

Bright electroluminescence from a conjugated dendrimer

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Photoluminescence and electroluminescence (EL) from a conjugated dendrimer consisting of three distyrylbenzene units linked by a central nitrogen atom as core and meta-linked biphenyl units as dendrons were investigated. The conjugated dendrimer emits green light and shows photoluminescence quantum efficiency of 9%. Bright electroluminescence was realized by using bilayer devices with blurred interface, which were fabricated by sequentially spin coating a neat dendrimer and a dendrimer doped with 2-(4-biphenyl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole (PBD). The devices have the following structure: indium tin oxide/3,4-polyethylenedioxythiophene-polystyrenesulfonate/dendrimer/ dendrimer:PBD/Al. By optimizing the concentration of PBD, the maximum brightness and EL quantum efficiency reach 4100 cd/m² and 0.17%, respectively. This is the best result reported so far on organic light-emitting diodes using dendrimer as an active material with an Al cathode. © 2002 American Institute of Physics.

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The development of photonic devices requires the use of a well-defined macromolecular architecture having a large section for energy absorption, extremely high quantum yield of fluorescence, good solubility and processability characteristics, and a degree of versatility that allows for the tuning of each of these properties such that the devices can be tailored for specific applications. Although conjugated polymers as active materials in photonic devices such as light-emitting diodes and lasers have been investigated widely,^{1,2} a major disadvantage of the linear polymer materials is lower luminescence quantum efficiency in solid state films relative to dilute solutions. The lower luminescence efficiency in films than in dilute solutions has been thought of being due to the formation of aggregates and excimers between chromophores,³ which may drastically reduce the possible efficiency of light-emitting devices. Although blending luminescent polymer into another host polymers may overcome the problem, and improve luminescence efficiency by energy transfer,⁴ there yet exists a problem of phase separation, and the energy transfer in the blends is not also very effective. On the other hand, doping different fluorescent dyes into polymer matrix for tuning emissive color in organic light-emitting diodes has proven to be a very effective strategy,⁵ but it is often complicated by undesirable interactions (i.e., energy transfer) between different dyes that typically results in emission predominantly from the smallest band gap dye in the blend. Moreover, in order to suppress detrimental self-quenching processes, the concentration of the doped dyes

must remain lower. This leads to the dependence of luminescence and electroluminescence (EL) efficiency of devices on dye dopant concentration. Therefore, it should be beneficial to design an organic luminescence material that not only the optical, electrical, and processing characteristics can be controlled, respectively, but also the chromophores are encapsulated within a protective organic matrix to prevent detrimental excimer formation and undesirable energy transfer.

Dendrimers, well-defined, hyperbranched macromolecules having numerous chain ends all emanating from a single core, have recently attracted considerable attention as a luminescence material for applications in organic light-emitting diodes and lasers⁶⁻⁹ because their branched architecture makes their three-dimensional structures highly controllable.¹⁰ Dendrimers may not only control optical, electrical, and processing characteristics well by cores, dendrons, and surface groups, and because the dendritic shells decrease the interactions between the cores and surrounding molecules, the formation of aggregates or excimers is also effectively reduced. At the same time, intramolecular energy transfer in the dendrimers is extremely efficient.¹¹

In this letter, we report a conjugated dendrimer designed for use in organic light-emitting diodes, and investigate its photoluminescence and electroluminescence characteristics. Bright electroluminescence was obtained from a bilayer device with structure of indium tin oxide (ITO)/3,4-polyethylenedioxythiophene-polystyrenesulfonate (PEDOT)/dendrimer/dendrimer: 2-(4-biphenyl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole (PBD)/Al. The organic layer was formed by sequentially spin coating a neat dendrimer layer and a dendrimer doped with PBD layer. Obviously, this device is dif-

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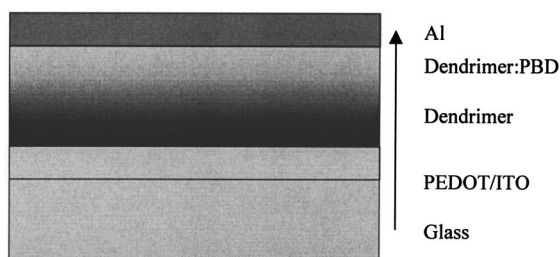
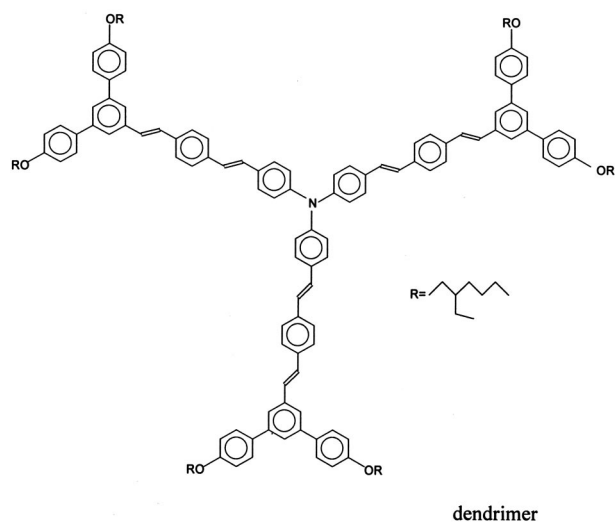


FIG. 1. Molecular structure of the dendrimer used in this study and device configuration of the blurred organic light-emitting diode.

ferent from conventional bilayer structures in which the interface layer is eliminated by interlayer mixing, leading to a blurred interface.

The molecular structure of the conjugated dendrimer and the device configuration used in this study are shown in Fig. 1. The conjugated dendrimer is a first generation dendrimer. It consists of three parts: three distyrylbenzene chromophores surrounding a nitrogen core, meta-linked biphenyl units as dendrons and alkoxy groups as surface groups. The device was fabricated in such a way that ITO with a thin layer of conducting polymer PEDOT was used as the anode. A neat dendrimer layer (10 mg/ml in tetrahydrofuran) was spin coated on the PEDOT/ITO coated glass substrate (~ 80 nm). Then, a dendrimer:PBD blend containing the same weight dendrimer (10 mg/ml) with different concentrations of PBD was spin coated onto the neat dendrimer film from the same solvent. The final bilayer film thickness is about 130 nm. Obviously, the lower neat dendrimer is partly dissolved. The device structure is very efficient in improving the performance of organic devices, which has been discussed in more detail in our article.¹² In this device, stable Al metal was used as the cathode. The thickness of the organic layer was measured using a surface profilometer. The light-current-voltage characteristics were measured using a Keithley source measure unit with a calibrated silicon photodiode. The EL spectra were measured using a charge coupled device spectrograph, and photoluminescence (PL) spectra were measured with a SPEX spectrophotometer. The absorption spectra were measured using Varian UV spectrophotometer. The device has an area of 2 mm^2 .

Figure 2 shows the absorption and PL spectra excited at

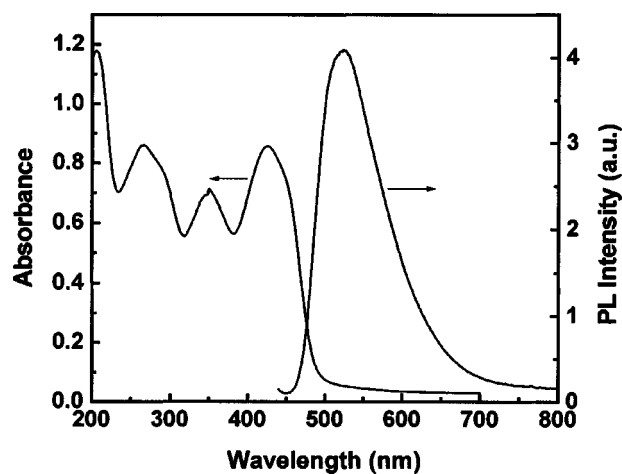


FIG. 2. Absorption and PL spectra of the neat dendrimer film.

425 nm of the neat dendrimer film. There are three main absorption feature peaks at 425, 350, and 260 nm, respectively. The absorption at 350 and 260 nm can be assigned to the biphenyl dendrons, whereas the absorption at 420 nm originates from the core. In the case of this dendrimer, the core and dendron bands are well separated and the absorption spectra can to a first approximation be expressed as a superposition of core and dendron absorption, leading to a broad absorption spectrum. It is worth noting that distyrylbenzene absorbs at 360 nm,¹³ whereas the observed absorption here peaks at 420 nm. This indicates that the electronic core region extends across the central amine region and is a result of delocalization between the three distyrylbenzene units in the core region. With difference from the absorption spectrum, the PL spectrum shows structureless single peak emission feature with a peak at 520 nm, as seen in Fig. 2. The same PL spectrum was measured by excitation wavelength of 350 and 260 nm at biphenyl dendron absorption band. The fact that the same PL spectra from the distyrylbenzene core are observed at different excitation wavelength demonstrates that the energy transfer from dendrons to cores is efficient in this dendrimer. The photoluminescence quantum efficiency of the neat dendrimer film was measured using an integrating sphere. The dendrimer shows PL quantum efficiency of 9%.

In Fig. 3, the EL spectrum of the device with a weight ratio of dendrimer/PBD of 1:0.8 is shown. The similar EL spectra from the devices with different concentrations of PBD are also observed. For comparison, the EL spectrum of an undoped single-layer device is also given in Fig. 3. It can be seen that the device with blurred interface shows the approximately same EL peak at 520 nm as that of undoped single-layer device and as PL spectrum of the neat dendrimer film, indicating that the EL emission in the device with blurred interface is from the conjugated dendrimer. However, it is observed that the device with blurred interface shows a narrower EL spectrum with respect to the undoped single layer. The narrow EL spectrum were also observed in mixed single-layer devices with structure of ITO/PEDOT/dendrimer:PBD/Al. Obviously, the emission in the device with blurred interface originates from the dendrimer in the doped PBD layer.

By optimizing the concentration of PBD, bright and ef-

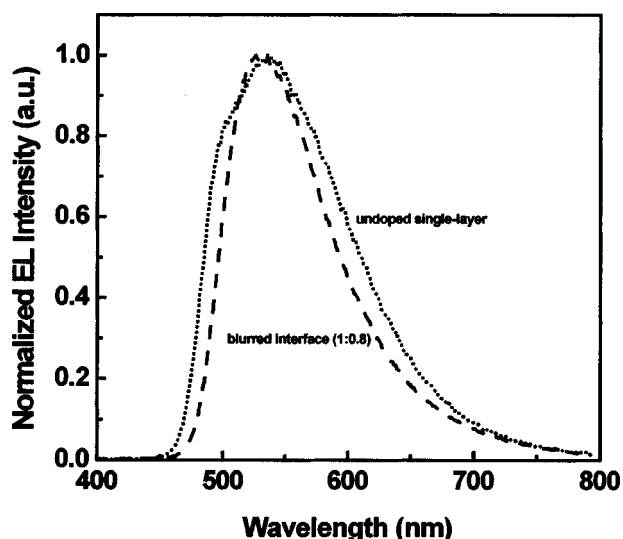


FIG. 3. Normalized EL spectra of ITO/PEDOT/dendrimer/dendrimer:PBD(1:0.8)/Al and ITO/PEDOT/dendrimer/Al.

efficient light-emitting diodes based on the conjugated dendrimer as emissive material have been obtained. Figure 4 illustrates a typical current–light–voltage characteristic of a device with PBD concentration of 1:0.8. The EL quantum efficiency as a function of current density is shown in the inset of Fig. 4. The maximum brightness reaches 4100 cd/m^2 , and the EL quantum efficiency of 0.1% is achieved at 11.5 V bias (1.32 A/cm^2). Depending on the concentration of PBD, EL quantum efficiency of 0.17% is obtained. Table I gives the performance including maximum brightness, EL quantum efficiency, and EL power efficiency of the devices with different concentrations of PBD. It can be seen that the maximum EL quantum efficiency is enhanced by a factor of 340, and the maximum brightness is increased by 820 times in the devices with the blurred interface with respect to that of undoped single-layer devices. In the undoped single-layer devices, the low brightness and efficiency result from the unbalanced injection and transport of electrons and holes, especially in the case of Al as the cathode,

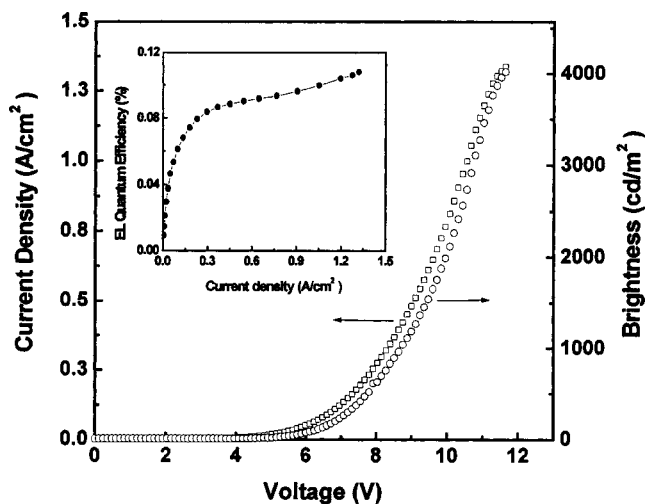


FIG. 4. Current–light–voltage characteristics of ITO/PEDOT/dendrimer/dendrimer:PBD(1:0.8)/Al device. The inset shows the EL quantum efficiency as a function of injection current.

TABLE I. Performance of ITO/PEDOT/dendrimer/dendrimer:PBD($x:y$)/Al devices with different concentrations of PBD.

$x:y$	Maximum brightness (cd/m^2)	Maximum EL efficiency (%)	Maximum power efficiency (lm/W)
1:0	5	0.0005	0.000 024
1:0.2	260	0.0055	0.0032
1:0.5	690	0.038	0.02
1:0.8	4100	0.10	0.09
1:1.0	2400	0.17	0.08
1:1.4	1800	0.07	0.04

where the emissive region is near to the cathode, leading to the excitons being strongly quenched. In these devices with a blurred interface, the significant improvement in brightness and efficiency is then attributed to this efficient device structure, in which exciton formation is improved by a microscopic networking of electron and hole transporting layers. This leads to the recombination region far from the quenching cathode and the efficient recombination of injected electrons and holes. The reduction of the brightness and efficiency at high concentration of PBD results from phase separation.

In conclusion, we have demonstrated the use of a conjugated dendrimer as efficient electroluminescent materials in organic light-emitting diodes. By utilizing a bilayer device with blurred interface, bright electroluminescence has been observed, and the maximum brightness and EL quantum efficiency reach 4100 cd/m^2 and 0.17%, respectively. Because of unique three-dimensional hyperbranched molecular structure, dendrimers have been considered as promising candidate material systems for fabricating efficient and stable light-emitting diodes, and may find applications in other photonic devices such as lasers, solar cells, fluorescent sensors, and frequency converters, etc.

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- J. H. Burroughes, D. D. C. Bradley, A. R. Brown, R. N. Marks, K. Mackay, R. H. Friend, P. L. Burn, and A. B. Holmes, *Nature (London)* **347**, 539 (1990).
- M. D. McGehee and A. J. Heeger, *Adv. Mater.* **12**, 1655 (2000).
- R. Jakubiak, C. J. Collison, W. C. Wan, L. J. Rothberg, and B. R. Hsieh, *J. Phys. Chem. A* **103**, 2394 (1999).
- S. Tasch, E. J. W. List, O. Ekström, W. Graupner, G. Leising, P. Schlichting, U. Rohr, Y. Geerts, U. Scherf, and K. Mullen, *Appl. Phys. Lett.* **71**, 2883 (1997).
- J. Kido, M. Kimura, and K. Kagai, *Science* **267**, 1332 (1995).
- M. Halim, J. N. G. Pillow, I. D. W. Samuel, and P. L. Burn, *Adv. Mater.* **11**, 371 (1999).
- J. M. Lupton, R. Beavington, M. J. Frampton, P. L. Burn, I. D. W. Samuel, and H. Bässler, *Phys. Rev. B* **63**, 155206 (2001).
- A. W. Freeman, S. C. Koene, P. R. L. Malenfant, M. E. Thompson, and J. M. J. Fréchet, *J. Am. Chem. Soc.* **122**, 12385 (2000).
- A. Otomo, S. Yokoyama, J. Nakahama, and S. Mashiko, *Appl. Phys. Lett.* **77**, 3881 (2000).
- C. J. Hawker and J. M. J. Fréchet, *J. Am. Chem. Soc.* **112**, 7638 (1990).
- A. Adronov, S. L. Gilat, J. M. J. Fréchet, K. Ohta, F. V. R. Neuwahl, and G. R. Heming, *J. Am. Chem. Soc.* **122**, 1175 (2000).
- D. Ma, J. M. Lupton, R. Beavington, P. L. Burn, and I. D. W. Samuel, *Adv. Funct. Mater.* **12**, 507 (2002).
- J. N. G. Pillow, M. Halim, J. M. Lupton, P. L. Burn, and I. D. W. Samuel, *Macromolecules* **32**, 5985 (1999).