Near-infrared electroluminescent diodes based on copper hexadecafluorophthalocyanine CuPcF$_{16}$

Zhaoqi Fan (范昭奇)[1]*, Chuanhui Cheng (程传辉)[1,2], Shukun Yu (于书坤)[2],

Kaiqi Ye (叶开其)[3], Daocheng Xia (夏道成)[1], Qinglong Bai (白青龙)[1],

Hesong Guan (管和松)[2], and Guotong Du (杜国同)[1,2]**

[1]*School of Physics and Optoelectronic Technology, Dalian University of Technology,*

Dalian 116023, China

[2]*State Key Laboratory of Integrated Optoelectronics, College of Electronic Science*

and Engineering, Jilin University, Changchun 130012, China

[3]*Key Lab of Supramolecular Structure and Materials, College of Chemistry, Jilin University,*

Changchun 130012, China

**E-mail: zhaoqijlu@yahoo.com.cn; ****e-mail: dugt@dlut.edu.cn*

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We demonstrate the near-infrared (NIR) organic light-emitting devices (OLEDs) based on copper hexadecafluorophthalocyanine (CuPcF$_{16}$) doped into 2,2,2"-(1,3,5-benzenetriyl)tris-[1-phenyl-1H-benzimidazole] (TPBI). The device structure is ITO/ NPB/ TPBI:CuPcF$_{16}$/BCP/Alq$_3$/Al. Room-temperature electroluminescence is observed at about 1106 nm due to transitions from the first excited triplet state to the ground state (T_1-S_0) of CuPcF$_{16}$. The result indicates that Förster and Dexter energy transfers play a minor role in these devices, while the direct charge trapping is the dominant mechanism. The absorption spectra of CuPcF$_{16}$ solution in pyridine and vacuum sublimed films on quartz have also been investigated.

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Organic light-emitting diodes (OLEDs) emitting visible light have been investigated considerably since the initial work by Tang *et al.*[1−5] Recently, there has been a growing interest in OLEDs that emit in the near-infrared (NIR) region (700−2500 nm)[6−13]. Highly efficient NIR OLEDs have been fabricated based on noble metal complexes (Pt complexes[6,7]). However, the emission wavelengths of these NIR OLEDs are not very long (700−800 nm) and still far from the 1.33- and 1.55-μm regions usually used in telecommunications. To date, attempts at achieving the materials emitting at wavelengths longer than 1 μm have been focused on organic complexes with trivalent rare earth ions (such as Er^{3+}[8,9], Tm^{3+}[10], Pr^{3+}[11]). Only a few organic materials containing no rare earth ions display electroluminescence (EL) characteristic at wavelengths longer than 1 μm[12,13]. We have reported NIR OLEDs emitting near 1.1 μm based on copper phthalocyanine (CuPc)[13]. Metal hexadecafluorophthalocyanines (MePcF$_{16}$) have also received a great deal of attention due to their interesting electron-transporting characteristics[14].

Copper hexadecafluorophthalocyanine (CuPcF$_{16}$) is n-conducting with high electron mobility ($\sim$0.03 cm^2/(V· s)) and also relatively stable[14]. This suggests that CuPcF$_{16}$ is practically useful to fabricate organic bipolar devices such as EL diodes. In this letter, the electrophosphorescence of CuPcF$_{16}$ peaking at about 1106 nm is observed at room temperature. The NIR OLEDs are fabricated by using CuPcF$_{16}$ doped into 2,2,2"-(1,3,5-benzenetriyl)tris-[1-phenyl-1H-benzimidazole] (TPBI). The emission band at NIR region is broader than that of the rare earth complexes with f-f inner core electron transitions[8,15]. Therefore, the NIR

OLEDs based on CuPcF$_{16}$ are much better for the broadband optical communication, NIR light sources, etc.

CuPcF$_{16}$ (80%, Aldrich) was purchased and further purified by vacuum sublimation before use. All the other materials (N,N'-di-1-naphthyl-N,N'-diphenylbenzidine (NPB), tris-(8-hydroxyquinoline) aluminum (Alq$_3$), 2,9-dimethyl-4,7diphenyl-1,10-phenanthroline(BCP), and TPBI) were also obtained commercially and used without further purification. Organic layers were deposited by vacuum ($< 1\times10^{-3}$ Pa) thermal evaporation onto a clean glass substrate precoated with an indium tin oxide (ITO) layer with a sheet resistance of $\sim$ 20 Ω/$\square$. A 30-nm-thick film of NPB served as the hole-transport layer. Next, a 40-nm-thick CuPcF$_{16}$-doped TPBI (0−15 wt.-%) layer was deposited as the light-emitting layer. A 20-nm-thick BCP layer was deposited as hole-blocking layer. A 20-nm-thick layer of Alq$_3$ was used to transport and inject electrons. Finally, a shadow mask comprising 3 × 3 (mm) openings was used to define the 120-nm-thick Al cathode. Absorption spectra were taken on a UV-3600 recording spectrophotometer (Shimadzu, Japan). Current versus voltage (I-V) measurements were obtained using a Keithley 2400 current-voltage source. The NIR EL signals were focused into a monochromator and detected with a liquid-nitrogen-cooled Ge detector, using standard lock-in techniques.

The absorption spectra of CuPcF$_{16}$ solution in pyridine and films on quartz (100 nm in thickness) are shown in Fig. 1. The absorption maxima for the Q band were observed at 679 nm with shoulders at 647 and 614 nm for solution. In the case of films, the absorption peaks at 651 and 793 nm corresponded to the Q band. According to the molecular exciton theory[16], the red shift of the
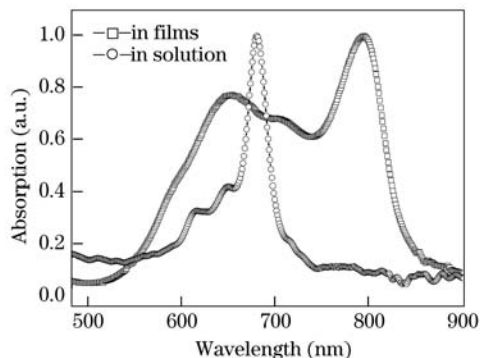
Fig. 1. Normalized absorption spectra of $CuPcF_{16}$ solution in pyridine and films on quartz substrate.

Q band in $CuPcF_{16}$ films (at 793 nm) compared with $CuPcF_{16}$ solution pointed to the edge-to-edge interaction between neighboring molecules.

Figure 2 shows the NIR EL spectra of OLEDs based on $CuPcF_{16}$ with different concentrations in TPBI at 10 mA at room temperature. As can be seen, the EL band with a peak at about 1106 nm extends to about 1400 nm. The emission was considered to be phosphorescence due to transitions from the first excited triplet state to the singlet ground state (T_1-S_0). In $CuPcF_{16}$ with large spin-orbit coupling, the strong inter-system crossing induced the phosphorescence. The inset shows the dependence of the intensity of $CuPcF_{16}$ emission at about 1106 nm on the $CuPcF_{16}$ concentration in TPBI. When the concentration of $CuPcF_{16}$ is higher than 5 wt.-%, the intensity of the emission decreases with the increasing doping concentration. The reason could be that the effect of triplet-triplet quenching becomes significant at higher concentration. The optimum concentration is 5 wt.-% and the external quantum efficiency of the device with this concentration is estimated to be between 1×10^{-4}% and 1×10^{-3}%. We have reported the EL emissions from $CuPc$[13], H_2Pc[17], and $ClInPc$[18] before. In the case of H_2Pc, the emissions were from H_2Pc monomers and aggregates. The emission wavelengths were shorter than 1 μm. In the case of $ClInPc$, the emission around 0.88 μm was molecular fluorescence due to transitions from the first excited singlet state to the ground state. In the case of $CuPc$ and $CuPcF_{16}$, the emission wavelengths were longer than 1 μm. These emissions were attributed to be molecular phosphorescence due to transitions from the first excited triplet state to the ground state.
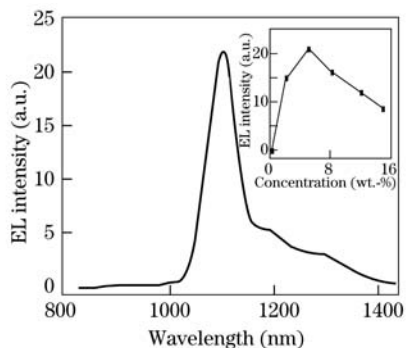
In phosphorescent heavy-metal complexes (such as CuPc and $CuPcF_{16}$) with large spin-orbit coupling, the strong inter-system coupling induced the phosphorescence. The fluorescent materials can only use singlet excitons, while the phosphorescent materials can use both singlet and triplet excitons. Highly efficient NIR OLEDs have been fabricated based on phosphorescent materials[6].

There were two possible ways for electrically exciting the guest ($CuPcF_{16}$) in the doped OLEDs: the energy transfer from host (TPBI) excited state and the sequential electron and hole capturing by $CuPcF_{16}$. In energy-transfer processes, the electrons and holes were firstly injected into the organic host material, producing either a singlet or a triplet exciton, and then the excitation was transferred to $CuPcF_{16}$ by Försteror Dexter process, respectively. In the charge trapping process, the guest ($CuPcF_{16}$) functioned as a recombination center for holes and electrons injected from anode (ITO) and cathode (Al), respectively, leading to the formation of a phosphorescent excitation.

The inset of Fig. 3. shows the energy band diagram of the $CuPcF_{16}$-doped TPBI-based OLEDs. The highest occupied molecular orbit (HOMO) and lowest unoccupied molecular orbit (LUMO) of $CuPcF_{16}$ are -5.9 and -4.6 eV, respectively, just falling within the band gap of TPBI. Therefore, the $CuPcF_{16}$ could function as both a hole trap and an electron trap. This implies that direct charge trapping plays an important role in the emission mechanism in these devices. Thus, it is proposed
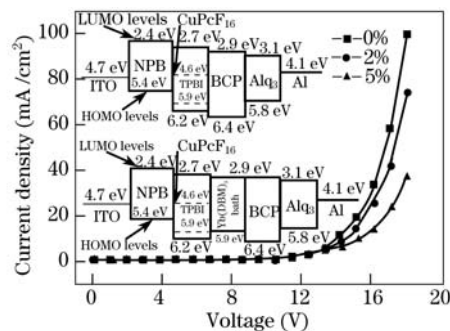

Fig. 3. Current density versus voltage for devices with the structure of ITO/NPB/TPBI:$CuPcF_{16}$/BCP/Alq_3/Al with different $CuPcF_{16}$ concentrations in TPBI. Inset: proposed energy level diagram of the devices based on $CuPcF_{16}$.
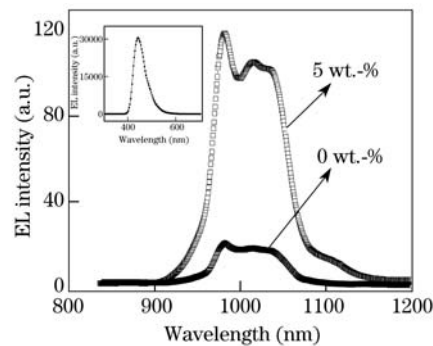

Fig. 4. NIR EL spectra of devices with the structure of ITO/NPB/TPBI:$CuPcF_{16}$/Yb(DBM)$_3$ bath/BCP/Alq_3/Al with different $CuPcF_{16}$ concentrations in TPBI. Inset: UV-vis EL spectrum of the undoped device with the structure of ITO/NPB/TPBI/BCP/Alq_3/Al.

Fig. 2. NIR EL spectra of devices based on $CuPcF_{16}$ doped into TPBI. Inset: NIR EL intensity versus concentration of $CuPcF_{16}$ in TPBI.

that the formation of the excited state occurs directly on $CuPcF_{16}$ by trapping holes injected from NPB and electrons injected from BCP. In order to confirm this, we fabricated the devices with the structure of ITO/NPB (30 nm)/TPBI:$CuPcF_{16}$ (x wt.-%, 40 nm)/Yb(DBM)$_3$ bath (30 nm)/BCP (20 nm)/Alq$_3$ (20 nm)/Al. Here, x (0 or 5) means the concentration of $CuPcF_{16}$ in TPBI. Figure 4 shows the NIR EL spectra of these devices. As can be seen, the NIR emission peaks at about 980, 1012, and 1038 nm are attributed to the $^2F_{5/2} \rightarrow ^2F_{7/2}$ transition of Yb^{3+} ion of Yb(DBM)$_3$ bath[15]. It is noted that the intensity of the NIR emission in the OLEDs with 5 wt.-% concentration of $CuPcF_{16}$ is increased by about 6 times compared with that of the OLEDs with 0 wt.-% concentration of $CuPcF_{16}$. This implies that carrier recombination effectively occurred at Yb(DBM)$_3$ bath layer in the OLEDs with 5 wt.-% $CuPcF_{16}$. The inset of Fig. 3 also shows the energy band diagram of these devices. When the concentration of $CuPcF_{16}$ is 0 wt.-%, the hole injection from NPB to TPBI is nearly prevented because of the energy difference between the HOMO levels of NPB and TPBI ($\sim$0.8 eV). Therefore, very few holes are transported to the Yb(DBM)$_3$ bath. When the concentration of $CuPcF_{16}$ is 5 wt.-%, most holes from NPB are directly trapped at $CuPcF_{16}$ and then transported to the Yb(DBM)$_3$ bath by hopping process rapidly. Therefore, the intensity of the emission from Yb(DBM)$_3$ bath is increased by about 6 times compare with that of undoped device and the emission at about 1106 nm from $CuPcF_{16}$ is very weak. If there is no Yb(DBM)$_3$ bath layer, most holes would be trapped at $CuPcF_{16}$ because the HOMO level of BCP located below the HOMO level of TPBI. These holes recombine with electrons trapped at $CuPcF_{16}$, leading to the formation of $CuPcF_{16}$ in an electronically excited state. So it is concluded that direct charge trapping plays an important role in the emission mechanism in the devices with the structure of ITO/NPB/TPBI:$CuPcF_{16}$/BCP/Alq$_3$/Al. The inset of Fig. 4 shows the ultraviolet-visible (UV-vis) EL spectrum of the undoped device with the structure of ITO/NPB/TPBI/BCP/Alq$_3$/Al. As can be seen, the blue emission at about 438 nm comes from NPB and there is nearly no emission at about 380 nm from TPBI. This indicates that very little exciton formation occurs on TPBI molecules. That is to say, very few TPBI molecules are excited, and thus energy transfer from TPBI to $CuPcF_{16}$ is very little. The results suggest that Förster and Dexter energy transfers play a minor role in these devices, and direct charge trapping is the dominant mechanism. In the current density versus voltage characteristics of the doped devices shown in Fig. 3, the increase of the device driving voltages with the $CuPcF_{16}$ concentration is the evidence of charge trapping mechanism on the $CuPcF_{16}$ molecules.

In summary, the NIR OLEDs based on $CuPcF_{16}$ doped into TPBI were fabricated. The emission at about 1106 nm corresponded to the phosphorescence of $CuPcF_{16}$ (T_1-S_0 transition). Förster and Dexter energy transfers play a minor role in these devices and direct charge trapping is the dominant mechanism.

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