

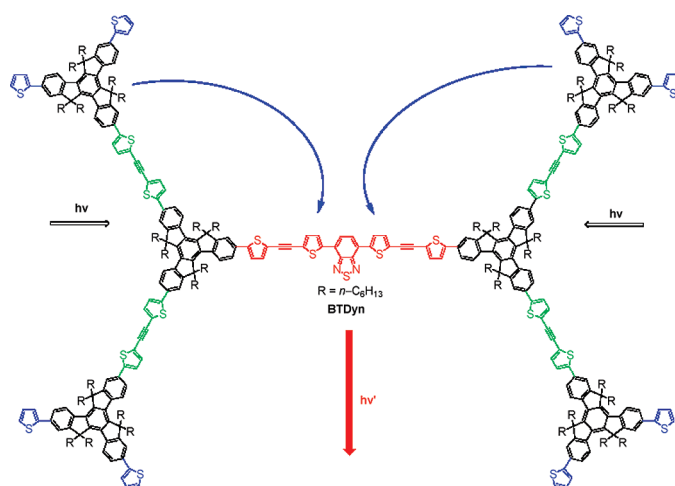
Solution-Processable Gradient Red-Emitting π -Conjugated Dendrimers Based on Benzothiadiazole as Core: Synthesis, Characterization, and Device Performances

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Received July 18, 2009



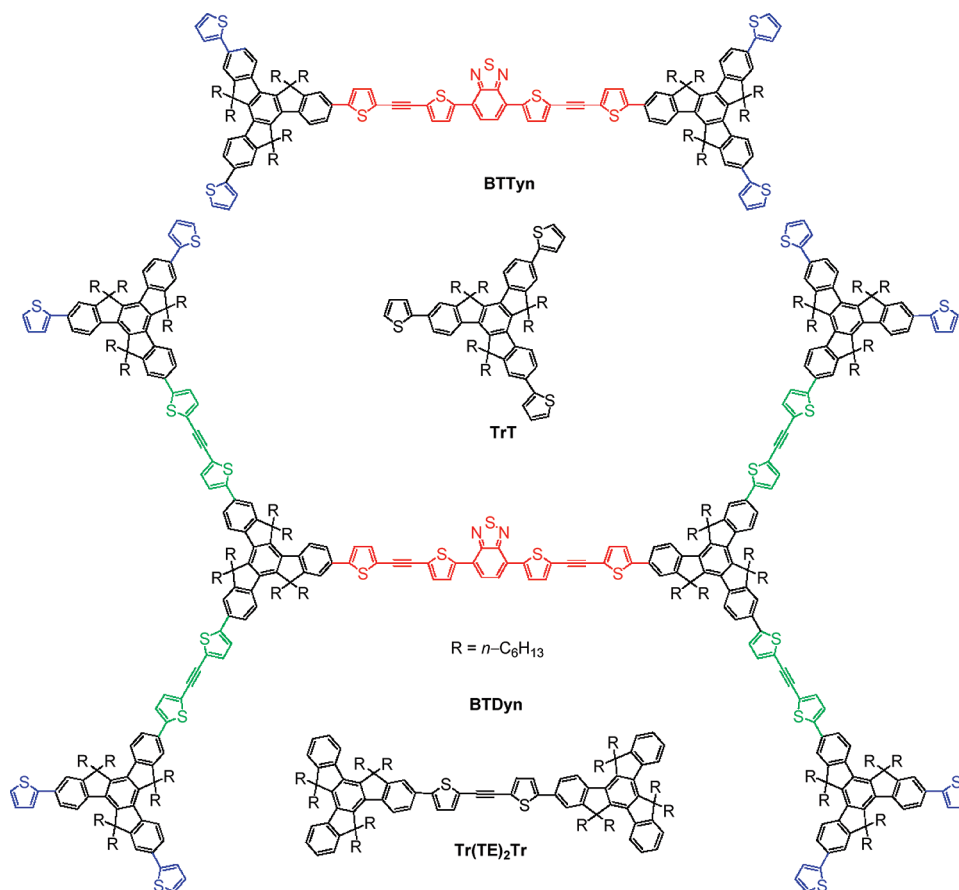
A family of gradient π -conjugated dendrimers, in which the 5,5,10,10,15,15-hexahexyltruxene unit is employed as the node, oligo(thienylethynylene)s (OTEs) are employed as light-harvesting branching units, and a 4,7-diaryl-2,1,3-benzothiadiazole is employed as the core, have been developed through the Sonogashira reaction in good yields. All dendrimers were fully characterized by ^1H and ^{13}C NMR, elemental analysis, and MALDI-TOF MS. Investigation of their steady-state and time-resolved photophysical properties revealed that the gradient dendritic scaffold resulted in efficient energy transfer and strong red emission. On the basis of the good solubility and excellent film forming properties, single-layer red-emitting diodes using these dendrimers as the active materials were fabricated by a simple solution spin-coating process. The moderate device performance was achieved; for example, the maximum luminance of 1290 cd/m^2 with a maximum luminescence efficiency of 1.07 cd/A was performed from **BTDyn**.

Introduction

In the field of organic light-emitting diodes (OLEDs), great efforts have been taken to develop new conjugated materials as well as to optimize device conditions in order to realize full color displays with high efficiency and long lifetime.¹ Among three-element color light-emitting materials, red-emitters with high brightness and good stability are scarce compared to the other two colors. More efforts are needed to achieve promising red-emitting materials. As an

alternative to polymers, π -conjugated dendrimers are also attractive as shape-persistent molecular architectures for electronic and optoelectronic devices.² They provide several advantages, like well-defined structures, facile purification by standard methods, and specific structure–property correlations.³ Moreover, the stepwise synthetic methodology of such a dendritic structure offers the possibility of incorporating gradient light-absorbing chromophores in each dendritic branch, making such dendrimers promising candidates

CHART 1. Chemical Structure of BTtyn, BTDyn, and Model Compounds



for light-harvesting materials.⁴ Several groups have utilized conjugated dendrimers as light-harvesting antenna, in which high-efficiency intramolecular energy transfer from the functionalized outside group to the core group has been reported.⁵ The energy accumulated at the core can be released either as core emission or deactivated by an electron-transfer process.⁶ The site-isolation effect provided by bulky dendrons minimized the undesired core–core interaction.⁷ A distinct feature of conjugated dendrimer is that the fluorescence quantum yield of the core chromophores may rapidly increase with increasing generation, an important requirement for organic light-emitting materials.

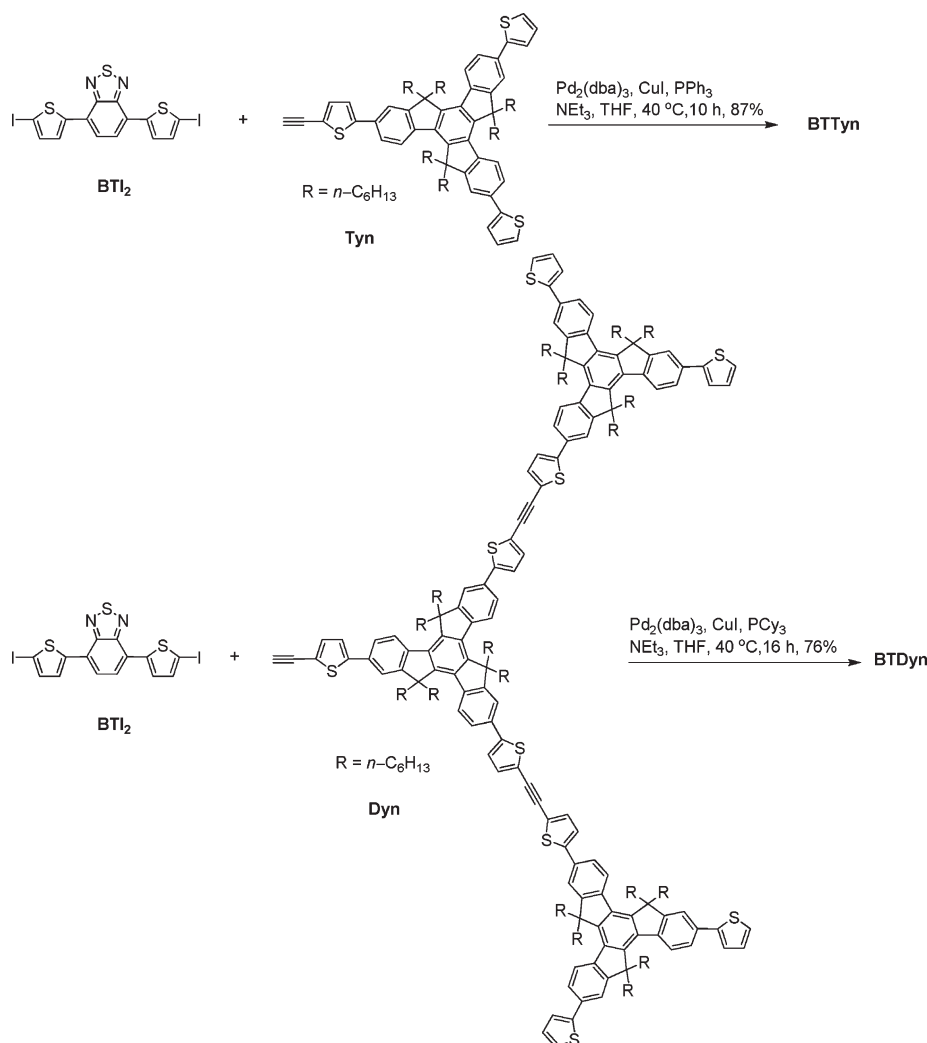
In our previous works, we reported a family of gradient-conjugated dendrimers constructed with 5,5,10,10,15,15-hexahexyltruxene units and oligo(thienylethynylene)s (OTEs) for light-harvesting purposes.⁸ The investigation of the

photophysical properties showed that those dendrimers have excellent energy funneling ability due to well-suited photoluminescence (PL) emission to excite the red-emitting core. As a further step, we explored the possibility of incorporating a red-emitting chromophore into the center of the molecules to harness the collected light energy. On the other hand, 4,7-diaryl-2,1,3-benzothiadiazole is known as a good acceptor unit in linear and dendritic-type molecules for organic light-emitting diodes, organic solar cells, organic field effect transistors, and two-photon absorption.⁹ However, few conjugated dendrimers containing a benzothiadiazole unit as the core have been applied to organic red-emitting

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SCHEME 1. Synthetic Route to BTTyn and BTDyn



diode. Therefore, we present here a new family of gradient π -conjugated dendrimers **BTTyn** and **BTDyn** as shown in Chart 1. The 5,5,10,10,15,15-hexaethyltruxene unit is employed as the node, oligo(thienylethynylene)s (OTEs) are employed as the light-harvesting branching units, and a benzothiadiazole is employed as the core. Our molecular design establishes an

efficient energy transfer framework leading to strong red emission. In this approach, the unique and nonplanar conjugated dendritic architecture has significant consequences on the fluorescence properties of core chromophores as well as their performances in optoelectronic devices. Our intention is to study the relationship between generation of the light-harvesting

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dendron and the energy-transfer process as well as device performance while keeping the basic dendrimer backbone and core unit unchanged. Finally, we describe their performances in solution-processable organic red-emitting diode and show that these molecules have drastically different electroluminescent behavior with different generation.

Results and Discussion

Considering the large number of reaction steps required to synthesize our dendrimers, we employ a convergent growth approach to avoid incomplete conversion in the key reaction step.¹⁰ Scheme 1 illustrates the synthetic approach to dendrimers **BTTyn** and **BTDyn**. The core unit can be introduced in the final step. Light-harvesting dendrons **Tyn** and **Dyn**, which contain part of the core segment, were reported in our previous work.⁸ **BTTyn** was synthesized through a Sonogashira reaction between **BTI₂** and the monoacetylene dendron **Tyn** in 87% yield.¹¹ Difficulty caused by large steric hindrance was encountered in the preparation of next-generation dendrimer **BTDyn**. After more active cocatalyst ligand PCy₃ was employed to suppress undesired homodimerization,¹² the convergent Sonogashira coupling between **BTI₂** and **Dyn** afforded **BTDyn** in 76% isolated yields, which was fairly acceptable considering the size of the desired dendrimer.

The dendrimers **BTTyn** and **BTDyn** are a deep red solid and readily soluble in common organic solvents such as CHCl₃, THF, and toluene. All compounds were purified by silica gel column chromatography, and their structures and purity were verified by ¹H and ¹³C NMR, elemental analysis, and MALDI-TOF MS. The MALDI-TOF MS spectrum of **BTDyn** showed the sharp molecular ion peak at *m/z* = 6995 Da (calcd *m/z* = 6995 Da), and another signal corresponding to dehexylated fragment [M - C₆H₁₃]⁺ (calcd *m/z* = 6910 Da, found *m/z* = 6910 Da) was clearly observed, which was similar to those of other truxene derivatives.¹³ These results clearly indicated the molecular identity and purity of **BTDyn**. The thermal properties of our dendrimers were analyzed by thermal gravimetric analysis (TGA). Both

TABLE 1. Photophysical Data of Our Dendrimers Both in Dilute THF Solutions and in Thin Films

compd	abs ^a		emis ^a		Φ _{PL} ^c (%)	τ (ns) ^d (χ ²)
	λ _{max} /nm soln (log ε)	abs ^b λ _{max} /nm films	λ _{max} /nm soln	λ _{max} /nm films		
BTTyn	343 (5.51);	345	631	643	25	2.0 (1.22) ^e 2.0 (1.19) ^f
	384 (5.23);	522				
	509 (4.98);					
BTDyn	343 (5.82);	347	631	638	25	2.0 (1.12) ^e 2.0 (1.20) ^f
	355 (5.82);	356				
	398 (5.83);	399				
	509 (4.98)	518				

^aIn THF solution (10⁻⁶ M). ^bIn thin films. ^cIn THF solution (*A* = 0.1) and rhodamine B as the standard. (Φ_{PL} = 0.65 in ethanol); ^dIn THF solution (10⁻⁶ M), the fluorescence decay was monitored at the maximum emission peak (631 nm). Time-resolved fluorescence of all compounds shows monoexponential decay. The percentage in parentheses indicates the contribution from that component. ^eEmission spectra were collected when excited at 343 nm. ^fEmission spectra were collected when excited at 509 nm.

dendrimers have high thermal stability with decomposition temperature higher than 380 °C in nitrogen atmosphere.

The photophysical properties of all dendrimers and model compounds were investigated to understand their energy-transfer properties. Photophysical data from both the solution and thin films are summarized in Table 1. The absorption and photoluminescence (PL) spectra in dilute THF solutions (ca. 10⁻⁶ M) are shown in Figures 1 and S1 (Supporting Information). The absorption spectra of the dendrimers showed two or three distinct absorption bands. In the short wavelength range, the absorption peak at about 343 nm in **BTTyn** and **BTDyn** was assigned to the periphery unit (part of compound **TrT**).¹³ Relative to the absorption peak of **Tr(TE)₂Tr** at about 394 nm, another absorption peak at about 398 nm for **BTDyn** was assigned to the middle branch **Tr(TE)₂Tr** segment.¹⁴ In the longer wavelength range, both **BTTyn** and **BTDyn** exhibited an absorption peak at about 509 nm and the similar absorbance intensity due to the same benzothiadiazole unit as the core group. A comparison of the 4,7-bis(2-thienyl)-2,1,3-benzothiadiazole unit (λ_{max} = 447 nm) with our dendrimers revealed that the terminal thiophene-functionalized truxene moiety participated in the conjugated system and thus induced obvious red shift.¹⁵ All these molecules have fairly large molar extinction coefficients at their absorption maxima, especially in the short wavelength range. Upon increasing the dendrimer generation, the molar extinction coefficient of the short wavelength absorption peak increases dramatically. Meanwhile, both dendrimers have an obviously higher value of molar extinction coefficient in shorter wavelength compared with that of the model compounds. For example, **BTDyn** has a high value of molar extinction coefficient (6.6 × 10⁵ M⁻¹ cm⁻¹) at 398 nm, as compared to that of the middle branch segment **Tr(TE)₂Tr** (1.4 × 10⁵ M⁻¹ cm⁻¹) at 394 nm. All results indicated that no ground-state interactions exist for our dendrimers.

The emission spectra of two dendrimers showed red-emission and similar intensity at about 631 nm when excited at 508 nm, as shown in Figure 2. Meanwhile, the emission maximum λ_{max} of reference compounds **TrT** and **Tr(TE)₂Tr**

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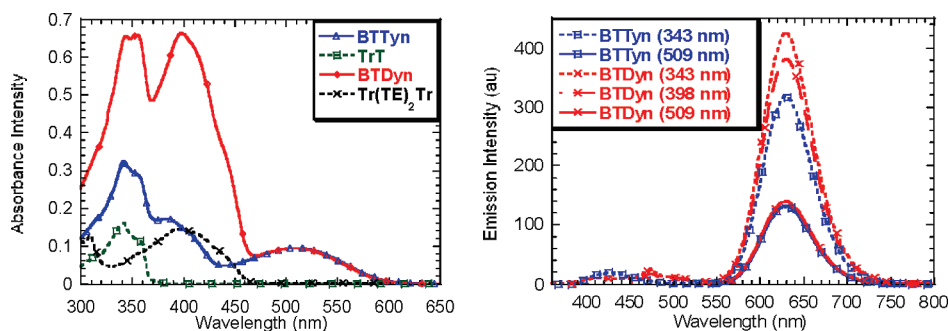


FIGURE 1. Absorption spectra of dendrimers **BTTyn**, **BTDyn**, and model compounds **TrT** and **Tr(TE)₂Tr** (left) and emission spectra of the dendrimers (right) in THF solutions (10^{-6} M). Emission spectra were recorded at different excitation wavelengths shown in parentheses.

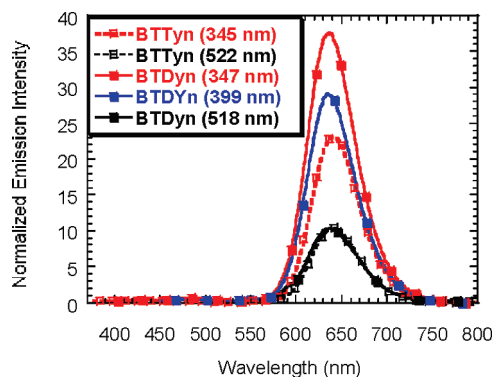


FIGURE 2. Comparison of emission spectra of dendrimers in thin films at different excitation wavelengths. The emission intensity of all spectra was normalized when dendrimers were excited at the longest wavelength absorption region.

is located at 383 and 460 nm, respectively.¹⁴ The fluorescence quantum yields (Φ_{PL}) of two dendrimers in dilute solutions were measured to be 0.25 when each solution was excited at 509 nm (absorbance values were ca. 0.1, rhodamine B as the standard, $\Phi_{\text{PL}} = 0.65$ in ethanol).¹⁶ Using 9,10-diphenylanthracene as standard, the fluorescence quantum yields of antenna parts in dilute THF solution were measured to be 0.54 for **Tyn**, 0.25 for **Tr(TE)₂Tr**, and 0.28 for **Dyn**. To study the effect of generation on the photon-harvesting ability of the dendrimers, the excitation spectra of our dendrimers were recorded by the monitoring the emission at 631 nm, and the spectra were normalized to a constant intensity value at 509 nm, which belongs to the absorption of core group. It was clearly observed that more photons were collected and transmitted from the periphery to the benzothiadiazole core while generation increased from **BTTyn** to **BTDyn**. Therefore, higher generation dendrimers with a larger number of branch groups will serve as better antenna.

An interesting aspect of our shape-persistent dendrimers is their highly efficient intramolecular energy harvesting behavior. The emission of the donor part, that is our dendritic part in **BTTyn** and **BTDyn**, overlaps well with the absorption of the acceptor core.¹⁴ This fulfills the prerequisite for the energy-transfer process according to the Förster mechanism.¹⁷ As shown in Figure 2, the maximum emission peaks were

excitation wavelength independent. When excited at 343 or 398 nm (the maximum absorption of the periphery group and the middle branch arm), the red-emitting emission came almost exclusively from the core units with weak residual fluorescence at the 380–500 nm. This result provides direct evidence that a highly efficient intramolecular energy transfer process from the periphery group to the red-emitting core. Meanwhile, the emission intensities excited at 343 nm for **BTDyn** were not only several times higher than those when excited at the core group (509 nm) for **BTDyn** but also higher than those excited at 343 nm for **BTTyn**, which clearly showed a different “antenna effect” in the different generation dendrimer.¹⁸ At the same time, it is indicated that the larger light-harvesting antenna with higher absorption coefficient of the dendron at the short wavelength is more efficient to improve the emission quantum yields of the core chromophore. To quantify the energy-funneling ability of our dendrimers, we measured the fluorescence quantum yields of **BTTyn**, **BTDyn**, and **TrT** upon excitation at 343 nm. The energy-transfer efficiency is deduced from the ratio between the fluorescence quantum efficiency of the residual emission ($Q_{\text{TrT(core)}}$) between 350 and 450 nm in dendrimers and that of **TrT** (Q_{TrT}) using the equation.^{5c}

$$\phi_{\text{ET}} = 1 - \frac{Q_{\text{TrT(core)}}}{Q_{\text{TrT}}} \quad (1)$$

Calculated results showed that the energy-transfer efficiency were 96% for **BTTyn** and 94% for **BTDyn**, respectively. Moreover, the energy-transfer rate could be calculated from the following equation.^{5b}

$$k_{\text{ET}} = \frac{1}{\tau_{\text{TrT}}} \left(\frac{1}{(1/\phi_{\text{ET}}) - 1} \right) \quad (2)$$

The energy transfer rate is $4.0 \times 10^9 \text{ s}^{-1}$ for **BTTyn** and $2.6 \times 10^9 \text{ s}^{-1}$ for **BTDyn**, respectively.^{8b} The high energy-transfer efficiency and fast energy-transfer rate can be ascribed to the large overlap between the emission of the gradient dendritic branch and absorption of the acceptor core, as well as their short distances.

Finally, to give more insight into such energy-transfer processes, the fluorescence lifetime of the dendrimers was measured in THF solutions using a time-correlated photon-counting instrument. The results are also shown in Table 1. The decay of the emission maximum of our dendrimers was

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TABLE 2. Electrochemical Onset Potentials and Electronic Energy Levels of Dendrimers

compd	$E_{\text{ox(onset)}}$ (V)	$E_{\text{red(onset)}}$ (V)	E_{HOMO} (eV)	E_{LUMO} (eV)	$E_{\text{g(cv)}}$ (eV)	$E_{\text{g(opt)}}$ (eV)
BTTyn	0.91	-1.12	-5.62	-3.59	2.03	2.00
BTDyn	0.93	-1.13	-5.64	-3.58	2.06	2.02

found to be well-fitted by monoexponential decay function when excited at 343 or 509 nm. Fluorescence lifetimes were all the same (2.0 ns) for **BTTyn** and **BTDyn**, whether obtained by excitation at the terminal group or core group. A comparison of the 4,7-bis(2-thienyl)-2,1,3-benzothiadiazole ($\tau = 14.6$ ns) with our dendrimers revealed that our dendron extends the effective conjugation length and thus induced the obvious decrease of fluorescence lifetime.¹⁹ We were unable to measure the lifetime of our dendrimer in the maximum emission band of our dendron due to weak residual emission. This suggests a highly efficient energy cascade process in which the final emission came from the red core chromophore.

We also obtained their thin films used for UV-vis and PL measurements by spin-coating of a toluene solution (ca. 10 mg/mL) onto quartz plates at 1000 rpm. Our dendrimers display good film-forming properties. All absorption spectra basically split into dendron absorption bands and core absorption bands. The maximum of the absorption peak was located at 522 nm (345 nm) for **BTTyn** and at 518 nm (347 nm, 399 nm) for **BTDyn**, which were very similar with those in dilute solutions, as shown in Figure S1 (Supporting Information). It indicated that no significant intermolecular aggregation occurred in the ground state due to the dendritic architecture and the large number of alkyl groups. The bandgaps of our dendrimers were estimated from the onset of the absorption spectra in thin films. **BTTyn** has a bandgap of 2.00 eV and **BTDyn** has a bandgap of 2.02 eV, which are very similar to each other. Relative to those in dilute solution, their emission spectra in thin films as shown in Figure 2 became broad, and the emission λ_{max} red-shifted by 12 nm for **BTTyn** and 7 nm for **BTDyn**. Such small shifts implied that intermolecular aggregation (usually observed for benzothiadiazole derivatives in thin films) was suppressed by the dendritic structure. Moreover, the energy-transfer process of our dendrimers seemed to be more efficient in thin films as the residual emission of our dendrimers between 380 and 530 nm present in the solution spectra when excited at short wavelength disappeared in the film emission, possibly due to additional contribution from intermolecular energy transfer.²⁰ Meanwhile, if we normalized the emission intensity of our two dendrimers when dendrimers were excited at the longest wavelength absorption region, we observed that the emission intensity excited at 345 nm for **BTDyn** was nearly two times higher than that when excited at 347 nm for **BTTyn**. It is indicated that the larger light-harvesting dendrimer seems to be a more suitable candidate for red-emitting materials.

For red-emitting diodes, the electrochemical properties of active compounds are essential.²¹ HOMO and LUMO

TABLE 3. Single-Layer OLED Device Performance of Our Dendrimers BTTyn and BTDyn

compd	voltage _{turn-on} (V)	EL λ_{max} (nm)	luminance _{max.} (cd/m ²) at voltage (V)	EL _{max} efficiency at voltage (V)
BTTyn	3.2	635	2260 (9.7)	0.11 (7.2)
BTDyn	9.1	630	1290 (23)	1.07 (14)

energy levels and the corresponding bandgap of these dendrimers in thin films were investigated by cyclic voltammetry on the Pt electrode. Figure S2 (Supporting Information) shows the cyclic voltammetric response of our dendrimers in thin films. Oxidation due to the peripheral group and reduction due to the central benzothiadiazole core show reversible processes, which indicates their high electrochemical stability suitable for both *p*- and *n*-doping. Relative to the Ag/Ag⁺ reference electrode, the onset oxidation and reduction potentials of the materials were 0.91 and -1.12 V for **BTTyn** and 0.93 and -1.13 V for **BTDyn**, respectively. From these values, the HOMO and LUMO and the bandgap of the dendrimers were calculated using the equations listed below.²²

$$\text{HOMO} = -e(E_{\text{ox(onset)}} + 4.71) \text{ (eV)} \quad (3)$$

$$\text{LUMO} = -e(E_{\text{red(onset)}} + 4.71) \text{ (eV)} \quad (4)$$

$$E_{\text{g(cv)}} = e(E_{\text{ox(onset)}} - E_{\text{red(onset)}}) \text{ (eV)} \quad (5)$$

The electrochemical data of our dendrimers are summarized in Table 2. The bandgaps of both dendrimers calculated from electrochemical measurements agree well with those obtained from the absorption spectra.

The motivation of design and synthesis of π -conjugated dendrimers **BTTyn** and **BTDyn** is to search for new benzothiadiazole derivatives as the red light emission layer in solution-processable organic light-emitting diodes. Hence, we used their films directly spin-coated from their solutions as emitting-layers to fabricate OLEDs devices with the structure of ITO/PEDOT(30 nm)/EML(**BTTyn** or **BTDyn**)/Ca (15 nm)/Al (150 nm). The thickness of the emission layer was about 50 nm for **BTTyn** or 80 nm for **BTDyn**. Device characteristics are summarized in Table 3, and the current-voltage and luminance-voltage curves of both dendrimers are shown in Figures S3 (Supporting Information) and 3. The EL λ_{max} of our dendrimers slightly blue-shifted in comparison with their corresponding PL λ_{max} . As shown in Table 3, the nonoptimized OLED device performance based on **BTDyn** exhibits good performance with the emission maximum at about 630 nm, a turn-on voltage of 9.1 V, a maximum luminance of 1290 cd/m², and a maximum luminescence efficiency of 1.07 cd/A. In comparison, the OLED fabricated from **BTTyn** exhibits a turn-on voltage of 3.2 V, a higher maximum luminance of 2260 cd/m², and a lower maximum luminescence efficiency of 0.11 cd/A. Apparently, increasing the dendrimer generation is beneficial for the device performance, with enhancement of 1 order of magnitude. Figure 3 also shows the EL spectra of our dendrimers **BTDyn** under different biases. As shown in Figure 3, both devices had red emission and hardly affected their EL spectra in the range

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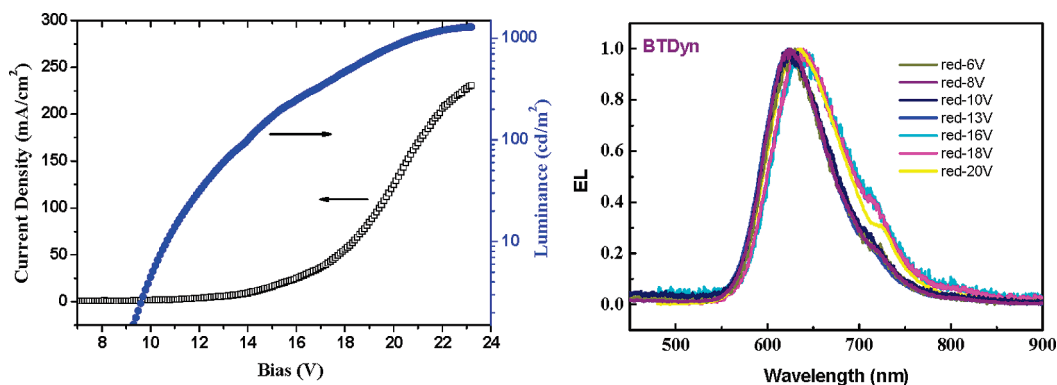


FIGURE 3. I–V–L characteristics for the single-layer device fabricated with dendrimer **BTDyn** (left) and EL spectra of our dendrimers **BTDyn** under different biases (right).

from 6 to 20 V for **BTDyn**. The results showed that **BTDyn** could be a potentially useful solution processable fluorophore for red OLEDs.

Conclusions

In conclusion, we have developed a family of gradient shape-persistent π -conjugated dendrimers **BTTyn** and **BTDyn** bearing red-emitting benzothiadiazoles derivatives as the core and truxene moieties as the nodes and OTEs as the branching arm for nondoped and solution processable organic light-emitting diodes. Detailed investigations on the steady-state UV–vis absorption and PL emission as well as time-resolved fluorescence spectroscopy of these dendrimers provide insight into the photophysical process in such dendrimers. The molecular architecture of our dendrimer with an energy-gradient dendron and a core unit suppresses undesired shortwavelength emission and leads to a stable red emission from these dendrimers, due to highly efficient energy transfer from the light-harvesting dendron to the core unit. Good device performance for single-layer solution processable organic light-emitting diodes based on these gradient-conjugated dendrimers is achieved. Moreover, the EL efficiency of dendrimer devices largely increases with increasing the concentration of light-harvesting OTEs and truxene moiety from **BTTyn** to **BTDyn**. Our work demonstrated that conjugated dendrimers with an excitation energy-transfer process open an avenue for application in electroluminescent devices. We note that our present synthetic strategy allows further functionalization at the periphery of the dendrimers with n-type (oxadiazole moieties) or p-type (triaryamine moieties) groups, which might improve the device performance. Related works and further modification of device configuration are ongoing in our laboratory.

Experimental Section

General Methods. Chemicals were purchased and used as received. ^1H and ^{13}C NMR spectra were recorded on an using CDCl_3 as solvent. Chemical shifts were reported in parts per million (ppm) relative to internal TMS (0 ppm) or residual CHCl_3 (7.26 ppm). MALDI-TOF MS spectra were recorded on a time-of-flight (TOF) mass spectrometer using a 337 nm nitrogen laser with dithranol as matrix. Differential scanning calorimetry analyses were performed on a calorimeter. Cyclic voltammetry was performed as follows: scan rate, 100 mV s^{-1} ;

working electrode, Pt disk; auxiliary electrode, Pt wire; reference electrode, Ag/Ag^+ ; supporting electrolyte, Bu_4NPF_6 (0.1 M, CH_3CN).

BTTyn. To a mixture of **BTI₂** (55 mg, 0.1 mmol), **Tyn** (246 mg, 0.22 mmol), $\text{Pd}_2(\text{dba})_3$ (4.9 mg), PPh_3 (2.6 mg), and CuI (1.0 mg) in anhydrous THF (40 mL) was added 40 mL of Et_3N . After 10 h at 40°C under nitrogen atmosphere, the mixture was poured into water. The aqueous layer was extracted with CH_2Cl_2 . The combined organic extracts were washed with brine and then dried over MgSO_4 . After removal of solvents under reduced pressure, the residue was purified by column chromatography (silica gel, petroleum ether/ CH_2Cl_2 , 10:1) to afford **BTTyn** as a red solid (0.22 g, 87%). ^1H NMR (CDCl_3 , 400 MHz, ppm): δ 8.36–8.38 (m, 6H), 8.08–8.09 (d, $J = 3.6$ Hz, 2H), 7.93 (s, 2H), 7.67–7.71 (m, 12H), 7.47–7.48 (d, $J = 3.6$ Hz, 4H), 7.40–7.43 (m, 4H), 7.36–7.37 (d, $J = 3.6$ Hz, 2H), 7.33–7.34 (d, $J = 3.6$ Hz, 4H), 7.15–7.17 (dd, $J = 4.8, 3.6$ Hz, 4H), 2.95–2.30 (m, 12H, CH_2), 2.13–2.14 (m, 12H), 0.88–0.94 (m, 72H). 0.58–0.62 (m, 60H). ^{13}C NMR (CDCl_3 , 100 MHz, ppm): δ 154.5, 154.4, 154.3, 152.4, 147.1, 145.3, 145.2, 145.1, 144.8, 140.8, 140.5, 139.6, 138.1, 138.0, 137.8, 133.5, 132.9, 132.5, 131.7, 128.1, 127.6, 125.6, 125.0, 124.9, 124.6, 124.1, 123.0, 122.9, 121.5, 119.3, 119.2, 89.0, 87.5, 55.8, 37.0, 31.4, 29.5, 23.9, 22.2, 13.8. MALDI-TOF MS (m/z): calcd for $\text{C}_{168}\text{H}_{196}\text{N}_2\text{S}_9$ 2529, found 2637 ($[\text{M} + \text{Ag}]^+$). Anal. Calcd for $\text{C}_{168}\text{H}_{196}\text{N}_2\text{S}_9$: C, 79.69; H, 7.80; N, 1.11. Found: C, 79.34; H, 7.98; N, 0.97.

BTDyn. To a mixture of **BTI₂** (30 mg, 0.054 mmol), **Dyn** (400 mg, 0.12 mmol), $\text{Pd}_2(\text{dba})_3$ (2.7 mg), PCy_3 (1.7 mg), and CuI (0.5 mg) in anhydrous THF (40 mL) was added 40 mL of Et_3N . After being stirred at 40°C under nitrogen atmosphere for 16 h, the mixture was poured into water. The aqueous layer was extracted with CH_2Cl_2 . The combined organic layers were washed with brine and then dried over MgSO_4 . After removal of solvents under reduced pressure, the residue was purified by flash column chromatography (silica gel, petroleum ether/ CH_2Cl_2 , 8:1) to afford **BTDyn** as a red solid (0.28 g, 76%). ^1H NMR (CDCl_3 , 400 MHz, ppm): δ 8.36–8.41 (m, 18H), 8.09–8.10 (d, $J = 3.6$ Hz, 2H), 7.93 (s, 2H), 7.70 (m, 36H), 7.47–7.48 (d, $J = 3.6$ Hz, 8H), 7.41–7.43 (m, 12H), 7.33–7.38 (m, 18H), 7.15–7.17 (dd, $J = 4.8, 3.6$ Hz, 8H), 2.98 (m, 36H), 2.12–2.16 (m, 36H), 0.88–0.97 (m, 216H), 0.59–0.62 (m, 180H). ^{13}C NMR (CDCl_3 , 100 MHz, ppm): δ 154.54, 154.52, 154.4, 154.3, 152.4, 147.0, 146.8, 146.7, 145.5, 145.3, 145.2, 145.1, 144.9, 140.8, 140.4, 140.3, 140.2, 139.66, 139.64, 138.1, 138.01, 137.95, 137.8, 133.5, 133.3, 132.9, 132.5, 131.9, 131.8, 131.7, 128.1, 127.9, 127.6, 125.6, 125.0, 124.9, 124.6, 124.3, 124.14, 124.10, 124.0, 123.1, 123.04, 122.99, 122.9, 121.8, 121.7, 121.6, 119.3, 119.2, 88.9, 87.7, 87.6, 87.5, 71.1, 55.9, 55.8, 37.0, 31.5, 29.5, 23.9, 22.2, 13.8. MALDI-TOF MS (m/z): calcd for $\text{C}_{476}\text{H}_{572}\text{N}_2\text{S}_{21}$ 6995, found 6995 (M^+). Anal.

Calcd for $C_{476}H_{572}N_2S_{21}$: C, 81.73; H, 8.24; N, 0.40. Found: C, 81.42; H, 8.42; N, 0.28.

Acknowledgment. This work was supported by the Major State Basic Research Development Program (Nos. 2006CB921602 and 2009CB623601) from the Ministry of

Science and Technology and National Natural Science Foundation of China.

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