Sensitized electrophosphorescence of infrared emission diode based on copper phthalocyanine by an ytterbium complex

Fei Yan, Wen Lian Li, Bei Chu, Tian Le Li, Wen Ming Su et al.

Related Articles

Degradation induced decrease of the radiative quantum efficiency in organic light-emitting diodes
APL: Org. Electron. Photonics 5, 199 (2012)

Degradation induced decrease of the radiative quantum efficiency in organic light-emitting diodes
Appl. Phys. Lett. 101, 103301 (2012)

High-efficiency organic light-emitting diodes utilizing thermally activated delayed fluorescence from triazine-based donor–acceptor hybrid molecules
Appl. Phys. Lett. 101, 093306 (2012)

High-efficiency organic light-emitting diodes utilizing thermally activated delayed fluorescence from triazine-based donor–acceptor hybrid molecules
APL: Org. Electron. Photonics 5, 198 (2012)

Magnetic-field dependent differential capacitance of polymer diodes
Appl. Phys. Lett. 101, 093303 (2012)

Additional information on Appl. Phys. Lett.

Journal Homepage: http://apl.aip.org/

Journal Information: http://apl.aip.org/about/about_the_journal

Top downloads: http://apl.aip.org/features/most_downloaded

Information for Authors: http://apl.aip.org/authors

Sensitized electrophosphorescence of infrared emission diode based on copper phthalocyanine by an ytterbium complex

Fei Yan, Wen Lian Li,[a),b)] Bei Chu,[a),c)] Tian Le Li, Wen Ming Su, Zi Sheng Su, Jian Zhuo Zhu, Dong Fang Yang, Guang Zhang, De Feng Bi, and Liang Liang Han
The Key Laboratory of the Excited State Processes, Chinese Academy of Sciences, 16-Dong NanHu Road, Economic Development Area, Changchun 130033, People's Republic of China and Graduate School of the Chinese Academy of Sciences, Beijing 100039, People's Republic of China

Chuan Hui Cheng, Zhao Qi Fan, Shu Kun Yu, and Guo Tong Du
National Integrated Optoelectronics Laboratory, College of Electronic Science and Engineering, Jilin University, Qianjin Street 2699, Changchun 130012, China

Taiju Tsuboi
Faculty of Engineering, Kyoto Sangyo University, Kamigamo, Kyoto 603-8555, Japan

By inserting a layer of (dibenzoylmethanato)$_3$-(bathophenanthroline)-ytterbium (Yb–C) between copper phthalocyanine (CuPc) emitting layer and electron transport layer, intense and broadband electroluminescence (EL) were achieved at 930–1300 nm spectral region in a phosphorescent EL device. The intensity and bandwidth are increased by about 50 and 4 times, respectively, compared with the EL device without Yb–C layer. The improvement in the EL intensity and band broadening were attributed to the energy transfer from Yb–C to CuPc and the overlapping of the Yb^{3+} near-infrared emission band with the CuPc emission band. © *2007 American Institute of Physics.*
[DOI: 10.1063/1.2811953]

The organic light emitting diodes (OLEDs) emitting visible light have been investigated considerably.[1–3] The electroluminescence (EL) of OLEDs at near-infrared (NIR) region also attracts increasing attention because of its applications in optical communication networks, low-cost NIR light sources, IR amplifiers, etc.[4–6] Rare-earth (RE) complexes[7–9] and noble metal complexes[10–12] (NMCs) have been studied as the NIR emitters. Of various NMC materials, copper phthalocyanine (CuPc) is a cheap heavy-metal complex and its emission band at NIR region is broader than that of the RE complexes with *f-f* inner core electron transitions. Therefore, the CuPc-based OLEDs are much better for the broadband optical communication, NIR light sources, etc.

Recently, we fabricated an EL device with CuPc doped in 4,4′-*N*,*N*′-dicarbazole-biphenyl (CBP) (called device-CBP, hereafter)[13] and observed NIR-EL band peaking at 1.1 μm. Its intensity, however, was weak and its NIR photoluminescence (PL) was not observed at room temperature (RT). The emission was assigned to relaxation from ^{3}MLCT.[14,15] On the other hand, we have observed a NIR emission at 960–1060 nm in EL spectrum that was attributed to the $^2F_{5/2} \rightarrow {}^2F_{7/2}$ transition of Yb^{3+} ion of Yb complex, (dibenzoylmethanato)$_3$-(bathophenanthroline)-ytterbium (Yb–C).[16] We compared the emission energy levels between CuPc molecule and Yb^{3+} ion, and found that the excited state $^2F_{5/2}$ (energy of $\sim 10.1 \times 10^3$ cm^{-1}) of Yb^{3+} locates above and close to the ^{3}MLCT state ($\sim 8.93 \times 10^3$ cm^{-1}) of CuPc. Therefore, it is expected that energy transfer from Yb^{3+} to CuPc leads to the enhancement of CuPc emission intensity if OLED device with CuPc and Yb–C complexes could be skillfully designed.

In this letter, we report an improvement in EL emission of CuPc-based OLED device, which was done using a new layer structure. The emitting layer (EML) of the OLED consists of two layers: (1) layer of CuPc-doped 4,7-diphenyl-1,10-phenanthroline (Bphen) and (2) layer of neat Yb–C. The two layers are attached to each other. By selecting an optimal concentration of CuPc, the NIR emission intensity was enhanced by factors of about 50 and the full width at half maximum (FWHM) of the emission band was broadened by about four times compared with the device-CBP.[13]

Yb–C was synthesized in our laboratory, while other chemicals were obtained from chemical companies. The PL and decay time of their symmetrical polycrystalline mixture with 0.1 wt % CuPc in Yb–C were measured by a spectrophotometer with a Spex 1403 photomultiplier with a boxcar averager, under excitation by a Nd doped yttrium aluminum garnet (Nd:YAG) laser at a wavelength of 532 nm. Organic films and Al cathode were deposited on indium tin oxide (ITO) glass substrate with a sheet resistance of 25 $\Omega/\square$ by thermal evaporation in vacuum chamber with a base pressure $<5.0 \times 10^{-4}$ Pa. The devices were encapsulated in drying N$_2$ atmosphere. The active area of each device is 2×3 mm^2. The EL spectra were obtained by the same method reported in Ref. 13. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels of Yb–C and Bphen were estimated from the cyclic voltammetry and absorption spectra, while the HOMO and LUMO levels of the others were obtained from literatures.[13,17,18]

Figure 1(a) shows the PL spectrum of a powder of Yb–C doped with 0.1 wt % CuPc at RT. It consists of two spectral bands of CuPc and Yb–C. The CuPc emission at 1120 nm is identical with the spectrum previously obtained at 4.2 K,[14] and the Yb–C spectrum at 985 nm from Yb^{3+} is consistent with that reported in Ref. 16. Relative emission intensity of CuPc increases with increasing doping level, as indicated in

Fig. 1(b). No emission was observed from the powder of 100% CuPc, probably by concentration quenching.

Taking into account the PL spectra of Fig. 1, we fabricated the following three kinds of OLED devices: Device I: ITO/TPD (40 nm)/Yb–C (30 nm)/TPBI (40 nm)/LiF (1 nm)/Al (150 nm); Series A: ITO/TPD (40 nm)/Bphen:CuPc(x wt %, 30 nm)/TPBI(40 nm)/LiF(1 nm)/Al(150nm); Series B: ITO/TPD (40 nm)/Bphen:CuPc(x wt % , 30 nm)/Yb–C(30 nm)/TPBI(40 nm)/LiF(1 nm)/Al(150nm). Here, x means concentration of CuPc in Bphen. TPD and TPBI denote N,N'-diphenyl-N,N'-bis (3-methylphenyl)-1,1′-biphenyl-4,4′diamine and 2,2′,2″-(1,3,5-benzenetriyl)-tri[1-phenyl-1-H-benzimidazole], respectively. Devices with various x values ($0 < x < 30$) were fabricated in both series A and B devices. Unlike the case of device-CBP, we use Bphen as host material for CuPc guest material and TPD as hole transport material. The reason why we selected Bphen as the host material is that high carrier injection and charge balance are expected because Bphen has high electron mobility (10^{-4} cm^2/V s) (Ref. 19) which is the same order as the hole mobility in TPD.[20] Series B devices, which have nondoped Yb–C layer between the Bphen:CuPc EML and TPBI electron transport layer (ETL), are fabricated since enhancement of CuPc emission intensity is expected by the energy transfer from Yb–C as mentioned already. Device I does not contain CuPc-doped Bphen layer. Besides, we also fabricated the same OLED as the device-CBP to compare the EL characteristics. We measured the intensity of EL from CuPc by changing CuPc concentration x variously in the devices series A and B. Maximum intensity was obtained at $x=10$ in series A and at $x=13$ in Series B. These optimized devices with $x=10$ and 13 in the series A and B are called devices II and III hereafter, respectively.

The CuPc EL intensity was found to enhance by about 50 and 2–3 times in devices III and II, respectively, compared with device-CBP. An example is shown in Fig. 2(a) where the EL spectra of device-III and device-CBP are shown, suggesting that Bphen is much better as the host material for CuPc guest than CBP. From Fig. 2(a), it is noted that the EL band of device III is four times broader than that of device-CBP, which is caused by the additional 950–1100 nm emission from Yb^{3+} in Yb–C layer. The EL band due to CuPc with an intense peak at 1120 nm has a sideband at the low energy which extends to 1500 nm. Like

this, it is found that device III gives the strong EL emission in wide spectral range from 910 to 1380 nm.

Figure 2(b) shows the EL spectra of devices I and II. These EL band shapes are quite similar to the bands observed in device III, indicating that the EL of device III is generated from each of CuPc and Yb–C layers. It is noted that the EL emission band of Yb–C is a little different from the PL band of Yb–C shown in Fig. 1(a). We understand its reason as follows. The $^2F_{5/2} \rightarrow {}^2F_{7/2}$ emission line shape of Yb^{3+} strongly depends on the site symmetry of Yb^{3+} ion because the Stark splitting of the $^2F_{5/2}$ and $^2F_{7/2}$ states strongly depends on the ligand field or crystal field around Yb^{3+}. The site symmetry of Yb^{3+} are quite different between Yb–C polycrystalline powder and neat Yb–C film in OLED device.

A considerable improvement was achieved in the EL intensity in device III when compared with the previous device-CBP. Several reasons are conceivable. One reason is the change of host material in the EML from CBP to Bphen with higher ET mobility. Another reason is the insertion of Yb–C layer between the CuPc EML and the TPBI ETL, which is an important factor as described below.

We replaced the Yb–C layer by other neat RE (RE:Tm, Nd, and Er)-complex materials with the same ligands in device III. The enhancement of EL intensity of CuPc, however, was not observed, showing that only the Yb complex is useful for the enhancement due to the good energy level match between the $^2F_{5/2}$ level of Yb^{3+} and the ^{3}MLCT level of CuPc.

Figures 3(a) and 3(b) show the proposed energy level diagrams of devices II and III, respectively. The LUMO level of Yb–C is lower by about 0.1 eV than that of TPBI. Therefore, the injected electrons from the cathode are easily transported into the Yb–C layer, while the interface of Bphen/Yb–C acts as a recombination zone for EL emission because Yb–C presents excellent ET ability.[21]

The LUMO level difference between Bphen and Yb–C is 0.4 eV. Such a high barrier for electrons is favorable in confining electrons in the Yb–C layer. The HOMO level difference between Bphen and TPD is 0.5 eV, while the HOMO level of CuPc locates at 0.3 eV above the HOMO level of TPD. Therefore, most holes from the TPD hole transport layer are directly trapped at CuPc and then transported to the Yb–C layer by hopping process at high bias. As a result, no EL emission appears from TPD in device III at high CuPc concentration.

As mentioned above, the direct carrier recombination at CuPc molecules is more difficult in device III than the recombination at Yb–C layer. Yb–C molecules are excited first
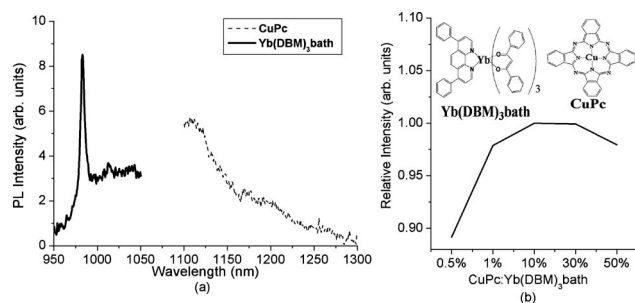

FIG. 1. The PL spectrum of a polycrystalline powder of Yb–C doped with 0.1 wt % CuPc which was excited with 532 nm Nd:YAG laser at room temperature. Since the intense 1064 nm laser line of the Nd:YAG laser overlaps in the spectrum, the spectrum is drawn after the subtraction of the 1064 nm line. (b) The dependence of intensity ratio of the 1120 nm CuPc emission to the 985 nm Yb^{3+} emission on the CuPc concentration in Yb–C powder mixed with CuPc. The inset shows the chemical structures of CuPc and Yb–C.
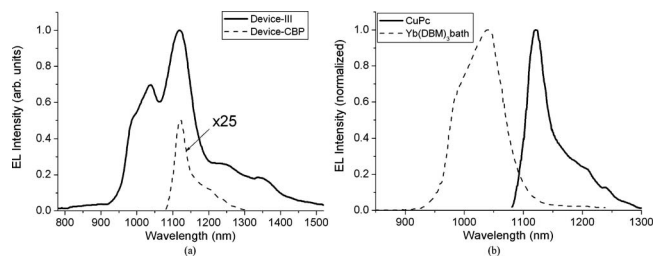

FIG. 2. (a) The EL spectra of OLED device III (upper spectrum) and device-CBP (lower spectrum). The spectrum of device-CBP is enlarged by 25 times. (b) The normalized EL spectra of OLED device I with an Yb–C EML (left) and device II with a CuPc EML (right).
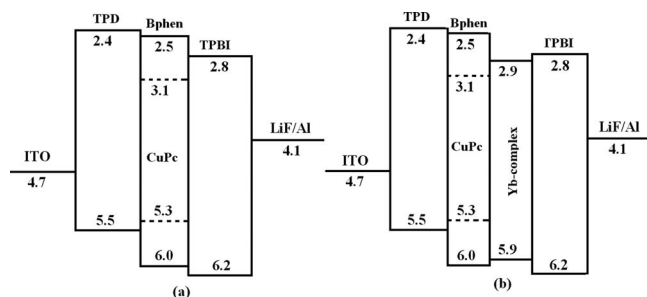
FIG. 3. Proposed energy level diagrams of (a) device II without Yb–C layer and (b) device III with Yb–C layer.

FIG. 4. Schematic energy transfer processes from Yb–C to CuPc, including the electronic transition responsible for the 985 nm Yb^{3+} emission of Yb–C and transition responsible for the 1120 nm CuPc emission. The left figure shows the excitation and the intramolecular energy transfer processes in the Yb–C.

and then its energy is transferred to CuPc molecules, leading to enhancement of EL intensity of CuPc, which is shown in Fig. 4. The excited Yb–C molecules transfer their energies of high-energy ligand triplet state (T_1) to the lower-energy $^2F_{5/2}$ level of Yb^{3+} ion, giving rise to Yb^{3+} emission. At the same time, a part of energies of the $^2F_{5/2}$ state is transferred to ^3MLCT state of CuPc. Therefore, two emission bands due to Yb^{3+} and CuPc appear simultaneously, resulting in broadband emission in a spectral range of 930–1360 nm.

The luminescence decay time was estimated as about 50 ns for CuPc (Ref. 15) and 11 μs for Yb^{3+} of Yb–C. The lifetime of the donor Yb^{3+} is much longer than that of the accepter CuPc, which restricts the back energy transfer from CuPc to Yb–C. Moreover, since the $^2F_{5/2}$ state of Yb^{3+} has such a long radiative time, the $^2F_{5/2}$ exciton would have a longer diffusion length, which makes the intermolecular energy transfer from Yb–C to CuPc possible. Taking into account that the T_1 level of Bphen locates at much higher energy than the $^2F_{5/2}$ state (see Fig. 4),[22] the sensitization occurs by the Förster energy transfer process from Yb–C to CuPc directly rather than the energy transfer from Yb^{3+} to CuPc through Bphen host indirectly.

Besides these devices, we fabricated another contrast OLED to check whether the EML structure is important to obtain high CuPc emission or not. The OLED is the same as device III except for the following points. The EML is Yb–C:CuPc in the contrast OLED while BPhen:CuPc/Yb–C in device III. Unlike the case of device III, no enhancement was observed for the CuPc EL intensity. This suggests that most carriers are trapped by CuPc molecules so the Yb–C emission becomes weak. As a result, the CuPc emission was not efficiently sensitized.

In summary, high EL intensity and broad bandwidth was obtained for 1.1 μm emission from CuPc-based device where CuPc is doped in Bphen host. The intensity and FWHM are increased by about 50 and 4 times, respectively, compared with the OLED device-CBP where CuPc is doped in CBP host and no Yb–C layer is inserted. The improvement in the EL intensity was attributed to the intermolecular energy transfer from the high energy $^2F_{5/2}$ state of Yb^{3+} in Yb–C to the ^3MLCT state of CuPc, while the broadening EL band was attributed to the overlapping of the Yb^{3+} emission band with the CuPc emission band. It is expected that the method of insertion of such a sensitizing Yb–Complex layer is not only useful for highly efficient NIR OLEDs but also
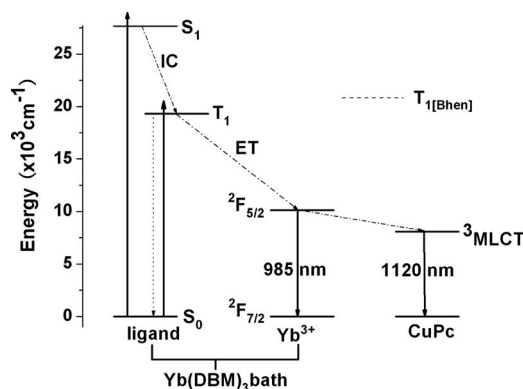
for the design of highly efficient OLED with visible emission.

[1] C. W. Tang and S. A. VanSlyke, Appl. Phys. Lett. **51**, 913 (1987).
[2] B. W. D'Andrade, J. Brooks, M. E. Thompson, and S. R. Forrest, Adv. Mater. (Weinheim, Ger.) **14**, 147 (2002).
[3] Y. R. Sun, N. C. Giebink, H. Kanno, B. Ma, M. E. Thompson, and S. R. Forrest, Nature (London) **440**, 908 (2006).
[4] H. Kajii, T. Taneda, and Y. Ohmori, Thin Solid Films **438**, 334 (2003).
[5] E. L. Williams, J. Li, and G. E. Jabbour, Appl. Phys. Lett. **89**, 083506 (2006).
[6] F. Meinardi, N. Colombi, R. Destri, W. Porzio, S. Blumstengel, M. Cerminara, and R. Tubino, Synth. Met. **137**, 959 (2003).
[7] Z. R. Hong, C. J. Liang, R. Li, F. X. Zang, D. Fan, and W. L. Li, Appl. Phys. Lett. **79**, 1942 (2001).
[8] F. X. Zang, W. L. Li, Z. R. Hong, H. Z. Wei, M. T. Li, and X. Y. Sun, Appl. Phys. Lett. **84**, 5115 (2004).
[9] R. J. Curry, W. P. Gillin, A. P. Knights, and R. Gwilliam, Appl. Phys. Lett. **77**, 2271 (2000).
[10] E. L. Williams, J. Li, and G. E. Jabbour, Appl. Phys. Lett. **89**, 083506 (2006).
[11] C. J. Yang, C. Yi, M. Xu, J. H. Wang, Y. Z. Liu, and X. C. Gao, Appl. Phys. Lett. **89**, 233506 (2006).
[12] C. Borek, K. Hanson, P. I. Djurovich, M. E. Thompson, K. Aznavour, R. Bau, Y. R. Sun, S. R. Forrest, J. Brooks, L. Michalski, and J. Brown, Angew. Chem. **119**, 1127 (2007).
[13] C. H. Cheng, Z. Q. Fan, S. K. Yu, W. H. Jiang, and X. Wang, G. T. Du, Y. C. Chang, and C. Y. Ma, Appl. Phys. Lett. **88**, 213505 (2006).
[14] K. Yoshino, M. Hikida, K. Tatsuno, K. Kaneto, and Y. Inuishi, J. Phys. Soc. Jpn. **34**, 441 (1973).
[15] P. S. Vincett, E. M. Voigt, and K. E. Rieckhoff, J. Chem. Phys. **55**, 4131 (1971).
[16] Z. R. Hong, C. J. Liang, R. G. Li, D. Zhao, D. Fan, and W. L. Li, Thin Solid Films **391**, 122 (2001).
[17] Y. Shirota, Appl. Phys. Lett. **65**, 808 (1994).
[18] J. M. Nunzi, C. R. Phys. **3**, 523 (2002).
[19] S. Naka and H. Onnagawa, Appl. Phys. Lett. **76**, 197 (2000).
[20] J. Kalinowski, N. Camaioni, P. Di Marco, V. Fattori, and A. Martelli, Appl. Phys. Lett. **72**, 513 (1998).
[21] F. X. Zang, O. Lengyel, W. L. Li, Z. R. Hong, Z. Liu, C. S. Lee, and S. T. Lee, Solid-State Electron. **50**, 1584 (2006).
[22] Q. Xin, W. L. Li, W. M. Su, T. L. Li, Z. S. Su, B. Chu, and B. Li, J. Appl. Phys. **101**, 044512 (2007).