

Energy Transfer in New D- π -A Conjugated Dendrimers: Their Synthesis and Photophysical Properties

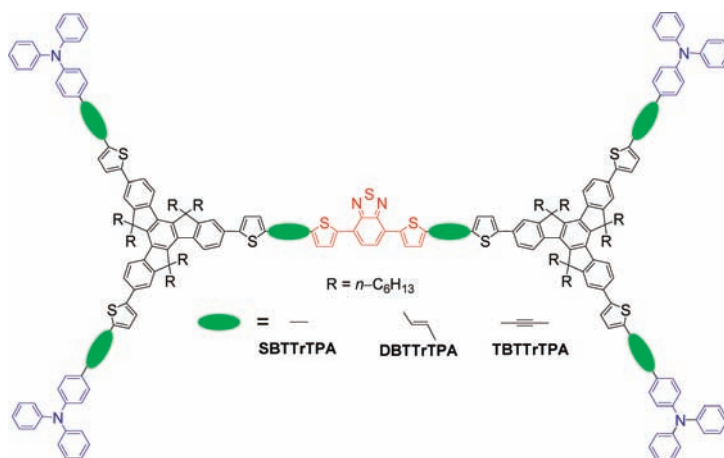
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ABSTRACT



A series of new D- π -A conjugated dendrimers based on benzothiadiazole and triphenylamine were developed via facile synthetic approaches. By changing the types of bridges between the different functional moieties of these dendrimers, their photophysical properties, especially the intramolecular energy transfer process, were effectively modulated.

π -Conjugated dendrimers integrating different functional groups represent a unique class of shaped-persistent macromolecules and show great application potential for the artificial light-harvesting system.¹ In our previous contributions, we reported a family of new gradient conjugated dendrimers, in which the photophysical properties, especially the intramolecular energy transfer efficiency, were modulated by the dendrimers' generation.² Herein, we develop a series of new D- π -A dendrimers composed of four triphenylamine moieties as the donor groups share one benzothiadiazole chromophore in the middle as the acceptor, through various conjugated spacers. The properties of donor-acceptor substituted conjugated dendrimers have been tuned by changing the structures of the donor, acceptor, and

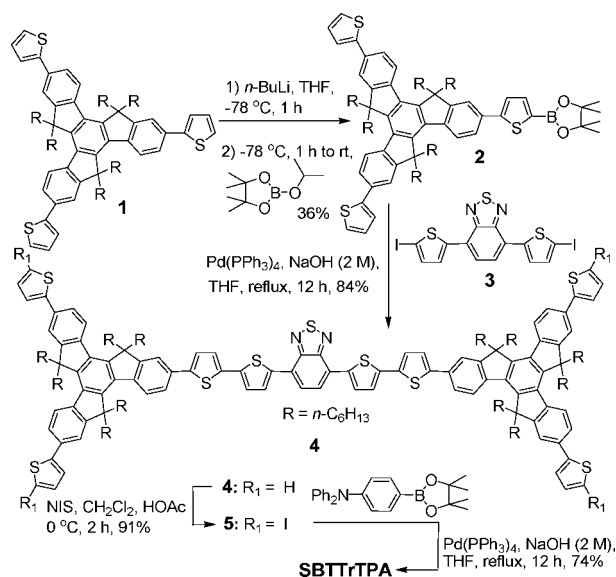
π -conjugated moieties.^{3,4} In our system, different conjugated bridges between the core and the periphery are integrated, which results in different effective conjugated lengths and electronic communication between the rim and the core. The

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aim of these systematic structural variations was to provide insight into the relationship between the effective conjugation length, the photophysical properties, and the intramolecular energy transfer process, which is conducive for the design of new optoelectronic materials in nonlinear optical devices or solar cells.

Scheme 1 illustrates the synthetic approaches to **SBTTrTPA**. Lithiation of **1**⁵ followed by reaction with 2-isopropoxy-4,4,5,5-

Scheme 1. Synthesis of SBTTrTPA



tetramethyl-1,3,2-dioxaborolane gave monoboronic ester **2** in 36% yield, while unreacted **1** was recovered. The diiodinated product **3** was obtained through the lithiation of 4,7-bis(2-thienyl)-2,1,3-benzothiadiazole with LDA at $-78\text{ }^{\circ}\text{C}$ followed by the addition of elementary iodine in 86% yield.⁶ Diiodo **3**

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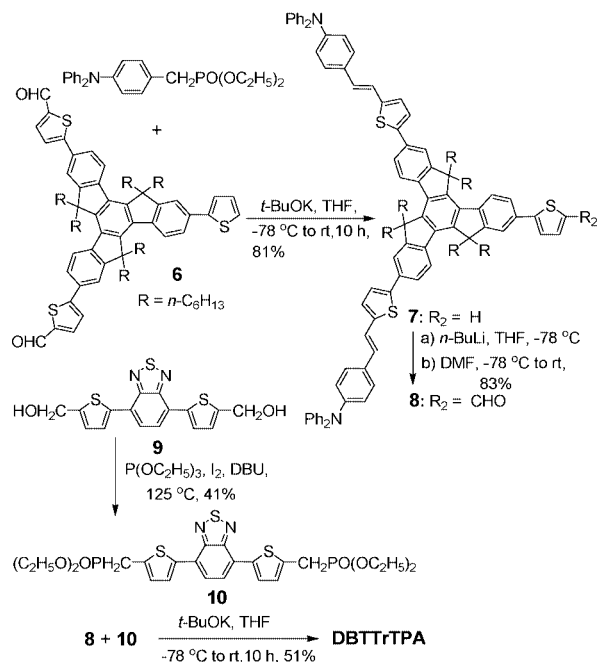
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was subjected to a Suzuki reaction with **2** catalyzed by $\text{Pd}(\text{PPh}_3)_4$ to afford **4** in 84% yield. Treating **4** with NIS afforded **5** in 91% yield. **SBTTrTPA** was obtained through the 4-fold Suzuki coupling between **5** and the monoboronic pinacol ester of triphenylamine in 74% yield.⁷

Scheme 2 illustrates the synthetic approaches to **DBTTrTPA**. Compound **7** with all *E*-configured double bonds was prepared

Scheme 2. Synthesis of DBTTrTPA



via Wittig–Horner reaction between **6**⁵ and diethyl 4-(diphenylamino)benzylphosphonate⁸ using *t*-BuOK in 81% yield. **7** was converted to the monoaldehyde **8** using *n*-BuLi and anhydrous DMF in 83% yield. **9** was obtained by reduction of 4,7-bis(5-formylthiophen-2-yl)-2,1,3-benzothiadiazole⁹ with NaBH_4 in 88% yield and then converted to diphosphonates **10** in 41% yield by treating **9** in triethylphosphate with iodine and DBU at $125\text{ }^{\circ}\text{C}$.¹⁰ **DBTTrTPA** was obtained through Wittig–Horner reaction between **7** and **10** in 51% yield.

Scheme 3 illustrates the synthetic approaches to **TBTTrTPA**. Compound **11**² reacted with 2-methylbut-3-yn-2-ol under standard Sonogashira reaction conditions to give **12** in 28% isolated yield, and unreacted **11** was recovered.¹¹ Another Sonogashira reaction between **12** and 4-ethynyl-*N,N*-diphenyl-

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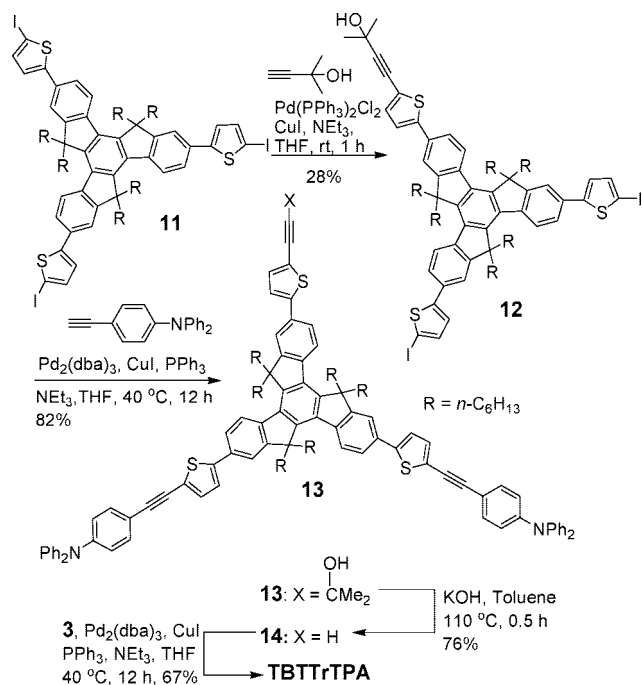
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Scheme 3. Synthesis of **TBTTrTPA**



laniline¹² afforded **13** in 82% yield. Removal of the protection group of **13** to give **14** was performed in refluxing toluene in 76% yield. **TBTTrTPA** was obtained through the Sonogashira reaction between **3** and **14** in 67% yield.

All new compounds were readily soluble in common organic solvents such as toluene, THF, and DMF. Their structures and purity were fully characterized and verified by ¹H and ¹³C NMR, elemental analysis, as well as MALDI-TOF MS (see the Supporting Information). The stereochemistries of all double bonds of **DBTTrTPA** and **7** were confirmed from the values of the coupling constant (*J*) between vinyl protons (ca. 16 Hz).

The photophysical properties of these dendrimers and model compounds **4** and **7** were investigated in dilute solutions and in thin films. Figure 1 shows their absorption and photoluminescent (PL) spectra in cyclohexane solution. Table 1 summarizes their photophysical data in both solutions and in thin films. All molecules show two distinct absorption bands. Absorption peaks were at 396 and 535 nm for **SBTTrTPA**, 421 and 552 nm for **DBTTrTPA**, and 391 and 512 nm for **TBTTrTPA**. By comparing the maximum absorption peak of **7** (421 nm) and **4** (344 nm, 535 nm), we assigned the absorption band in the shorter wavelength region to the four end-capping triphenylamine units in these dendrimers. Another absorption peak for **SBTTrTPA**, **DBTTrTPA**, and **TBTTrTPA** was assigned to the π - π^* absorption band of the benzothiadiazole core. Among three dendrimers, **DBTTrTPA** exhibited the longest effective conjugation length along the molecule. In comparison with

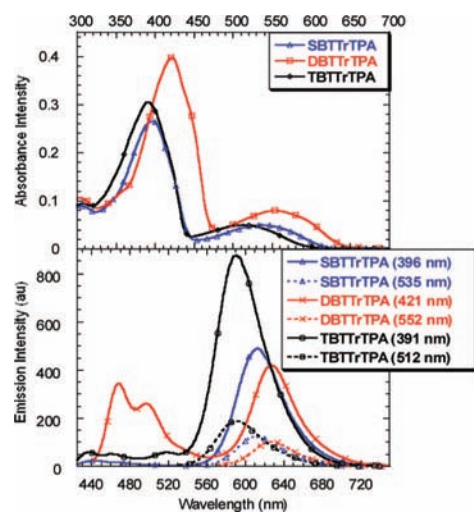


Figure 1. Absorption and PL spectra of three dendrimers in cyclohexane solution (10^{-6} M). PL spectra recorded at different excitation wavelengths shown in every parenthesis.

SBTTrTPA, the insertion of vinylene units results in a red-shift of ca. 20 nm and a higher value of molar extinction coefficient, beneficial to the light-harvesting process.¹

Table 1. Photophysical Properties of Dendrimers and Model Compounds in Solutions and in Thin Films

compd	$\lambda_{\text{max}}^{\text{abs.}}$ ^a nm (log ϵ)	$\lambda_{\text{max}}^{\text{emis.}}$ ^a nm	$\lambda_{\text{max}}^{\text{abs.}}$ ^b nm	$\lambda_{\text{max}}^{\text{emis.}}$ ^b nm	$\Phi_{\text{PL}}\%$
SBTTrTPA	396(5.42)	614	405	658	8 ^c
	535(4.70)		552		
DBTTrTPA	421(5.60)	628	426	670	3 ^c
	552(4.90)		567		
TBTTrTPA	391(5.48)	592	397	628	16 ^c
	512(4.71)		521		
4	344(5.28)	614	345	660	9 ^c
	535(4.70)		553		
7	421(5.30)	468	426	512	64 ^d

^a In cyclohexane solution (10^{-6} M). ^b In thin films. ^c In cyclohexane solution and rhodamine B ($\Phi_{\text{PL}} = 0.65$ in ethanol) as the standard. ^d In cyclohexane solution and Coumarin 152 ($\Phi_{\text{PL}} = 0.21$ in ethanol) as the standard.

The maximum emission wavelengths λ_{max} in cyclohexane solutions for **SBTTrTPA** to **TBTTrTPA** were 614, 628, and 592 nm, respectively. Red shifts of the fluorescence spectra were observed for **SBTTrTPA** and **DBTTrTPA** compared with **TBTTrTPA**, confirming the more effective conjugation through single bond and double bond bridges. Compound **4** exhibited an emission feature similar to that of **SBTTrTPA** (see Figure S1, Supporting Information). The fluorescence quantum yields (Φ_{PL}) of these dendrimers in dilute cyclohexane solution were measured to be 8% for **SBTTrTPA**, 3% for **DBTTrTPA**, and 16% for **TBTTrTPA** (Rhodamine B as the standard, $\Phi_{\text{PL}} = 0.65$ in ethanol).¹³ Although **DBTTrTPA** has the longest

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effective conjugation length, its fluorescence quantum yield was dramatically lower than others, which might be related to the nonluminescent property of oligothiophenevinylenes.¹⁴ Moreover, the maximum emission peaks were excitation wavelength independent. For **SBTTrTPA** and **TBTTrTPA**, when excited at 394 or 391 nm (the maximum absorption peaks of the periphery group), the emission came almost exclusively from the core units (see Figure 1). The residual fluorescence from the periphery group in the range from 400 to 550 nm became very weak, which indicated a highly efficient intramolecular energy transfer process from the outside to the core. In addition, the emission intensities excited at the periphery group were several times higher than those when excited at maximum absorption of the core units, showing clearly an antenna effect.¹⁵ When **DBTTrTPA** was excited at 421 nm, residual fluorescence in the short wavelength region was clearly observed. The energy transfer efficiencies were calculated to be 74% for **SBTTrTPA**, 82% for **DBTTrTPA**, and 79% for **TBTTrTPA**, respectively.^{3c} Note that **DBTTrTPA**, despite the obvious residual fluorescence in the short wavelength region, has the largest energy transfer efficiency. These seemingly conflicting results be caused from the very high PL quantum yield (64%) of the donor unit and the comparatively low PL quantum yield of the acceptor unit (3%) in this molecule.

To gain further insight into the photophysical process within these dendrimers, we investigated their absorption and emission behaviors in different solvents. The absorption spectra are nearly independent of solvent polarity in our D- π -A dendrimers, except for a slight red shift in methanol due to aggregation. This result indicated a negligible intramolecular interaction between donor and acceptor chromophores in the ground states.^{3g} 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. As shown in Figure 2 and Table S1 (Supporting Information), the

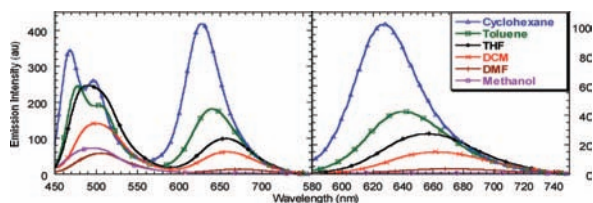


Figure 2. Emission spectra of **DBTTrTPA** in various solvents at 10^{-6} M. Emission spectra were obtained upon excitation at 421 nm (left) or 552 nm (right).

maximum emission peak of **DBTTrTPA** changed from ca. 628 nm in cyclohexane to ca. 672 nm in methanol along with a

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successively decreased fluorescence intensity. These results suggest that the excited states of our molecules possess more polar character than the ground state. Meanwhile, the residual emission exhibits less sensitive solvent dependence than those of the red-emitting region, which means that the energy transfer efficiency was also affected by the solvent polarity.

The absorption and PL spectra of these three dendrimers in thin films were also measured and shown in Figure S19 (Supporting Information). The thin films used for absorption and emission measurements were obtained by spin coating toluene solutions (ca. 10 mg/mL) onto quartz plates at 1000 rpm. All compounds exhibited excellent film forming properties. Absorption peaks were observed for **SBTTrTPA**, **DBTTrTPA**, and **TBTTrTPA** at 552 (405), 567 (426), and 521 nm (397 nm), respectively. The absorption spectra of molecules in thin films retain most of the spectral features in solution and exhibit a red shift compared with those obtained from cyclohexane solution. The PL spectra of these molecules in thin film became very broad, and maximum peaks were obviously red-shifted compared with those in cyclohexane solutions, similar to those in DMF solution. For example, red shifts of 44 nm for **SBTTrTPA** and 36 nm for **TBTTrTPA** were observed, respectively, indicating the formation of excimer in the solid state. Moreover, **DBTTrTPA** exhibits nearly nonluminescent property in thin film. The strong fluorescence quenching can be attributed to its lowest PL quantum yield in solution and additional intermolecular interaction in thin films.¹⁶

In conclusion, we have developed a series of new π -conjugated dendrimers based on benzothiadiazole as the core, truxene derivatives as the conjugated bridge, and triphenylamine as the end-group through various cross-coupling reactions in good yields. Their UV–vis absorption and PL properties are significantly affected by the electronic nature of the π -conjugated bridge, which provides an effective tool to fine-tune their functional properties. In addition, solvent polarity also proves to be an effective tool to modulate the energy transfer efficiency in these dendrimers. All dendrimers show excellent light-harvesting ability. Further experiments to explore their nonlinear optical properties and applications in organic solar cells are in progress in our laboratory.

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Supporting Information Available: Experimental procedures, ¹H and ¹³C 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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