White Light Electroluminescence from a Dendritic Europium Complex

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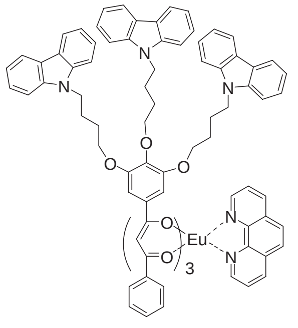
A novel dendritic europium complex Eu(TCPD)$_3$(Phen) with carbazole units as the periphery has been prepared and the device ITO//NPB//CBP:Eu(TCPD)$_3$(Phen)//BCP//Mg:Ag gave out white light with the CIE coordinate (0.333, 0.348) at 16.2 V and maximum external quantum efficiency of 1.1%.

White electrophosphorescent light device (EPhLED) is interesting for applications in planar displays and lighting devices.[1] The luminescence of lanthanide(III) complexes is unique in their high color purity, long lifetimes, and insensitivity to environmental quenching. These advantages have attracted considerable efforts in the development of luminescent materials.[2] To date, the most often reported approach to generate white EPhLED relying on combination of several emitting organic molecules to fully span the entire visible spectrum has the inherent defects.[1,3] Firstly, different efficiencies of energy transfer to each dopant in the mixture are leading to an imbalance in white color with brightness. Secondly, white light-emitting devices based on multiple independent emitters have to face the color variety throughout the life of the device due to differential aging of different components.[1] Specially speaking, white electroluminescent spectra using triplet excimers to make up for green and red bands are very broad and strongly dependent on the concentration of dopants.[3]

Nowadays, researches on dendrimers are very fashionable for designing solution-processable emitters.[4] In comparison with dendritic iridium complexes,[4a,4b] the research over europium dendrimers is in shortage except several dendritic europium complexes limited to simple non-functional peripheries.[5] Moreover, little work was done about white light EPhLED made from dendritic europium complexes with functionalized dendrons.

In this letter, we synthesized a novel dendritic europium complex Eu(TCPD)$_3$(Phen)[6] (shown in Scheme 1), and a device ITO//NPB//CBP:Eu(TCPD)$_3$(Phen)//BCP//Mg:Ag was fabricated. With carbazole units assembled around europium ions to "communicate" via an energy transfer interaction to form a light-harvesting antenna, Eu(TCPD)$_3$(Phen) emitted a brighter pure red photoluminescence, and the corresponding device emitted white electrophosphorescent light. In our design, the phenanthroline ligand was incorporated to enhance the electron transport of the material, and three carbazole fragments were appended to the diketonate ligand with intention of improving hole transport ability. Meanwhile, carbazole units are the source for blue and green emission by forming exciplex with CBP and β-diketonate, respectively. Also, it could adjust the HOMO and LUMO of the ligand TCPD and Eu(TCPD)$_3$(Phen) to match NPB (N,N'-bis(1-naphthyl)-N,N'-diphenyl-1,1$'$-biphenyl-4,4$'$-diamine) with less energy gap favorable to the injection of holes from NPB to the emitting layer.



Scheme 1. Chemical structure of Eu(TCPD)$_3$(Phen).

Eu(TCPD)$_3$(Phen) excited at 360 nm in THF shows a sharp characteristic emission at 615 nm with a full width at half maximum (FWHM) of 7 nm (Figure 1) and lifetime of 137 µs,[6] in addition to other four shoulders. All the five peaks at 586, 591, 615, 651, and 702 nm are exhibited corresponding to $^5D_0 \rightarrow {}^7F_j$ ($j = 0$–4) transitions, respectively.[7] As seen in Figure 1 (curve d), the luminescence of ligand TCPD consists of the blue band, which might be contributed from the emission of carbazole units due to the similar spectrum profile at the same region (curve b in Figure 1), and the green emission band of the exciplex formed between TCPD. Compared to PL spectrum of carbazole (curve b), trace emission coming from carbazole units linked to Eu(TCPD)$_3$(Phen) is observed because the luminescence of carbazole units is strongly quenched due to its large overlap with the absorption of Eu(TCPD)$_3$(Phen) (curve a), which indicates an efficient singlet-singlet Förster-type energy transfer in the complex. The photoluminescence efficiencies of Eu(TCPD)$_3$(Phen) in CH_2Cl_2 and powder film are 1.4 folds higher than that of relative parent Eu(III) complex without carbazole dendron.

Figure 2 shows the current density–voltage–luminance characteristics of the device with Eu(TCPD)$_3$(Phen) doping concentration of 2.5 wt % in CBP (4,4$'$-N,N'-dicarbazole biphenyl). EL spectrum of the device is shown in the inset. Notably, the device gave a white emission with three peaks at 487, 563, and 610 nm, and the CIE coordinate of (0.333, 0.348) at the applied voltage 16.2 V (Figure S3 in Supporting Information). With the increase of driving voltage, the color of the emission was changed towards the pure white color. In addition to an original red peak from the europium complex at 610 nm, the band at 400–530 nm likely arises from the exciplex or excimer between CBP and carbazole which is well-coincided with the blue region of the PL spectrum of CBP film doped with Eu(TCPD)$_3$(Phen) (2.5 wt %) (curve f). The ligand of TCPD emitting green light in solution or film should be responsible for the emission band at 530–580 nm.

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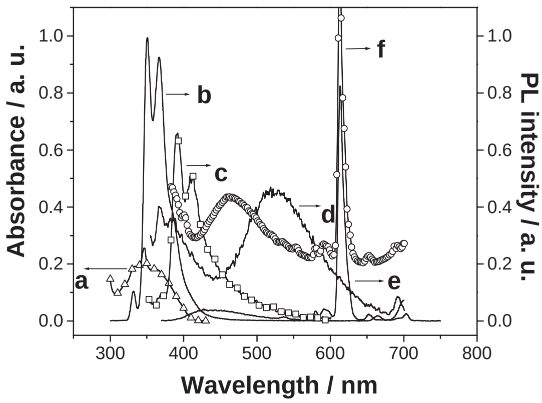

Figure 1. Absorption in THF of (a) Eu(TCPD)$_3$(Phen) (2×10^{-5} mol/L). PL of (b) Carbazole (2×10^{-6} mol/L), (c) BPPD (2×10^{-5} mol/L), (d) TCPD (2×10^{-5} mol/L), (e) Eu(TCPD)$_3$(Phen) (2×10^{-5} mol/L), and (f) CBP film doped with Eu(TCPD)$_3$(Phen) (2.5 wt %). Notice: Curve f is offset for clarity.

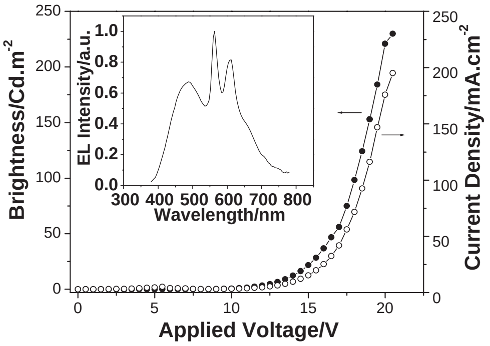

Figure 2. Current density–voltage–luminance curves of ITO//NPB(50 nm)//CBP:Eu(TCPD)$_3$(Phen)(60 nm)//BCP(50 nm)//Mg:Ag(80 nm).

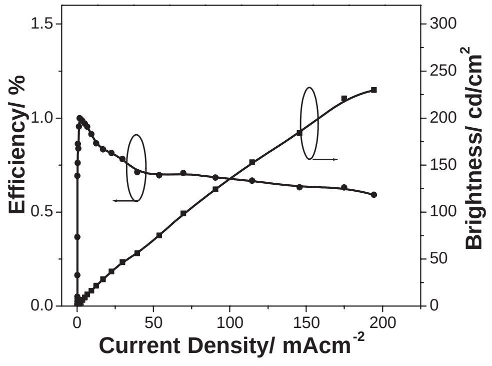

Figure 3. EL efficiencies as a function of current density of ITO//NPB(50 nm)//CBP:Eu(TCPD)$_3$(Phen)(60 nm)//BCP(50 nm)Mg:Ag(80 nm).

The luminance drastically increased with the increasing current density (Figure 3). It was very pleasant to find that the external quantum efficiency was relatively high and decreased rather slowly when the current density was over 50 mA/cm^2. When the current density reached 100 mA/cm^2, the efficiency still kept more than 0.7% and was prior to the white light-emitting devices reported previously.[8] The external quantum efficiency reached 1.1% with a luminance of 3.4 cd/m^2 and a current density of 1.7 mA/cm^2 at 10.5 V. A maximum luminance of 229 cd/m^2 was achieved at 20.5 V and 194 mA/cm^2 with an onset driving voltage near 10 V.

In summary, a novel dendritic europium complex Eu(TCPD)$_3$(Phen) was synthesized with a periphery of carbazole units. With the light-harvesting and energy-transferring ability of the periphery, Eu(TCPD)$_3$(Phen) emitted brighter pure red luminescence in CH_2Cl_2. The device fabricated with Eu(TCPD)$_3$(Phen) emitted white light with the CIE coordinate of (0.333, 0.348) and maximum external quantum efficiency 1.1%.

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