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Nonconjugated Red-Emitting Dendrimers with p-Type and/or n-Type Peripheries

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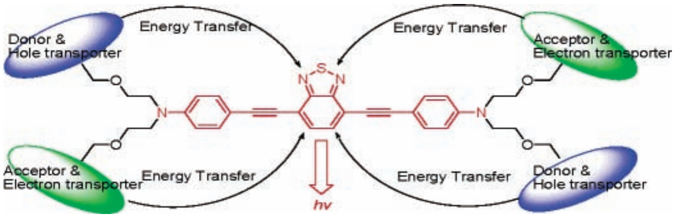
ABSTRACT



Dendron-encapsulated materials having a benzo[*c*][1,2,5]thiadiazole-based red-emitting core and p-type and/or n-type peripheries were synthesized. Intra- and intermolecular energy transfer from the peripheries to the core were found to be peripheries dependent. Red-emitting electroluminescent devices with promising performance were fabricated.

Organic materials with some specified functions have been widely used in optoelectronic devices such as organic light-emitting diodes (OLEDs),[1] organic field effect transistors (OFETs),[2] and organic photovoltaic cells.[3] Among these, molecules posscessing multi functional groups are of particular interest. Dendrimers are ideal in this aspect due to easy integration of different functional groups.[4] We have been interested in dendrimers for electroluminescent application because of the following advantageous characteristics of the dendrimers: (1) encapsulation of the emitting segment to avoid self-quenching of fluorescence or phosphorescence, i.e., site isolation; (2) emission enhancement via energy transfer from peripheries to the emittimg core, i.e., antenna effect;[5] (3) integration of the carrier-transport with the emitting units may simplify the device structure; (4) a spin-coating technique for the device fabrication may be possible for the dendrimers of larger molecular weights; and (5) white-light-emitting devices are possible via blending of dendrimers with different chroma.

There have been many reports on polymeric electroluminescent materials incorporating both electron- and hole-transporting moiety in order to effectively confine the excitons.[6] In recent years, fluorescent[7] and phosphorescent[8] dendrimers also attracted attention. A recent report by Burn and Samuel[9] on electrophosphorescent dendrimers nicely illustrated that host-free dendrimer-based OLEDs could have efficiency approaching that of the best OLEDs with phosphorescent dopants.[10] Systematic investigation of light-

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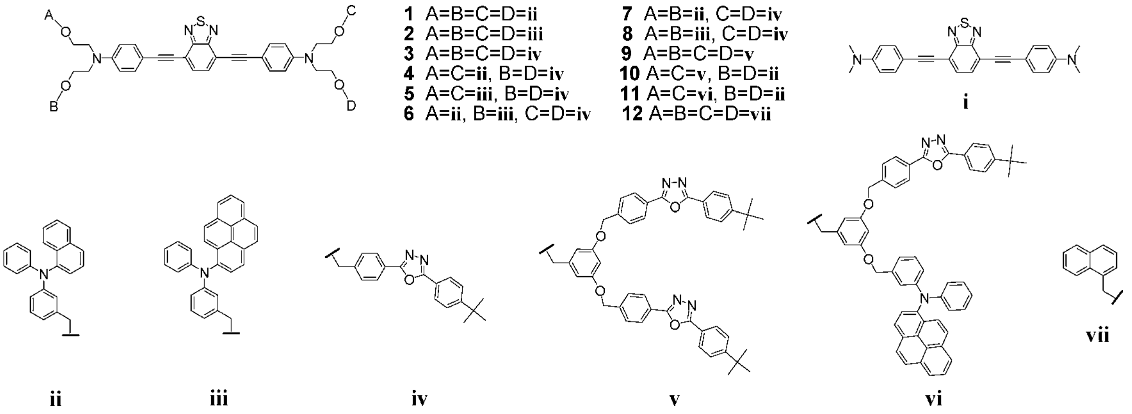
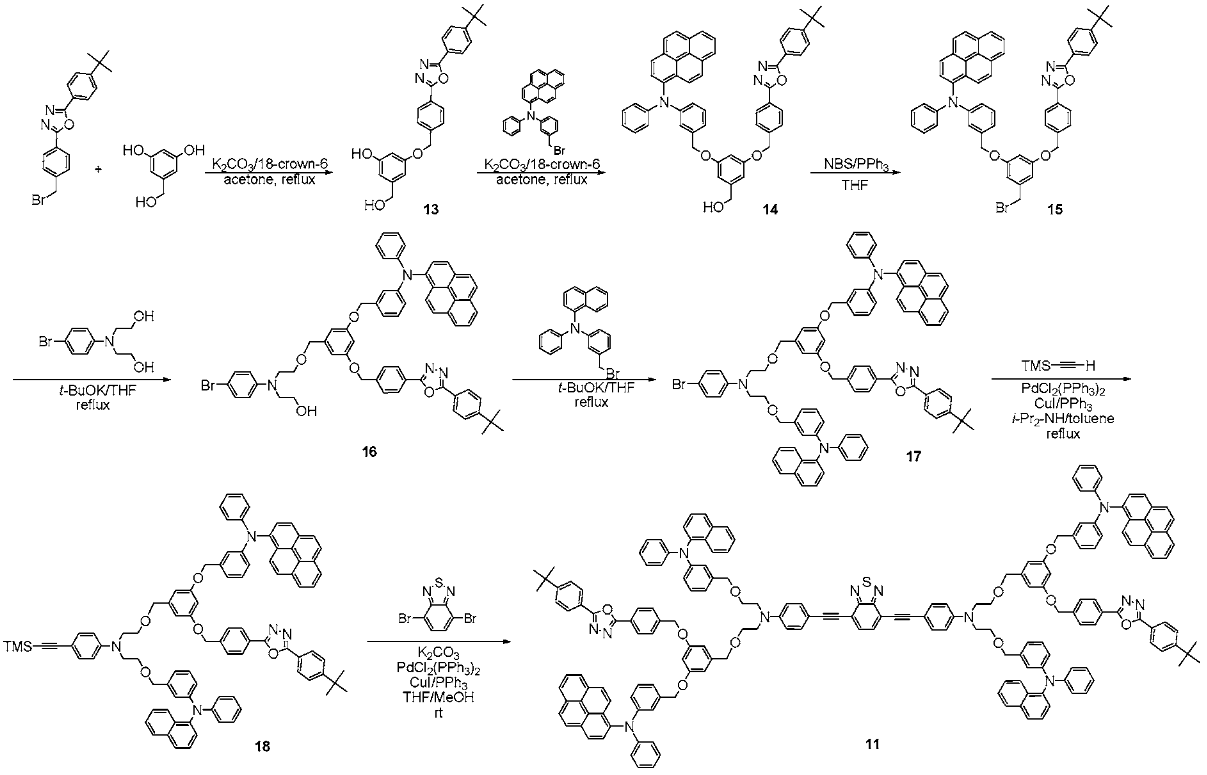


Figure 1. The structures of the p-type and/or n-type functionalized dendrimers and model units.

emitting dendrimers cotaining n- or p-carrying dendrons, or both, are still scanty.[11] We therefore set out to synthesize dendrimers containing red-emitting core and pheripheral n- and/or p-carriers. In this paper, we report dendrimers with a red-emitting core, 4,7-bis(*p*-aminophenylethynyl)benzo[*c*]-[1,2,5]thiadiazole, and peripheral n-carrier, 2,5-diaryl-1,3,4-oxadiazole, and/or p-carrier, triarylamine moieties. OLED devices fabricated by spin-coating will be also discussed.

Benzyl bromides, **ii**-Br, **iii**-Br,[12] and **iv**-Br,[13] were used to construct the dendrimers via the convergent method according to the literature procedure (Figure 1).[14] The representative synthetic route is outlined in Scheme 1. (1) Williamson ether syntheses[15] with 3,5-dihydroxybenzyl alcohol and benzyl bromide (**iv**-Br) to produce the hydroxylmethyl compound (**13** and **14**), (2) conversion of **14** to the benzyl bromide derivative **15** with NBS/PPh_3, (3) Williamson ether syntheses using **15** with 2-[(4-bromophenyl)(2-hydroxyethyl)amino]-ethanol to form aryl bromide (**16** and **17**), (4) conversion of **17** to the acetylene derivative **18** via Sonogashira coupling reaction,[16] and (5) the Sonogashira coupling reaction of dibromobenzo[*c*][1,2,5]thiadiazole with aryl acetylene provide the desired dendrimer (**11**). Williamson ether synthesis in step 1 can be conducted with K_2CO_3/18-crown-6 as the base. However, *t*-BuOK has to be used in step 3. In step 3,

Scheme 1. The Representative Synthetic Route of the Dendrimers



both hydroxy groups can be alkylated when **ii**-, **iii**-, and **iv**-Br were used. In contrast, only monoalkylated product was obtained for larger dendrons (e.g. **vi**-Br). Such an outcome allows incorporation of three different peripheral units, and compound **11** was isolated in 20% yield.

The photophysical data of the dendrimers and the model compounds (**i** for the core; **ii**-Br, **iii**-Br, and **iv**-Br for the peripheries) are compiled in Table 1. Compound **i** has a broad peak at ~330 nm attributable to the $\pi \rightarrow \pi^*$ transition of the benzothiadiazolyl unit, and a featureless broad band at ~500 nm due to the charge transfer from the amines to benzothiadiazolyl unit. Compounds **ii**-Br, **iii**-Br, and **iv**-Br have their characteristic $n \rightarrow \pi^*$ and/or $\pi \rightarrow \pi^*$ absorption bands: **ii**-Br, 296, 342 nm; **iii**-Br, 302, 380 nm; **iv**-Br, 296 nm. Owing to the nonconjugation nature between the core and the peripheries, the absorption spectra of the dendrimers are nearly the sum of the core and the peripheries. The intensity of the absorption band from peripheries increases as the generation of the dendron grows. The representative absorption spectra are shown in Figure 2.

Table 1. Physical Properties of the Compounds

compd	λ_{abs}, nm	λ_{em}, nm	Φ_f,[a] %	T_d, °C	HOMO,[b] eV	LUMO, eV
1	303, 325, 500	680	50	366	5.22	3.06
2	313, 361, 382, 502	682	50	371	5.27	3.12
3	294, 497	674	74	362	5.23	3.05
4	295, 342, 498	672	65	361	5.23	3.06
5	275, 303, 382, 500	677	51	359	5.24	3.07
6	295, 500	678	58	372	5.27	3.11
7	294, 354, 383, 500	675	58	374	5.26	3.09
8	295, 303, 500	678	55	387	5.23	3.06
9	294, 498	668	40	324	5.23	3.02
10	294, 352, 498	673	47	342	5.23	3.06
11	295, 358, 382, 501	686	43	353	5.27	3.12
i	324, 494	684	56	220	5.24	3.09
ii-Br	296, 342	435	68	237	5.41	2.19
iii-Br	302, 380	470	13	267	5.29	2.41
iv-Br	296	358	57	251	6.80	3.08

[a] Quantum yield was measured in CH_2Cl_2 relative to Nile Red (78%) in acetonitrile. Corrections due to the change in solvent refractive indices were applied. [b] Highest occupied molecular orbital (HOMO) energy was calculated with reference to ferrocene (4.8 eV). The band gap was derived from the observed absorption onset, and the lowest unoccupied molecular orbital (LUMO) energy was derived from subtracting the band gap from the HOMO.

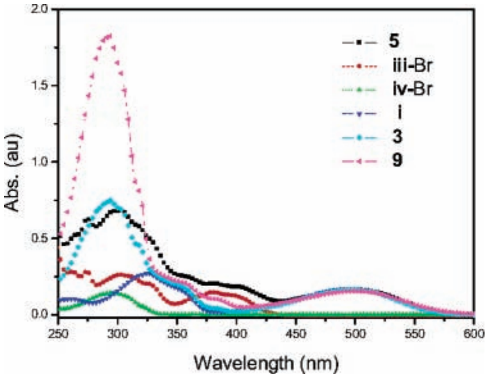


Figure 2. Absorption spectra of **5**, **iii**-Br, **iv**-Br, **i**, **3**, and **9** in CH_2Cl_2.

The fluorescence of **i** is quenched dramatically at a higher concentration or in polar solvents, implying the strong charge-transfer character in the excited state. The concentration quenching of the fluorescence was greatly suppressed in the dendrimers. For examples, **3** and **i** have comparable fluorescence quantum yield in CH_2Cl_2 at a concentration of 5×10^{-7} M, while the quantum yield of **i** drops to ~50% of that of **3** at a concentration of 10^{-5} M (Figure S1). Apprantly, the bulky dendron more effectively blocks the intermolecular interaction. All these dendrimers are red emitting in CH_2Cl_2 upon excitation at the charge-transfer band. In contrast to the absorption spectra, the emission wavelength of the dendrimers increases as the solvent polarity increases. For example, the λ_{em} values of compound **i** increase in the order toluene (615 nm) < CH_2Cl_2 (684 nm) < CH_3CN (750 nm), and so do those of compound **3**, toluene (616 nm) < CH_2Cl_2 (674 nm) < CH_3CN (724 nm). The dipolar nature of the excited state also results in significant quenching of the fluorescence in more polar solvents. For example, the Φ_f values for **i** and **3** are as follows: toluene (92%) < CH_2Cl_2 (57%) < CH_3CN (0.2%) for **i**; toluene (96%) < CH_2Cl_2 (74%) < CH_3CN (0.1%) for **3**. Encapsulation of the core by the dendrons gains further support from comparison of the film state λ_{em} and Φ_f between **i** ($\lambda_{em} = 642$ nm, $\Phi_f = 8\%$) and **3** ($\lambda_{em} = 693$ nm, $\Phi_f = 28\%$).

Energy transfer from the periphery to the core was investigated via steady-state absorption and emission spectroscopy. Spectral overlap between the emission band of the donor and the absorption band of the acceptor is a prerequisite for energy transfer to occur between the two. There is significant overlap between the emission spectra of **ii**-Br or **iii**-Br and the $\pi \rightarrow \pi^*$ of **i**, or between the emission spectra of **iv**-Br and the charge-transfer absorption band of **i** (Figure 3). A representaive emission spectrum is shown in Figure 4. The mixture of ***n***-Br (***n*** = **ii**, **iii**, or **iv**) and **i** was examined for the possibility of energy transfer between the donors and the acceptors. At a concentration of 5×10^{-6} M in CH_2Cl_2, strong emission of ***n***-Br accompanied the emission of **i**. Only at a concentration of $>5 \times 10^{-5}$ M was the emission of ***n***-Br completely suppressed (Figure S2). Energy transfer from the peripheries to the core in the dendrimers occurs both intra-

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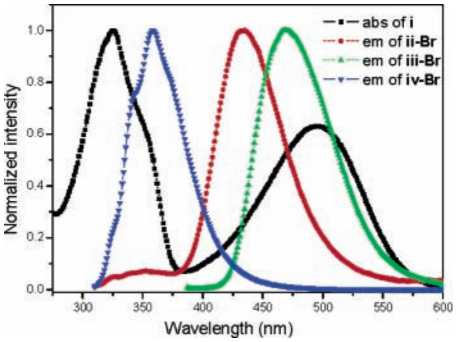

Figure 3. Absorption of the core and emission of the peripherals in CH_2Cl_2 upon the excitation of 342 nm for **ii**-Br, 380 nm for **iii**-Br, and 296 nm for **iv**-Br.

and intermolecularly. The intramolecular energy transfer is incomplete at a concentration below 10^{-5} M for all the dendrimers. When the dendrimers of 5×10^{-5} M concentration were excited at the peripherals' absorption bands (**ii**-Br, 342 nm; **iii**-Br, 380 nm; **iv**-Br, 296 nm), the emission came solely from the benzothiadiazole-based core at around 680 nm except for those containing pyrenylamines.

Different antenna effects or energy transfer efficiencies were observed among dendrimers **1**, **2**, and **3**. The antenna effect is prominent in **1**, and the emission intensity is higher for excitation at **ii** than at the core. In **2**, the antenna effect is also evident and the emission intensity is higher for excitation at **iii** than at the core. However, significant residual emission due to **iii** implies that the relative orientation of **iii** and the core is not ideal for complete energy transfer. In contrast, **3** exhibits lower emission intensity upon excitation at **iv** than at the core. There is less efficient energy transfer in **9** than in **3**, possibly due to the longer distance between **iv** and the core, and/or more facile nonradiative relaxation in the former.

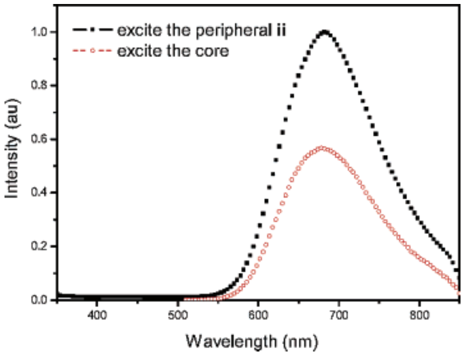

Figure 4. Emission spectra of **1** in CH_2Cl_2 upon the excition of 342 nm for **ii** and 498 nm for the core.

Electroluminescent devices[17] of configuration ITO/ PEDOT:PSS (80 nm)/compound n (40 nm)/BCP (10 nm)/Alq_3 (20 nm)/LiF (1 nm)/Al (200 nm) (PEDOT:PSS = polyethylenedioxythiophene:polystyrene-sulfonic acid; ***n*** **= 2, 3)** were fabricated. Both devices have pure red emission (CIE: $(x,y) = (0.63, 0.37)$ for **2** and (0.66, 0.34) for **3**) characteristic of the compound. The nonoptimized device performance appears to be promising: **2**, $V_{on} = 3.5$ V, $\eta_{ext,max} = 1.88\%$, $\eta_{p,max} = 2.13$ lm/W, $\eta_{c,max} = 2.37$ cd/A; **3**, $V_{on} = 4.0$ V, $\eta_{ext,max}$ 1.50%, $\eta_{p,max} = 0.96$ lm/W, $\eta_{c,max} = 1.17$ cd/A. In comparison, the device fabricated from **12**, which has no carrier transporting moieties in the peripheries, has much lower performances: $V_{on} = 5.0$ V, $\eta_{ext,max} = 0.07\%$, $\eta_{p,max} = 0.03$ lm/W, $\eta_{c,max} = 0.06$ cd/A. Apparently, carrier-transport in the molecules studied here is beneficial to raising the device performance. A more detailed study is needed, however.

In conclusion, red-emitting dendrimers with a red-emitting core encapsulated with peripheries capable of carrier transporting have been synthesized. Interesting energy transfer and antenna effects were verified for these compounds. Red-emitting electroluminescence of good performance was also fabricated from these compounds.

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Supporting Information Available: Synthetic procedures and characterization details for the new compounds (Figures S1 and S2). This material is available free of charge via the Internet at http://pubs.acs.org.

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[17] PEDOT:PSS was inserted between ITO and the dendrimers to help the hole injection. The layer of PEDOT:PSS was first spin-coated on a glass substrate with patterened ITO glass as a hole injection layer and then dried in an oven at 100 °C for 1 h. A solution containing **2**−**4** in dichloroethane was then spin-coated as the emitting layer of 40 nm thickness. On the coated emitting layer, 1 nm of LiF and 200 nm of Al as electrode were thermally deposited sequentially under vacuum.