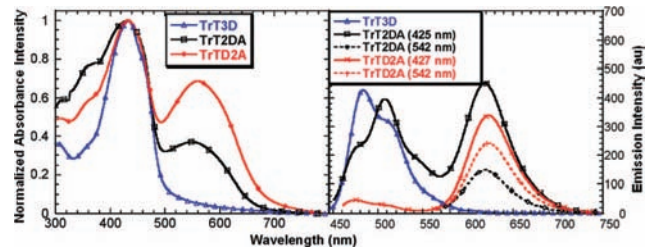


Figure 1. Absorption and PL spectra of **TrT3D**, **TrT2DA**, and **TrTD2A** in cyclohexane solution (10^{-6} M). PL spectra were recorded at different excitation wavelengths shown in parentheses. Emission spectrum of **TrT3D** is on a reduced scale (1%).

in these compounds.[12] The molar extinction coefficient of this absorption peak in longer wavelength increased about 2 times from **TrT2DA** (0.61×10^5 M^{-1} cm^{-1}) to **TrTD2A** (1.3×10^5 M^{-1} cm^{-1}). Figure 1 also shows the photoluminescent (PL) spectra of these star-shaped molecules in cyclohexane solutions. A maximum emission peak at 484 nm was observed from **TrT3D**. Under excitation at 425 nm, for **TrT2DA**, two emission bands at ca. 510 and 619 nm were observed; however, for **TrTD2A**, the emission band at ca. 484 nm was dramatically quenched, and the emission band comes almost exclusively from the acceptor units (623 nm). This result indicated a highly efficient intramolecular energy-transfer process from the donor branch to the acceptor branch. For **TrT2DA**, residual fluorescence in the short wavelength region was clearly observed due to its relatively high content of donor groups compared with that of **TrTD2A** and the high quantum efficiency of **TrT3D**. Under excitation at 542 nm, only one emission band was observed both from the PL spectra of **TrT2DA** and **TrTD2A**. At the same concentration, the emission intensities under excitation at 425 nm were ca. 1.5 times for **TrTD2A** and 3 times for **TrT2DA** higher than those under excitation at 542 nm, respectively, which indicated an effecive antenna effect in our molecules.[13] Moreover, the fluorescence quantum yields (Φ_{PL}) of **TrT3D** in dilute cyclohexane solution were measured to be 71%; however, after introduction of the acceptor unit, Φ_{PL} was dramatically decreased to 1.5% for **TrT2DA** and 1% for **TrTD2A**.[14] The excitation wavelength for the quantum yield measurements was 542 nm for **TrTD2A** and **TrT2DA** and 425 nm for **TrT3D**, respectively.

The absorption spectra of our D-π-A star-shaped molecules were nearly independent of solvent polarity. However, their emission spectra exhibited distinct solvent dependence. Less pronounced vibronic structure and larger Stokes shift were observed with the increase of the solvent polarity (see the Supporting Information). For example, the maximum emission peak of **TrTD2A** changed from ca. 623 nm in cyclohexane to ca. 662 nm in DMF. Moreover, the emission

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above 600 nm was obviously quenched with increase of the polarity of the solvents, which indicated that such D-π-A star-shaped molecules possessed more polar character at the excited states than at the ground state.

Figure 2 shows the absorption and PL spectra of these three molecules in thin films. The thin films used for

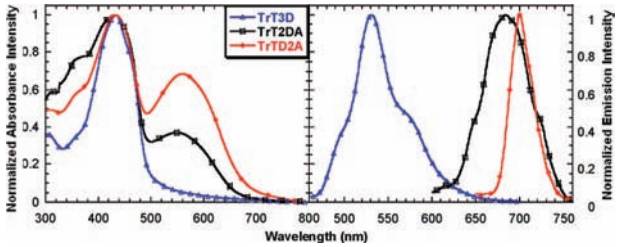

Figure 2. Absorption and PL spectra of star-shaped molecules in thin films. PL spectra recorded under excitation at the absorption λ_{max} wavelength at room temperature.

absorption and emission measurements were obtained by spin-coating toluene solutions (ca. 10 mg/mL) of our star-shaped molecules onto quartz plates at 1000 rpm. All compounds exhibited excellent film-forming properties. The absorption of three molecules in thin film showed almost the same features as those in dilution solution, although their absorption λ_{max} slightly red-shifted. The absorption features of **TrT2DA** and **TrTD2A** covered almost the whole visible region from 250 to 700 nm. As shown in Figure 2, **TrT3D** showed strong emission with the maximum λ_{max} at 531 nm; however, the emission of **TrT2DA** and **TrTD2A** in thin film was almost totally quenched when excited either at shorter (433 nm) or at longer wavelength (550 nm). These results indicated that a highly efficient intra- and intermolecular energy transfer in thin films occurred from the donor branch to the acceptors, and the strong fluorescence quenching was attributed to the poor PL quantum yield of **TrT2DA** and **TrTD2A** and strong intermolecular interaction in thin films.[15] Such photophysical property is beneficial for active materials in solar cells.

The energy bandgaps of our star-shaped molecules in thin films were determined from the onset of their absorption spectra to be 2.25 eV for **TrT3D**, 1.80 eV for **TrT2DA**, and 1.70 eV for **TrTD2A**. The cyclic voltammetry of **TrT3D** and **TrT2DA** shows irreversible oxidation peaks at 1.67 and 1.25 V vs Ag/AgCl. **TrTD2A** exhibits good reversible oxidation waves peaking at 1.06 V vs Ag/AgCl. In comparison with **TrTD2A** (0.78 eV), **TrT2DA** showed a higher oxidation potential onset (0.86 eV), which indicated that the oxidative potential enhanced with the increase of the content of the acceptor unit in these molecules, which caused an obvious change in HOMO and LUMO energy level of the corresponding molecules. The oxidation potential onset for **TrTD2A** was closed to that of 4,7-bis(5-(5-hexylthiophen-2-yl)thiophene-2-yl)benzo[1.2.5]thiadiazole (about 0.80 eV);[16] however, it was reduced relative to that of **TrT3D** (1.12 eV), which was because that **TrTD2A** and **TrT2DA** had the longer effictive conjugation length compared with Tr3D. The calculated HOMO and LUMO level were −5.52/−3.27 eV for **TrT3D**, −5.26/−3.46 eV for **TrT2DA**, and −5.18/−3.48 eV for **TrTD2A**.[17] Molecular modeling was employed to study the electronic properties of these molecules. The conformation of these molecules is shown in Figure S10 of the Supporting Information.

In conclusion, we have developed a series of new solution-processable star-shaped D-π-A organic molecules via facile synthetic approaches in good yields. Their absorption and PL features are significantly modulated by changing the content of the acceptor in our molecules. **TrTD2A** and **TrT2DA** in thin films show a broader and stronger absorption band in the range of 250 to 700 nm, which covers the whole visible region. These results indicated that the two acceptor branches of **TrTD2A** are conductive to increase the intermolecular interaction and light-harvesting ability.[18] These results show that **TrTD2A** and **TrT2DA** are good candidates for solution-processable organic solar cells. The photoinduced electron-transfer studies with regard to another electron acceptors such as C60 and further experiments to explore their applications in organic solar cells are in progress in our laboratory.

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Supporting Information Available: Experimental procedures and ^{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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