Electroluminescence of Phenothiazine-Labeled Dendrimer Encapsulated 2-{2-[2-(4-Dimethylamino-phenyl)-vinyl]-6-methyl-pyran-4-ylidene}-Malononitrile Derivative: Effect of the Density of Phenothiazine Dendron

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Summary: Red light emitting dendrimer (3) was synthesized by reacting 2-[2,6-bis-(2-{4-[bis-(6-hydroxy-hexyl)-amino]-phenyl}-vinyl)-pyran-4-ylidene]-malononitrile (2) with 3,5-bis-{3,5-bis-[2-(10-hexyl-10*H*-phenothiazin-3-yl)-vinyl]-benzyloxy}-benzoic acid (1). The red emitting core dye capable of electronic excitation *via* Förster energy transfer was encapsulated by phenothiazine (PTZ) dendrons. The multi-layered devices showed a luminance of 210 cd/m^2 at 321 mA/cm^2 (11.7 V) for the dendrimer only and 295 cd/m^2 at 246 mA/cm^2 (11.4 V) for the dendrimer with 3 wt% of PTZ dendron. The EL quantum efficiency ($\eta_{ext} = 0.79\%$) increased after doping an additional amount of PTZ dendron into the dendrimer.

Keywords: absorption; dendrimer; electroluminescence; energy transfer; phenothiazine; photoluminescence

Introduction

Electroluminescence (EL) devices using small molar mass organic materials have become the most popular technology that have already been employed in practical applications such as flat-panel or flexible display devices.[1–10]

Recently, functional dendrimers have been proposed to prepare multichromophoric material systems that possess unique molecular architecture and characteristics. It has been found that the photophysical properties of the core such as the absorption and emission behaviors can be fine-tuned by modifying the environmental moieties around the core.[11,12] In order to improve the EL efficiency, periphery-to-core energy transfer systems, based on light harvesting Π-conjugated dendrimers have often been prepared.[13–15] EL dendrimers exhibit a unique feature that is attractive for use in EL devices. The peripheral groups assist in core isolation as well as optimal geometry formation for an improved light harvesting property.[16–22] The site-isolation effect provided by bulky dendrons minimizes the undesired core-core interaction. Moreover, by systematically modifying the structures of a peripheral dendron, the overall energy transfer efficiency of EL devices can be optimized.

In this work, we report the photophysical and EL properties of the dendrimer consisting of phenothiazine (PTZ) peripheral moieties and red emitting cores. We found that the electron-rich phenothiazine ring is an excellent light harvesting molecular dendritic wedge whose PL emission is well suited to excite the red emitting core.

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We also investigated the density effects of the PTZ dendron either in the periphery or as a dopant on the PL and EL characteristics.

Experimental

Detailed synthetic procedures for the dendrimer and dendron will be reported elsewhere.

Absorption spectra of film samples and chloroform solution (conc. 1×10^{-5} mole/L) were obtained using a UV-vis spectrometer (HP 8453, PDA type) in the wavelength range of 300–800 nm. PL spectra were recorded with an AMINCO-Bowman series-2 luminescence spectrometer.

The multi-layer diodes have a structure of ITO/PEDOT:PSS (40 nm)/emitting layer (50 nm)/BCP (10 nm)/Alq_3 (40 nm)/LiF (1 nm)/Al (100 nm), respectively. The conducting PEDOT layer was spin-coated onto the ITO-coated glasses in an argon atmosphere. The emitting dendrimer layer then was spin-coated onto the thoroughly dried PEDOT layer using the solution (conc: 5wt%) in monochlorobenzene. For multi-layer devices, 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP) and tris(8-hydroxyquinoline) aluminium (Alq_3) layer were vacuum-deposited using a VPC-260 (ULVAC, Japan) vacuum coater and a CRTM-6000 thickness monitor (ULVAC, Japan) onto the emitting dendrimer layer. Finally, LiF (1 nm)/Al (100 nm) electrodes were deposited onto the Alq_3 layer under the same condition.

EL spectra of the dendrimer samples were also acquired on an AMINCO-Bowman series 2 luminescence spectrometer. I-V characteristics were measured using an assembly consisting of dc power supply (Hewlett-Packard 6633B) and a digital multimeter (Hewlett-Packard 34970A). Luminance was measured by using a Minolta LS-100 luminance meter. The thickness of the dendrimer was determined by a TENCOR P-10 surface profilometer.

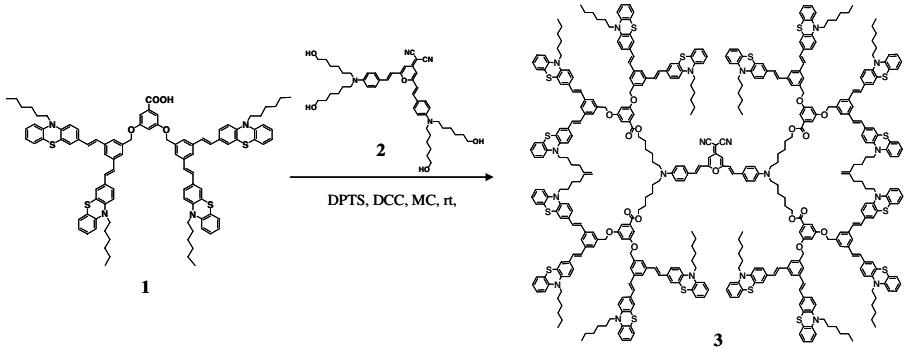
Results and Discussion

General Properties of Dendrimer

The synthetic route to prepare 3 can be found in Scheme 1. The syntheses of the PTZ precursor compounds and 1 were reported in our previous work.[23,24] 2 was encapsulated with sixteen PTZ dendrons. PTZ groups were attached to four hydroxyl groups in the core, 2 to yield a 2^{nd} generation dendrimer, 3. The reaction was conducted by DCC catalyzed esterification. The PTZ dendron and red emitting core were connected through a nonconjugated alkylene spacer in order to isolate the photophysical properties of the two moieties. The newly synthesized dendrimer is well soluble at room temperature in common organic solvents such as chloroform, THF, and chlorobenzene and it displays good self-film forming property. The glass transition temperature (T_g) of the dendrimer, 3 was obtained by DSC are 83.5°C. No melting behavior upto 300°C was observed in the DSC thermogram of the dendrimer.

Figure 1 illustrates the absorption spectrum of 2 and PL spectra of 1 and 3 in thin films on fused silica glass. The dendrimer, 3 exhibits distinct dual absorption maxima in the film state: one at around 386 nm and the other over a longer wavelength region at 506 nm, which are attributed to the Π–Π* transitions of 1 and the transition from the core dye, 2.[25,26]

The absorption spectrum of 2 and emission spectrum of 1 using spin-cast films displays a large overlap, which implies a higher efficiency of energy transfer in the dendrimer. In the spectrum (c), No emission at 500 nm is considered to originate from the PTZ dendron and the strong emission at 630 nm is the result of the energy transfer from the PTZ dendron to the core dye. It is noted that the coupling of the PTZ moiety and the core dye to form an energy donor-acceptor complex quenches the emission of the PTZ moiety. [13,27,28] In order to study the effect of dendronized dopant on PL behaviors, the emission spectra were recorded with the concentration of PTZ dendron, 1.



Scheme 1.
Synthesis of dendrimer 3. *DPTS: 4-(dimethylamino)-pyridinium 4-toluenesulfonate, DCC: N,N-dicyclohexylcarbodiimide, MC: methylene chloride.

(see Figure 2) As the concentration of the dendron increases, PL intensity becomes larger and the peak at 500 nm grows gradually. That is due to the residual PL emission of PTZ dendron. The maximum emission can be observed at a lower wavelength than that of the pristine dendrimer. It can be expected that doping the PTZ dendron can induce higher EL performance of the devices.

Electroluminescence Properties

We used the dendrimer for light emitting diodes (LEDs) as an emissive material in a multi-layered device. Poly(ethylene dioxythiophene):poly(styrene sulfonic acid) (PEDOT:PSS) thin film was deposited on indium tin oxide (ITO) as the anode for facilitating hole injection and the dendrimer was coated on it as an emissive layer. A thin film of 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP) with a thickness of 10 nm was subsequently vapor deposited on the dendrimer as a hole blocking material to confine exciton recombination and limit the loss of the faster moving holes to the cathode.[29,30]

This was followed by the sequential deposition of a 40 nm electron injection layer of tris(8-hydroxyquinoline) aluminum (Alq_3)[31] and a LiF(1 nm)/Al electrode sequentially. We found that the EL device with BCP/Alq_3 layers were much more efficient than those without these layers. We prepared two devices using the dendrimer only (sample I) and dendrimer with 70 wt% PTZ dendron (sample II).

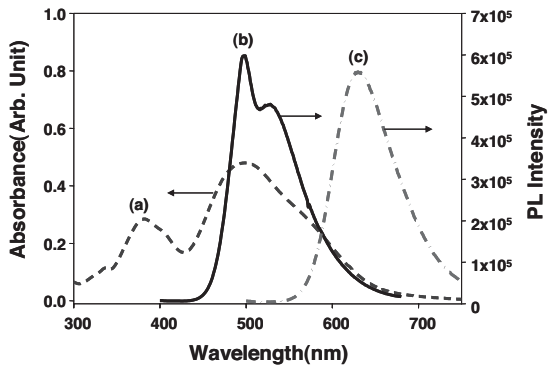


Figure 1.
(a) UV-vis absorption spectrum of 2. (b) and (c) are PL spectra of 1 and 3 in film states.

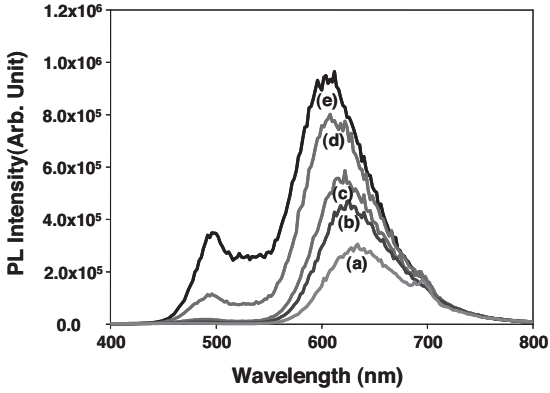


Figure 2.
PL spectra of the dendrimer samples with the doping concentration of the PTZ dendron. (a) pristine dendrimer. (b) 50 wt% doped sample, (c) 70 wt% doped sample, (d) 90 wt% doped sample, (e) 95 wt% doped sample.

Figure 3 shows the EL emission spectra of the devices with the sample I and sample II at a fixed bias voltage. The EL spectrum of the sample I is quite similar to the PL spectrum suggesting that the same excited-state species is responsible for both the PL and EL emissions.

At a fixed bias voltage, the characteristic red emissions of the samples I and II with a maximum EL emission at 630 and 618 nm are observed, respectively. A characteristic feature of the EL spectra of the sample I is that no leakage of holes into the BCP and Alq_3 layers diminishes the blue/green emission. This indicates that the exciton recombination zone is located in the emitting dendrimer layer. BCP is crucial for confining the charge recombination in the emissive layer of the dendrimer and preventing from undesired emissions from Alq_3. On the contrary, the EL spectrum of the sample II displays a shifted emission at 618 nm and weak emission around 500 nm at which the PTZ dendron has PL emission. It means that excitation energy is not transferred to the core perfectly and self-decay from the singlet state occurs.

When the EL spectrum was converted into chromaticity coordinates on the CIE 1931 diagram, a highly saturated red

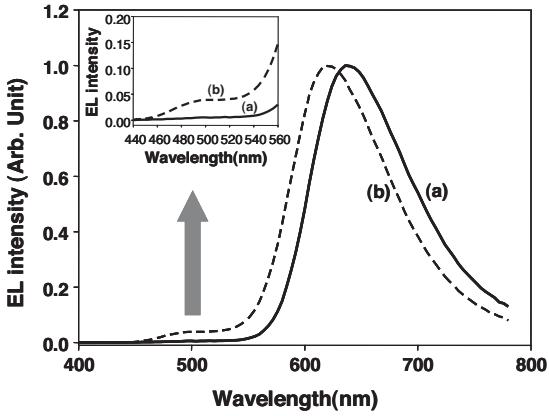


Figure 3.
EL spectra of multi-layered devices. (a) dendrimer only, (b) dendrimer with 70 wt% of PTZ dendron.

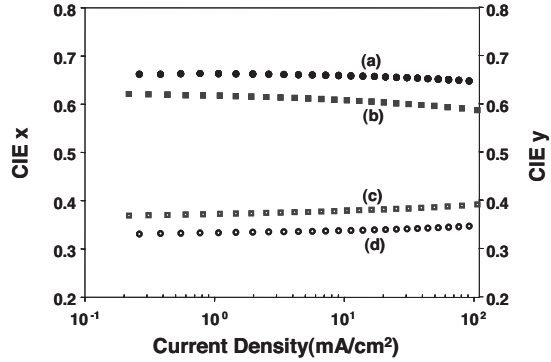


Figure 4.
Stability of the chromaticity depicted by CIE coordinates. (a) x, sample I; (b) x, sample II; (c) y, sample II, (d) y, sample I.

emission from 3 was obtained ($x = 0.64$, $y = 0.34$), which is almost consistent with the National Television System Committee (NTSC) standard for red color ($x = 0.67$, $y = 0.33$). The coordinates of the dendrimer, 3 with 70wt% of PTZ dendron, which displays orange-red emissions are $x = 0.63$ and $y = 0.36$ in a low current density range. In Figure 4, the stability of chromaticity was measured with the current density. The pure dendrimer device showed much better persistency in the chromaticity.

The current-voltage and luminance-voltage curves of the dendrimer samples (I and II) are shown in Figure 5. The turn-on voltages (electric fields) of the two LEDs were in the range of 11.4–11.7 V (2.28–2.34 MV/cm). The multi-layered devices showed a luminance of 210 cd/m^2 at 321 mA/cm^2 (11.7 V) for the sample I and 295 cd/m^2 at 246 mA/cm^2 (11.4 V) for the sample II. Higher luminance in the sample II is expected from the enhanced PL behavior. It can be conjectured that it is

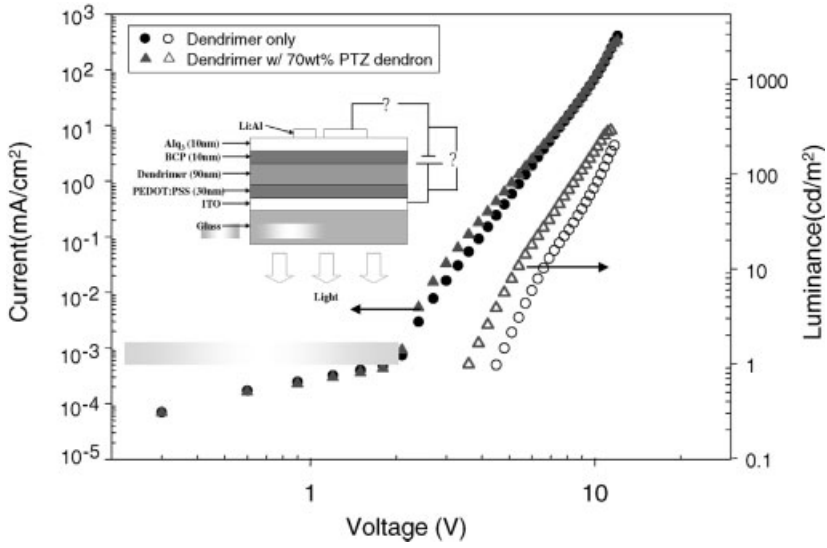


Figure 5.
Dependence of current density and luminance on the applied voltage, *sample: (a) sample I (circle), (b) sample II (triangle).

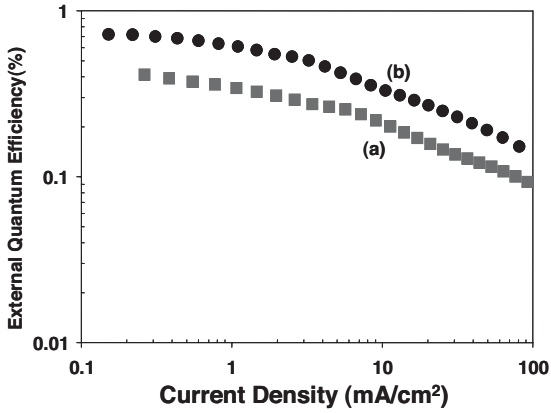


Figure 6.
Dependence of external quantum efficiency on the current density. *sample: (a) sample I (square), (b) sample II (circle).

due to high density of exciton formation and more efficient energy transfer from the more light harvesting moiety to the core.

External quantum efficiency of EL devices were determined to be 0.41% (at 0.26 mA/cm^2) and 0.79% (at 0.15 mA/cm^2) for the sample I and II, respectively. (see Figure 6) It should be noted that the sample II clearly showed a higher efficiency unequivocally at a relatively lower current density. In a higher electric field, a quenching effect was induced that was observed to reduce the efficiency.

Conclusion

We have described the properties of a new PTZ branched dendrimer bearing a red emitting moiety as a core. Although the dendrimers displayed simultaneous PL emissions at 500 and 580 nm for 3 from both structural components in a chloroform solution, they exhibited quite a significant suppression of the PL intensity from the PTZ dendron in the solid state.

When we fabricate multi-layered devices by inserting a thin layer of electron injecting Alq_3 layer and hole blocking BCP layer between the emitting dendrimer layer and the cathode, we observe a significant improvement in the EL efficiencies. Doping the PTZ dendron ito the dendrimer induces higher luminance and quantum efficiency than that of the dendrimer device.

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