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Dendrimer-Containing Light-Emitting Diodes: Toward Site-Isolation of Chromophores

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The doping of organic light-emitting diodes (OLEDs) with low concentrations (∼1 wt %) of efficient fluorescent[1,2] or phosphorescent[3] dyes has proven to be a very effective strategy for achieving excellent and tunable color quality in devices without compromising their electrical properties.[2] Color tuning is generally effected by either modifying the dopant, fabricating multilayer devices,[4] or by combining several dopants within a single emissive layer to obtain a synergistic emission.[1e,5] The latter strategy is perhaps the most attractive in terms of its modularity and simplicity, but it is often complicated by undesirable interactions (i.e., energy transfer) between lumophores that typically results in emission predominantly from the lowest band gap dye in the system. Moreover, since the dopant loading levels in the device must remain low in order to suppress detrimental self-quenching processes (i.e., excimer formation) both the luminescence and external quantum efficiencies of these devices go through a maximum with respect to dye dopant concentration. Therefore, it should prove beneficial to encapsulate the lumophores within a "protective" organic matrix, effectively isolating them to prevent detrimental excimer formation and energy transfer.[6]

We now report a new family of chromophore-labeled dendrimers designed for use in single-layer light-emitting diodes. By building on the design of Moore et al.,[7] these dendrimers possess peripheral redox-active triarylamines (TAA) that are responsible for hole transport (HT) and are the loci of exciton formation. Since both the dendrimer backbone and the core fluorophores have comparatively high redox potentials, charge transport is expected to occur solely through the hole-transporting TAA moieties and the accompanying electron transporting oxadiazole, 2-(4-biphenyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole, **3**.[1] Transfer of energy to the highly luminescent acceptor fluorophores at the core of the dendrimer via a Förster process, subsequently results in emission exclusively from the acceptors.[8,9] Related dendrimer-based OLEDs have been reported recently;[7,10] however, our work is the first to rely upon Förster energy transfer from charge carriers on the periphery of the dendrimer to a fluorescent dye at the core. The photophysical behavior and the device characteristics of our dendrimers are described using a combination of solution- and solid-state photoluminescence (PL) and electroluminescence (EL) studies, a partial discussion of which has recently appeared.[11] In addition to devices formulated with a single type of dendrimer, some preliminary results for those containing mixtures of two dendrimers with different emissive dyes are described as a novel approach toward modular, color-tunable OLED systems.

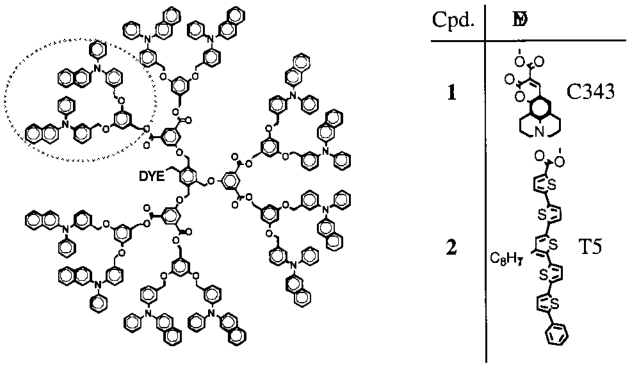
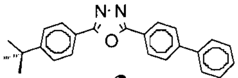


Figure 1. Emissive, HT dendrimers **1** and **2**. The monodendron (TAA) used for PL studies is shown by the dashed ellipse.



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Dendrimers **1** and **2** were prepared according to conventional convergent methodology.[12,13] These [G-2] dendrimers possess 12 peripheral TAA groups surrounding a single central dye-labeled core (see Figure 1). The coumarin (C343) and pentathiophene

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(13) All dendritic materials were characterized using a combination of spectroscopic and chromatographic techniques. For example, dendrimer **2**: ^{1}H NMR: (CDCl$_3$) δ 0.85 (br t, 3H, $J = 7.0$ Hz, $\mathrm{CH_2C}H_3$), 1.24−1.53 (m, 12H, $\mathrm{(CH_2)_6}$), 2.71 (br t, 2H, $\mathrm{C}H_2\mathrm{(CH_2)_6}$), 4.74−4.89 (m, 24H, $\mathrm{ArC}H_2\mathrm{O}$), 5.08−5.14 (m, 20H, $\mathrm{ArC}H_2\mathrm{O}$), 5.29 (s, 2H, $\mathrm{ArC}H_2\mathrm{O}$), 6.36 (br m, 7H, thiophene), 6.50 (m, 14H, ArH), 6.95−7.24 (m, 213H, ArH and thiophene), 7.59 (m, 2H, ArH), 7.64 (s, 1H, thiophene). ^{13}C NMR: (CDCl$_3$) δ 14.13, 22.66, 25.63, 29.25, 29.37, 29.55, 31.86, 66.85, 69.78, 101.78, 107.18, 120.47, 121.88, 122.90, 123.06, 123.48, 124.40, 124.44, 124.50, 125.59, 126.21, 126.91, 127.50, 128.90, 128.95, 129.29, 129.51, 130.03, 131.77, 134.32, 137.76, 137.94, 145.20, 147.53, 147.94, 158.29, 159.83, 165.01. MS (MALDI-TOF) *m*/*z* [M]$^+$ 5734, found 5734.

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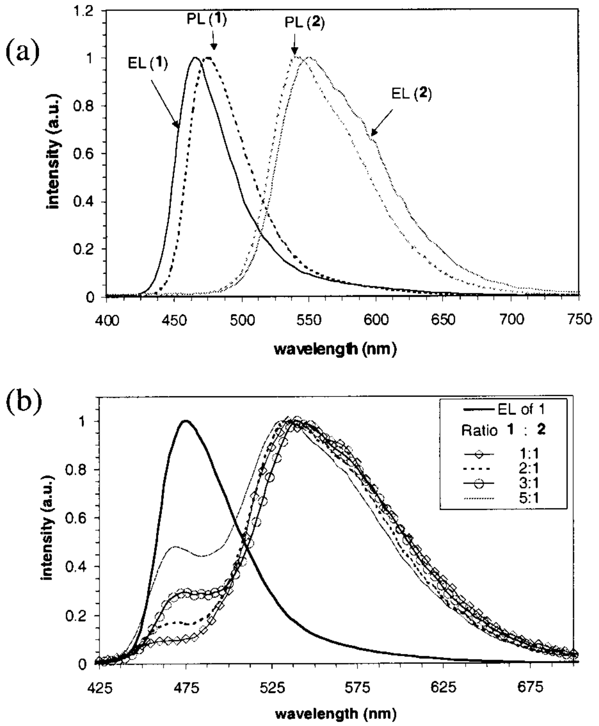

Figure 2. (a) Solid-state PL and EL of **1** and **2**. (b) EL of dendrimer blends.

(T5)[14] acceptor lumophores were chosen because of the extensive overlap of their respective absorption bands at 446 and 425 nm, with the emission band of the TAA moieties at 425 nm. In addition, their high molar absorptivities, 44 000 and 49 000 M^1 cm^{-1}, respectively, ensured that energy could be efficiently accepted.

Both solution- ($CHCl_3$ and CH_3CN) and solid-state (thin films on glass) PL studies revealed that energy-transfer efficiencies within **1** and **2** were essentially quantitative. Excitation of the peripheral amines at 310 nm resulted in emission exclusively from the core lumophores, C343 and T5, respectively (Figure 2a). Thus **1**, which has a $\lambda_{max}(em) = 480$ nm, appears blue, while **2** has a green luminescence at 550 nm. Two-component, single-layer OLEDs consisting of either dendrimer **1** or **2**, and the electron-transporting oxadiazole **3**[1f] were prepared. The EL spectra of both dendrimers were essentially identical to their PL spectra (Figure 2a).[15] In all cases, only intense emission from the respective core lumophores at 470 and 560 nm was observed in the absence of emission from either **3** (390 nm) or the peripheral amines (425 nm). Moreover, these devices exhibited external quantum efficiencies of 0.012 and 0.12%, respectively.

Next, a series of four single-layer devices containing mixtures of **1** and **2** were prepared wherein the total concentration of dendrimer remained constant (**1** + **2** = 10% w/v = 0.1 mmol of dye per gram of film), while their proportions were varied (1:1, 2:1, 3:1, and 5:1). The external quantum efficiencies are comparable to devices made with **1** only. The EL spectrum of the 1:1 mixture of **1** and **2** exhibits a dominant band originating from T5 centered at ~540 nm, accompanied by a small, but discernible, emission band from C343 at ~470 nm (Figure 2b). As the fraction of C343-labeled dendrimer **1** in the blend is increased, an expected linear increase in its EL is observed. It is evident that Förster energy transfer from C343 to the lower band gap T5 is responsible for the significant decrease in C343 emission relative to T5. The Förster radius for energy transfer between these chromophores was later calculated to be ~35−38 Å, which exceeds the separation afforded by the surrounding [G-2] monodendrons.[16]

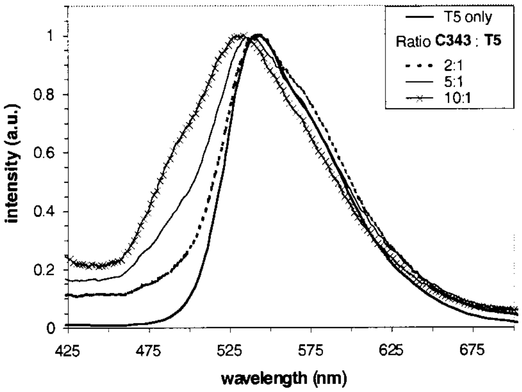

Figure 3. PL spectra of T5 as well as "free" C343 and T5 blends in TAA.

While the dendritic shells of **1** and **2** are too small to afford complete dye site isolation, a significant degree of site isolation is clearly achieved as shown in comparative experiments with films containing blends of the "free" chromophores C343 and T5 (Figure 3). The total dye concentrations of C343 and T5 in these films are the same as in the mixed dendrimer films. The PL spectra of the mixed dendrimer films are essentially identical to the EL spectra shown in Figure 2b. Comparison of the PL spectra of the two types of thin film is preferable to comparing the EL spectra, since the EL emission may be affected by charge trapping or other processes unrelated to energy transfer.[1,2] For all C343:T5 ratios in the free dye films, essentially T5 emission is observed regardless of the proportions of dyes, with the C343 band only seen as a weak shoulder on the T5 emission band. In contrast, the mixed dendrimer films give clearly resolved and steadily increasing C343 bands as the ratio of **1**:**2** is increased.

In conclusion we have introduced a new family of emissive, hole-transporting dendrimers, within which essentially quantitative energy transfer from periphery to the core is observed in both PL and EL measurements. Moreover, initial experiments toward color-tunable OLEDs in devices containing mixtures of dendrimers **1** and **2** demonstrate that a degree of site isolation of the central dye is afforded by the smal,l surrounding dendrons. While it is clear that larger dendritic shells are required for *complete* site-isolation of the core dyes, we have demonstrated that dye encapsulation is a potentially simple and powerful strategy for the manipulation of properties in optoelectronic devices. Further investigations into the use of larger dendrimers and alternative polymer architectures[17] that should afford a greater degree of core isolation and ultimately facilitate color tuning via dye mixing are currently underway.

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[15] Devices were prepared by spin casting 1,2-dimethoxyethane solutions of either dendrimer **1** or **2**, and PBD **3** (10 mg/mL each) onto glass substrates patterned with ITO (anode) (thickness = 800−900 Å). The MgAg cathode was vapor deposited (Mg:Ag (9:1) cathode (500 Å) + 1000 Å of Ag. All devices were operated at ambient atmosphere, had moderate turn-on voltages (12−15 V).

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