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Infrared and visible emission from organic electroluminescent devices based on praseodymium complex

Ziruo Hong,[a] Chunjun Liang,[a] Ruigang Li,[a] Faxin Zang,[a] Di Fan,[a] and Wenlian Li[a),b)]
*Laboratory of Excited States Processes, Chinese Academy of Sciences, Changchun, 130021,
People's Republic of China*

L. S. Hung and S. T. Lee
*Department of Physics and Material Sciences, City University of Hong Kong, Hong Kong,
People's Republic of China*

Praseodymium(dibenzoylmethanato)$_3$(bathophenanthroline) [Pr(DBM)$_3$bath] was employed as an emitting and electron transport layer, and N,N′-diphenyl-N,N′-bis(3-methylphenyl)-1, 1′-biphenyl-4,4′-diamine (TPD) as a hole transport layer in organic electroluminescent (EL) devices. Bilayer device TPD/Pr(DBM)$_3$bath and trilayer devices TPD/TPD:Pr(DBM)$_3$bath/Pr(DBM)$_3$bath with a different ratio of TPD to the Pr-complex were fabricated. Emission bands at 608 nm ($^1D_2 \rightarrow {}^3H_6$), 890 nm ($^1D_2 \rightarrow {}^3F_2$), 1015 nm ($^1D_2 \rightarrow {}^3F_3$), 1065 nm ($^1D_2 \rightarrow {}^3F_4$) and 1550 nm ($^1D_2 \rightarrow {}^1G_4$) originating from the internal $f-f$ transitions of a Pr^{3+} ion were observed from EL devices using both bilayer and trilayer structures. Decreasing the ratio of TPD to the Pr-complex, the emission of the $^1D_2 \rightarrow {}^3H_6$ transition was promoted and that from the exciplex suppressed, which was explained in terms of energy transfer from the ligand to the central ion. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1391239]

Earlier photoluminescence (PL) study[1] on rare earth (RE) complexes showed that emissions of RE ions originated from the excitation of ligands. Inner $4f$ electronic transitions of RE ions demonstrate miscellaneous spectroscopic properties, emitting photons covering the spectral region from the ultraviolet to infrared (IR). The introduction of RE complexes into organic electroluminescent (EL) devices is due to its narrow-band emitting spectra for practical information display and possibly high EL quantum efficiency.[2,3] Electroluminescence from trivalent Eu-, Tb-, Tm-, and Dy complexes, including red, green, blue, and white light emissions in the visible range, has been reported in our previous work.[4–7] Meanwhile, considering the potential use for optical fiber communication and organic laser output, infrared emission from organic EL devices based on tris-(8-hydroxyquinoline)erbium (ErQ)[8,9] and Nd(DBM)$_3$bath,[10] as well as a Yb(DBM)$_3$bath,[11] has been reported recently.

There are two single electrons in the $4f$ orbital of trivalent praseodymium (Pr^{3+}) ion, giving rise to a series of divided electronic states. Luminescence of Pr^{3+} in an inorganic medium consists of these multiplets, covering ultraviolet/visible/IR wavelength range. Many studies concentrated on luminescent dynamics and other properties of Pr^{3+} in inorganic matrices for its potential and practical use for laser, light communication in silicon fiber and phosphor,[11] while little attention was cast on Pr^{3+} in organic compounds, especially in the field of organic EL. Quantum efficiency of more than 1 has been reported for Pr^{3+} lumi-

nescence when excited by 185 nm light.[12] Therefore, using a Pr complex as an emitter can be a way to improve the quantum efficiency of an EL device, even above 100%.

In this letter, we choose a praseodymium (dibenzoylmethanato)$_3$(bathophenanthroline) (Pr(DBM)$_3$ bath), which shows good carrier injection and transport properties, as an electron-transport and emissive material. EL emissions in visible and near IR range were achieved.

A Pr(DBM)$_3$bath was synthesized according to the traditional method in our laboratory.[13] N,N′-diphenyl-N, N′-bis(3-methylphenyl)-1,1′-biphenyl-4,4′-diamine (TPD) was employed as hole-transport material. A Pr$_6$O$_{11}$ (99.95%), bath, TPD, DBM, and other reagents are commercially available and used without further purification. Organic layers and Ag:Mg (1:10) alloy cathode were successively deposited onto clean indium-tin oxide glass substrate (sheet resistance ~100 Ω/□) in the same vacuum run under 1×10^{-4} Pa. The evaporation and co-evaporation rate of materials was monitored *in vacuo* with quartz crystal monitors. Made-up EL devices were hermetically sealed in nitrogen without exposure to air prior during testing. A typical emitting area for EL devices is 3×4 mm^2. The brightness measurement was performed by a 1980 A spot photometer. The near-IR (700–1700 nm) and visible (400–700 nm) spectra were measured on a modified Biorad PL-9000 FT spectrometer equipped with a liquid-nitrogen-cooled Ge detector and a Hitach-4000 fluorescence spectrophotometer, respectively.

Five types of devices were made, shown as follows: Device 1, TPD/Pr(DBM)$_3$bath, device 2, TPD/TPD: Pr(DBM)$_3$bath(10:1)/Pr(DBM)$_3$bath, device 3, TPD/TPD: Pr(DBM)$_3$bath(1:1)Pr(DBM)$_3$bath, device 4 with blurry interfaces, TPD/TPD:Pr(DBM)$_3$bath(1:3)/Pr(DBM)$_3$bath, and device 5 with clear-cut interfaces, TPD/TPD: Pr(DBM)$_3$bath(1:3)Pr(DBM)$_3$bath. The ratio values that ap-
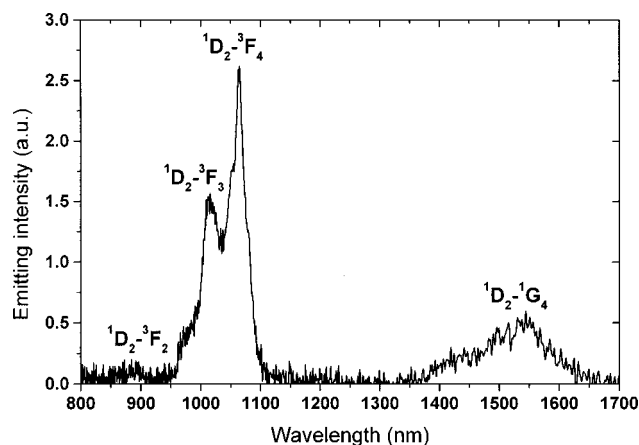

FIG. 1. IR emission spectrum of Pr^{3+} ion in EL device 4 ITO/TPD/TPD: Pr(DBM)$_3$bath(1:3)/Pr(DBM)$_3$bath/Ag:Mg at a current density of 90.5 mA/cm^2 is shown.

pear in the device structure refer to the weight ratio of the TPD:Pr complex. The thickness of TPD, TPD:Pr(DBM)$_3$bath, and Pr(DBM)$_3$bath films is 30 nm, 40 nm, and 60 nm, respectively.

For all the devices, infrared emissions consisting of three bands at about 1015 nm, 1065 nm, and 1550 nm were observed and assigned to $^1D_2 \rightarrow ^3F_3$, $^1D_2 \rightarrow ^3F_4$, and $^1D_2 \rightarrow ^1G_4$ transitions of a Pr^{3+} ion, respectively.[14] The absence of infrared emission at about 1320 nm corresponding to $^1G_4 \rightarrow ^3H_3$ indicates that the nonradiative process with phonon assistance dominates the relaxation of $^1G_4$ manifold energy levels. Therefore, emitting peaks at 1014 and 1065 nm are originated from $^1D_2$, not $^1G_4$.

It should be noted that the two blurry interfaces of the TPD/mixed layer and the mixed layer/Pr(DBM)$_3$bath are achieved by adjusting the evaporating speed of an individual material and play an important role in improving EL performance from the Pr^{3+} ion, and decreasing drive voltage. Device 5 requires higher drive voltage than device 4 to achieve the same current density. Under a fixed experimental condition, including the same current density flowing though the devices and identical positioning of the devices for spectral examination, it was verified that, with the optimization of a

device structure and fabrication, better performance could be obtained and stronger IR emission from Pr^{3+} shown in Fig. 1 was recorded for device 4 at a current density 90.5 mA/cm^2 under 12 V. $^1D_2 \rightarrow ^3F_2$ transition was also observed in this spectrum, also suggesting an improved performance of device 4. From our optimized device 4, IR emission is detectable when current density is 4.5 mA/cm^2 under 8 V. The $I-V$ curve of device 4 shown in Fig. 2 suggests good carrier injection and transport properties, although the mixed layer is inserted between the TPD and Pr-complex layers. Bilayer device 1 exhibits strong broad-band emission in the visible range and its emission in the IR range is obviously weaker than that of devices 2, 3, and 4. The effect of a clear-cut interface that increases the drive voltage of EL devices may be due to the difference between the molecular condensed states of the three organic layers during step-by-step deposition.

The visible emission spectra of EL devices with a different structure and mixed ratio of TPD:Pr complex are shown in Fig. 3. All EL devices exhibit a broad band ranging from 450 to 700 nm, which we are convinced is the exciplex emission as shown in our previous work.[15] By normalizing the emission spectra of the three devices according to the peak corresponding to the $^1D_2 \rightarrow ^3H_4$ transition of a Pr^{3+} ion, one can see that the emitting peak at 608 nm has become dominant in the visible spectra by increasing the doped ratio of the Pr complex in the mixed layer. The $^3P_0$ level located at about 21 000 cm^{-1} (Ref. 14) is a little higher than T_1 of DBM (20 500 cm^{-1}).[1] Therefore, the energy transfer from the ligand to $^3P_0$ is energetically forbidden and confirmed by the fact that only the $^1D_2 \rightarrow ^3H_4$ transition appears throughout 400–700 nm. The brightness of devices 1 and 4 at 15 V is 210 cd/m^2 and 50 cd/m^2, respectively. The exciplex emission seems brighter than that of a Pr^{3+} ion using cd/m^2 as a unit for luminescence, mainly due to the fact that human eyes are more sensitive to green light than red. Our conclusion is that the bilayer structure favors the exciplex emission and the mixed layer benefits emission from transition of Pr^{3+} ion, including both the visible and IR range. It is evident that a greater population of the $^1D_2$ state can be achieved by inserting a mixing layer of electron- and hole- transport materials.

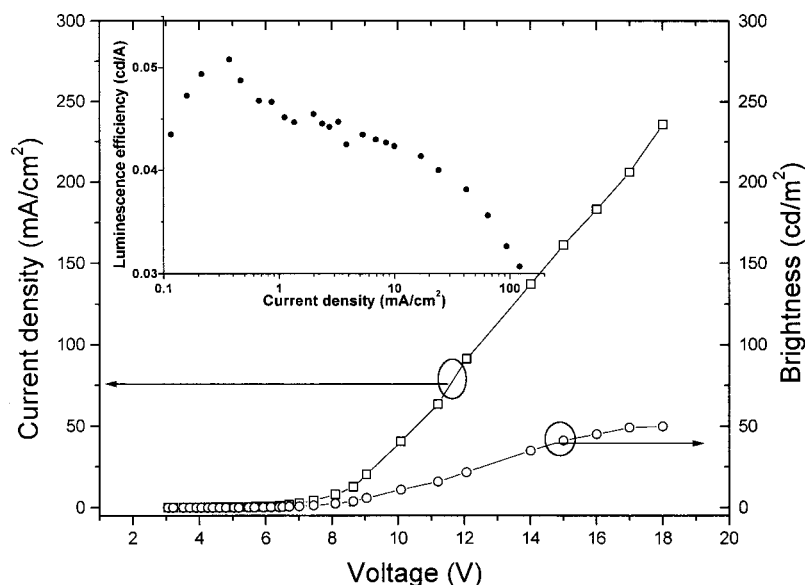FIG. 2. Current density and brightness dependence on the drive voltage of device 4, ITO/TPD/TPD: Pr(DBM)$_3$bath(1:3)/Pr(DBM)$_3$bath/Ag:Mg are shown. The inset is dependent on the visible luminescent efficiency of the current density.
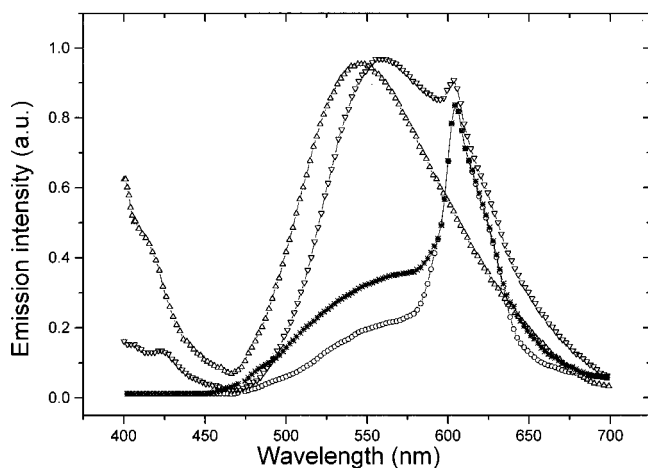
FIG. 3. Emission spectra of EL devices, device 1 TPD/Pr(DBM)$_3$bath (up triangle), device 2 TPD/TPD:Pr(DBM)$_3$bath(10:1)/Pr(DBM)$_3$bath (down triangle), device 3 TPD/TPD:Pr(DBM)$_3$bath(1:1)/Pr(DBM)$_3$bath (star), and device 4 TPD/TPD:Pr(DBM)$_3$bath(1:3)/Pr(DBM)$_3$bath (circle) in the visible range, at a drive voltage 9 V are shown.

The fact is that in the visible range, the f–f transition from a Pr^{3+} ion in a Pr(DBM)$_3$bath film, Pr-complex: TPD mixed film with different ratio, and Pr(DBM)$_3$bath powder sample under UV or blue light excitation is extremely weak. This reveals a small probability of energy transfer from the excited ligand to the central ion and/or radiative transition from the $^1D_2$ level. Strong PL and EL from the $^5D_0$ level of the europium complex with exactly the same ligands as a Pr(DBM)$_3$bath are based on a suitable energy difference between the T_1 of DBM and ^5D_J ($J=0, 1$) which enabled efficient energy transfer, and large emissive probability of $^5D_0$.[1,4] By using an Eu complex in place of Pr(DBM)$_3$bath in device 4, only the strong emission of an Eu^{3+} ion was observed.[4] A comparison between Pr(DBM)$_3$bath and Eu(DBM)$_3$bath leads to a reasonable explanation for the aforementioned results. The exciplex emission of all devices based on the TPD and Pr complex indicates invalid energy transfer from the T_1 state of DBM to the $^1D_2$ level. It may be partly ascribed to the lack of an intermediate energy level which optimizes energy transfer, like the $^5D_1$ in an Eu^{3+} ion.

The luminescent efficiency dependence on the current density of device 4 in which Pr^{3+} luminescence is predominant as shown in Fig. 3. The efficiency rises first and then drops down slightly when the current increases from 0.1 to 20 mA/cm^2 with a peak value at 0.3 mA/cm^2. A more rapid decrease occurs when the current exceeds 20 mA/cm^2, which may be due to the unstable nature of a RE(DBM)$_3$bath.[4] This result is quite different compared to the quick reduction of Eu(TTA)$_3$phen-based EL devices in previous reports,[16] and therefore, are evidence for invalid intramolecular energy transfer. But it remains unclear that the ratio of emission intensity from the exciplex to that from a Pr^{3+} ion is almost constant when the current increases. Assuming that the energy transfer from the ligand to the central ion is the bottleneck for Pr^{3+} luminescence, the ex-

ciplex emission should have been enhanced more than the emission from the Pr^{3+} ion when the current density increases.

For devices 1 and 2, when the drive voltage increases, an emitting band at about 410 nm from TPD, similar to the PL spectrum of a TPD film, appears and the emissive color changes slightly. On the other hand, no TPD emission is observed from devices 3 and 4 under same voltage or even higher. The TPD emission from devices 1 and 2 could be due to the fact that a high exciton density in the recombination zone at a larger current density enables radiative relaxation processes through TPD. The clear-cut interface in device 1 and the low Pr complex concentration in device 2 result in a carrier accumulation and hence a high exciton density. For devices 3 and 4, the mixing layer with a thickness of 40 nm acts as a recombination and emission zone a high exciton density can be eluded. The authors propose the concept of a mixing layer here, not doping, because there is no obvious host–guest relationship between TPD and the Pr complex, and the ratio of TPD to Pr complex changes extensively.

In conclusion, a series of organic EL devices based on a Pr complex were fabricated and intensive EL emissions in the IR and visible ranges, including exciplex emission and radiative transitions of Pr^{3+} were observed. Both the IR and visible emission intensity from Pr^{3+} was improved by the introduction of a TPD-Pr(DBM)$_3$bath mixing layer and blurry interface. Strong exciplex emission was attributed to the invalid energy transfer from the ligand to the central ion. Varying the ratio of a TPD:Pr complex intensified transitions from the $^1D_2$ level to the lower ones in both the visible and IR spectra, and suppressed the exciplex emission, although the exciplex emission cannot be erased completely.

[1] G. A. Crosby, R. E. Whan, and R. M. Alire, J. Chem. Phys. **34**, 743 (1961).
[2] J. Kido, H. Hayase, K. Hongawa, K. Nagai, and K. Okuyama, Appl. Phys. Lett. **65**, 2124 (1996).
[3] J. Kido, W. Ikeda, M. Kimura, and K. Nagai, Jpn. J. Appl. Phys., Part 2 **35**, L394 (1996).
[4] C. J. Liang, D. Zhao, Z. R. Hong, D. X. Zhao, X. Y. Liu, W. L. Li, J. B. Peng, J. Q. Yu, C. S. Lee, and S. T. Lee, Appl. Phys. Lett. **76**, 67 (2000).
[5] W. L. Li, J. Q. Yu, G. Sun, Z. R. Hong, Y. Yu, Y. Zhao, J. B. Peng, and T. Tsutsui, Synth. Met. **91**, 263 (1997).
[6] Z. R. Hong, W. L. Li, D. X. Zhao, C. J. Liang, X. Y. Liu, J. B. Peng, and D. Zhao, Synth. Met. **111**, 43 (2000).
[7] Z. R. Hong, W. L. Li, D. X. Zhao, C. J. Liang, X. Y. Liu, J. B. Peng, and D. Zhao, Synth. Met. **104**, 165 (1999).
[8] R. J. Curry and W. P. Gillin, Appl. Phys. Lett. **74**, 798 (1999).
[9] R. J. Curry and W. P. Gillin, Appl. Phys. Lett. **75**, 1380 (1999).
[10] Y. Kawamura, Y. Wada, Y. Hasegawa, M. Iwamuro, T. Kitamura, and S. Yanagida, Appl. Phys. Lett. **74**, 3245 (1999).
[11] J. L. Sommerdijk, A. Bril, and A. W. De Jager, J. Lumin. **8**, 341 (1974).
[12] Y. Kawamura, Y. Wada, M. Iwamuro, T. Kitmaura, and S. Yanagida, Chem. Lett. **2000**, 280 (2000).
[13] L. R. Melby, N. J. Rose, E. Abramson, and J. C. Caris, J. Am. Chem. Soc. **86**, 5117 (1964).
[14] G. H. Dieke, *Spectra and Energy Levels of Rare Earth Ions in Crystals* (Wiley, New York, 1968); *American Institute of Physics Handbook*, 3rd ed. (McGraw–Hill, New York, 1972), pp. 7–25.
[15] C. J. Liang, D. Zhao, Z. R. Hong, R. G. Li, W. L. Li, and J. Q. Yu, Thin Solid Films **371**, 207 (2000).
[16] C. Adachi, M. A. Baldo, and S. R. Forrest, J. Appl. Phys. **87**, 8049 (2000).