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Chromophore-labeled Dendrimers for Use in Single-layer Light-emitting Diodes

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SUMMARY: Two novel chromophore-labeled dendrimers are presented and their incorporation into two-component, single layer organic light emitting diodes (OLEDs) is described. The photoluminescence (PL) spectra, both in solution and in the solid state, demonstrate that Förster energy transfer from the donor chromophores on the dendrimers periphery to the acceptors located at the core is highly efficient, and affords emission exclusively from the core dyes, either coumarin 343 or a benzene-capped pentathiophene. When these dendrimers are doped into single layer OLEDs, the electroluminescence (EL) is nearly identical to the photoluminescence described above, indicating once again exclusive emission from the core chromophores.

Introduction

Although relatively efficient light-emitting diodes containing largely organic constituents were prepared more than a decade ago by Tang and VanSlyke,[1] it was not until Holmes and Friend's discovery of the electroluminescence properties of poly(phenylenevinylene)[2] (PPV) that organic polymers began to play a significant role in the field. Since then a multitude of polymeric systems, mainly π-conjugated polymers, have demonstrated their potential for use in organic light-emitting diodes (OLEDs). The benefits of polymers, namely their ease of introduction into devices *via* spin casting, good film forming properties, and tunable luminescence properties by judicious manipulation of substituents and side chains, makes them excellent choices in both single- and multi-layer OLEDs.

More recently, dendritic macromolecules have been employed in OLEDs either as the hole[3] or electron[4] transporting components (HT and ET, respectively), or as single-component emitters.[5] The latter system, studied by Moore and coworkers, demonstrates the control dendrimers can bring to optoelectronic devices. In their

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work, rigid phenylacetylene dendrimers functioned not only as ETs, but also as macromolecular scaffolds, maintaining the relative positions of both the HT surface groups and the emitters at the core. In all cases, a strong correlation between the photoluminescence (PL) and electroluminescence (EL) spectra was observed, indicating emission solely from the dye core. This paper describes the luminescence properties of multi-component, single-layer OLEDs containing modularly designed, chromophore-labeled dendrimers **1** and **2**.

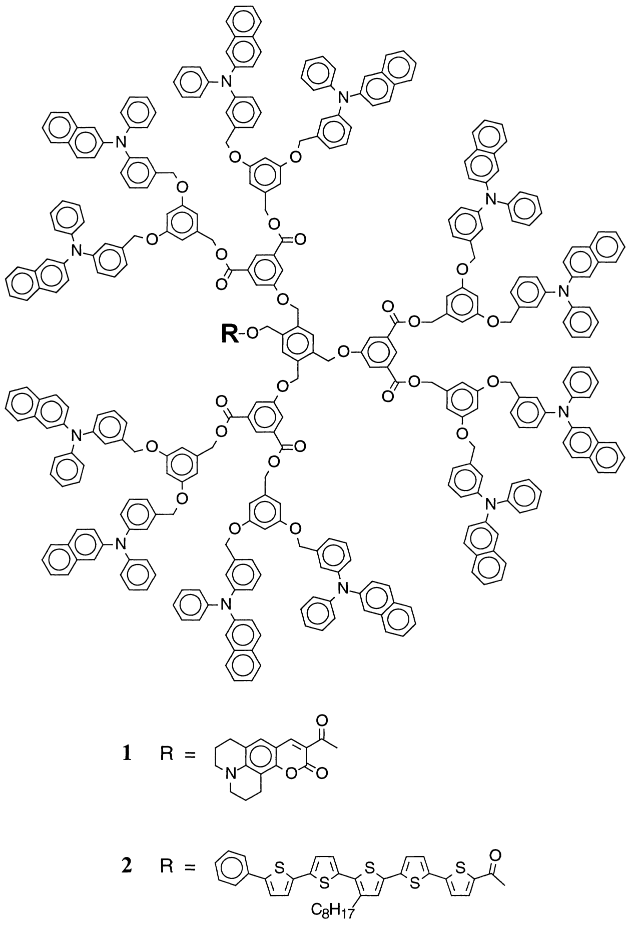

Figure 1. Chromphore-labeled HT-dendrimers.

Results and Discussion

For our studies, two chromophore-labeled dendrimers, **1** and **2**, were prepared. Both possess exactly 12 triarylamine (TAA) surface chromophores capable of hole transport, and an emissive dye core. The dyes, coumarin 343 (C343) for **1** and a benzene-capped pentathiophene (T5) for **2**, were chosen because their λ_{max}(abs) are between 420 and 430 nm which coincides exactly with the λ_{max}(em) of the TAA surface groups (425 nm). This excellent overlap between the absorption and emission bands is a requisite for efficient Förster energy transfer, the presumed primary mechanism of energy movement leading to emission from our devices. We have already demonstrated that Förster energy transfer between coumarin dyes positioned at the periphery and focal point of poly(benzyl ether) dendrimers can occur with efficiencies near 100%.[6] In addition, the carboxylate moieties present on each dye allowed them to be attached to their respective dendrimers using the same reaction conditions. The synthesis of these dendrimers will be presented elsewhere.

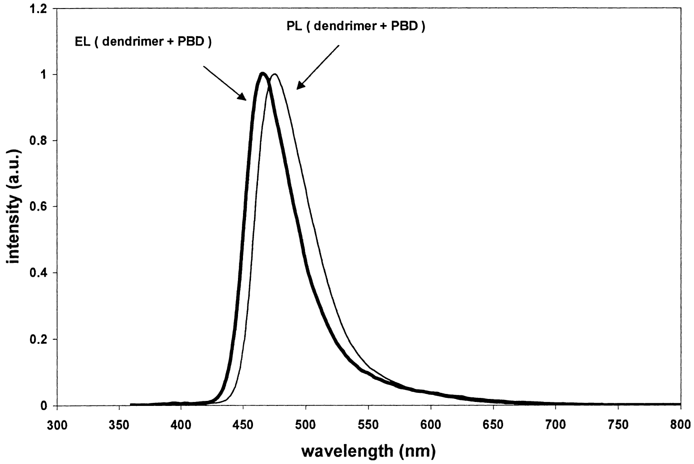

Figure 2. Photo- and electroluminescence of dendrimer **1**.

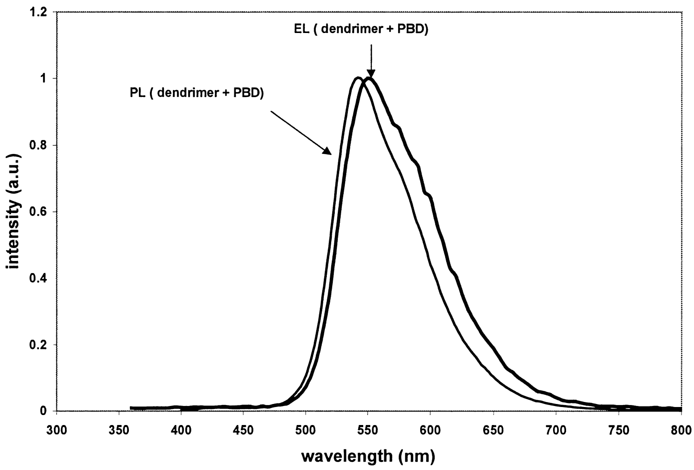

Figure 3. Photo- and electroluminescence of dendrimer **2**.

Photoluminescence properties. The potential of these dendrimers to function in OLEDs was assessed by first examining their photoluminescence (PL) properties. Direct irradiation of the peripheral TAA chromophores (λ_{max} = 309 nm) resulted in emission solely from the core dyes, C343 and T5 (see PL in Figures 2 and 3, respectively), both in solution (CH_2Cl_2 and CH_3CN) and in solid films on glass substrates [both in the presence and absence of 2-(4-biphenyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole (PBD) **3**]. The energy transfer efficiency within these systems is estimated to exceed 98%.

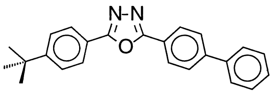

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Figure 4. Molecular ET **3**.

Electroluminescence properties. When incorporated into devices (as described below), both dendrimers **1** and **2** exhibited remarkable EL spectra. As seen in Figures 2 and 3, the EL of both dendrimers correlated almost identically with their respective PL spectra indicating emission solely from the C343 and T5 dyes, respectively.

Given the placement of functional groups within the dendrimer, it seems likely that the charged species generated upon application of a potential, recombine near the dendrimers surface and result in the formation of excitons, whose energy in rapidly transferred to the dye located at the core. Radiative relaxation of the dye then produces the observed fluorescence.

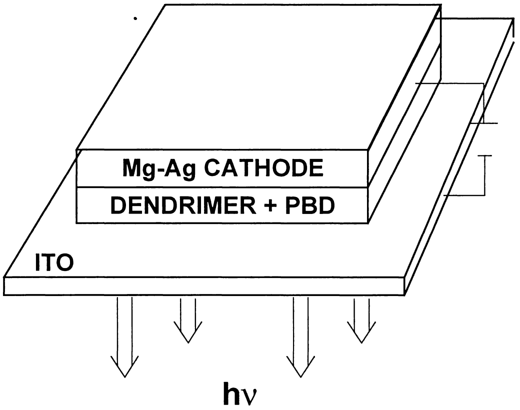

Figure 5. Configuration of the two-component, single-layer devices.

Device fabrication. All of the devices described herein are two component, single layer devices consisting of either dendrimer **1** or **2**, and molecular ET **3** (Figure 5). Preparation involved spin casting a solution of the components (~10 mg/mL each) onto a patterned ITO wafer, followed by vapor deposition of the metal cathode. Dendrimer films cast from glyme (40 seconds @ 2000 rpm) were consistently pinhole-free and had an average ellipsometric thickness of approximately 800-900 Å. Films cast from $CHCl_3$, THF, and 1,4-dioxane were inferior with respect to both quality and thickness. The Mg-Ag (~ 9:1) cathode was deposited to a thickness of approximately 500 Å, and subsequently capped with an additional 1000 Å of Ag. Most of the devices had moderately high turn-on voltages between 12-15 V, and could be driven at voltages exceeding 30 V.

Conclusion

In summary, we have prepared a new family of dendrimers, labeled with hole transporting amines at their periphery and with emissive dyes at the core. Highly efficient Förster energy transfer from the donors on the surface to the acceptors/emitters at the dendrimers core was demonstrated through photoluminescence studies, both in solution and in the solid state. Analogous energy conveyance/emission processes were observed in two component, single layer OLEDs incorporating these dendrimers, resulting in exclusive emission from the coumarin and oligothiophene core dyes.

Using the same modular design, many other HT donor/dye acceptor pairs can be employed to achieve almost any color of emission. Moreover, we expect that the physical separation of dyes by the sheer steric bulk of the surrounding dendrimer should allow several different dye-containing dendrimers to be mixed, thus affording a color tunable system. We are currently working toward the preparation of such dendrimers.

Acknowledgements

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