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Observation of 1.5 μm photoluminescence and electroluminescence from a holmium organic complex

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Electroluminescence (EL) and photoluminescence in both the visible and near-infrared spectral range were observed from a holmium(dibenzoylmethanato)₃(bathophenanthroline) [Ho(DBM)₃bath]. Five peaks at 580 nm, 660 nm, 980 nm, 1200 nm, and 1500 nm, respectively, were attributed to the internal 4*f* electronic transitions of the Ho³⁺ ions. Except for the emissions of the Ho³⁺ ions, a broadband exciplex emission from 480 nm to 670 nm appeared in the EL cases. The emission intensity of the exciplex at organic interface showed a tendency to saturation beyond a certain driving voltage, while the emissions of the Ho³⁺ ions kept increasing. This evolution of visible EL spectra was discussed in terms of the extension of the charge recombination zone. The 1500 nm emission corresponding to the ⁵F₅→⁵I₆ transition suggests that the Ho(DBM)₃bath is a potential candidate for optical communications.

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Trivalent rare-earth (RE) complexes, which featured linelike emissions, high luminescent efficiency, and easy synthesis, have been introduced into the field of organic light-emitting diodes (OLEDs).¹ Generally, the excitation of RE ions takes place through the intramolecular energy transfer from the lowest excited triplet (*T*₁) of ligands to the 4*f* levels of RE ions. Taking advantage of participation of the triplet excitons and efficient singlet-to-triplet crossing, one may expect high electroluminescence (EL) efficiency from the RE complexes.²

Recently, much attention has been paid to OLEDs based on near-infrared (NIR) emitting materials, including semiconducting nanocrystals,³ small molecule organic materials,⁴ and RE complexes⁵ because of their practical application for polymer-based optical amplifiers and electrically pumped organic infrared devices. The NIR emissions from trivalent Nd, Yb, Er, and Pr complexes have been reported in both photoluminescence (PL) and EL cases.^{6–9} Among these infrared emissions, the 1500 nm emission was particularly attractive for its good agreement with the efficient working window of a quartz fiber. As a result, the development of materials operating at 1500 nm has become an interesting subject. Moreover, the demonstration of the 1500 nm EL emission from Er-complex-based OLEDs on a silicon substrate was reported,¹⁰ suggesting a promising way toward the silicon-integrated OLEDs in the NIR range.

The NIR emissions of Ho³⁺ ion, which resulted from transitions between the abundant energy levels below the ⁵S₂, ⁵F₄, have become an attractive subject recently.^{11,12} In this letter, we report the NIR EL and PL of a holmium(dibenzoylmethanato)₃(bathophenanthroline)

[Ho(DBM)₃bath], which consisted of three peaks at 980 nm, 1200 nm, and 1500 nm, respectively. The 1500 nm emission corresponding to the ⁵F₅→⁵I₆ transition with a considerable bandwidth indicated the potential application of Ho(DBM)₃bath for the optical communication systems.

To achieve efficient excitation of the Ho³⁺ ion and good electron injection/transporting properties,¹³ dibenzoylmethanato (DBM), which has *T*₁ (20 300 cm⁻¹) above the ⁵S₂, ⁵F₄ levels, was selected as the first ligand. Bathophenanthroline (Bphen) was employed as the second ligand for its good electron mobility.¹⁴ Raw materials including Ho₂O₃ (99.95%), Y₂O₃ (99.95%), DBM (98%), and Bphen (99%) were from Aldrich and were used without further purification. RE complexes were synthesized following the traditional method¹⁵ and used as emitting and electron-transporting materials. N,N'-diphenyl-N,N'-bis(3-methylphenyl)-1,1'-biphenyl-4,4'-diamine (TPD) was selected as the hole-transporting material. Organic films were deposited onto an indium-tin-oxide (ITO) glass substrate (100 Ω/□) successively by thermal evaporation in a vacuum chamber at 2×10⁻⁴ Pa, followed by a 150-nm-thick Mg:Ag (10:1) alloy cathode in the same vacuum run. The film thicknesses and the deposition rate were monitored by quartz oscillators. Deposition rates were ~0.2 nm/s for organic films and ~1 nm/s for the cathode. The made-up devices were encapsulated in a glove box in a dried nitrogen ambient and the typical emitting area was 3×4 mm². To measure the NIR (800–1600 nm) and visible (400–780 nm) emission spectra, a Biorad PL-9000FT spectrometer equipped with a liquid-nitrogen-cooled Ge detector and a Hitach-4000 fluorescence spectrophotometer were utilized. The absorption spectrum of 1-μm-thick Ho(DBM)₃bath film also evaporated thermally was measured with a SHIMADZU ultraviolet–visible NIR scanning spectrophotometer. For the

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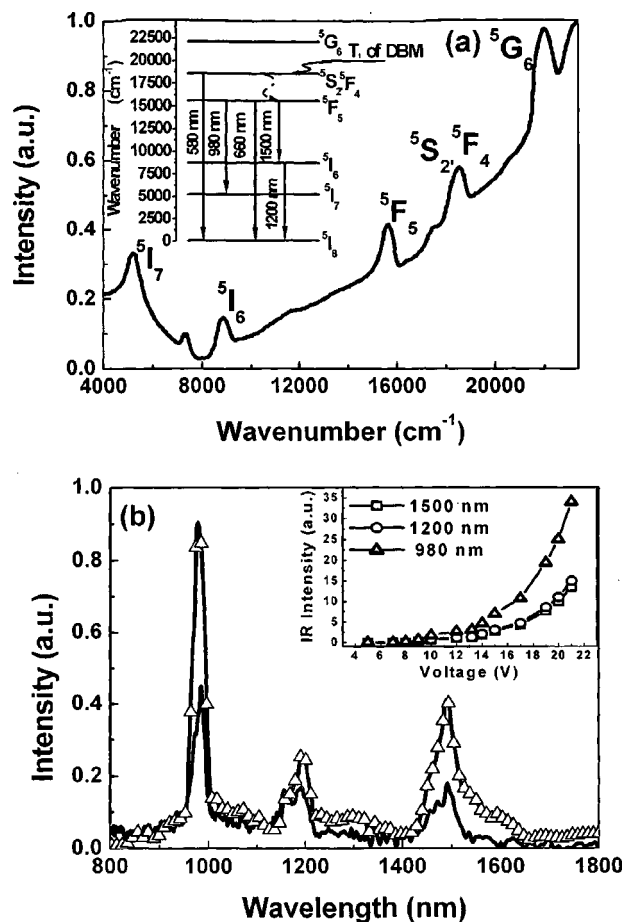


FIG. 1. (a) The absorption spectrum of Ho(DBM)₃bath film, inset of (a): The energy diagram illustrating the luminescent mechanism of Ho³⁺ ions. (b) The NIR EL spectrum (solid line) of TPD/Ho(DBM)₃bath device at 19 V and PL spectrum (up-triangle line) of Ho(DBM)₃bath film excited by the 514 nm line of Ar⁺ laser, inset of (b): The dependence of integrated intensity of NIR peaks on driving voltage.

PL measurement in the NIR range, a 514-nm Ar-ion laser with an incident energy density of 50 mW/cm² was used as the excitation source.

Figure 1(a) shows the absorption spectrum of the Ho(DBM)₃bath film. Absorption peaks corresponding to the f - f transitions of Ho³⁺ ions overlapped the absorption edge of the ligand. The energy diagram of the Ho³⁺ ion in the complex was hence determined as shown in the inset of Fig. 1(a). All energy levels of Ho³⁺ ions coincided with that in inorganic matrices.¹¹ Note that the absorption at 7000 cm⁻¹ was due to the residue O-H groups in the complex.¹⁶

In Fig. 1(b), three peaks at 980 nm, 1200 nm, and 1500 nm were observed under 514-nm-laser excitation, which were attributed to the $^5F_5 \rightarrow ^5I_7$, $^5I_6 \rightarrow ^5I_8$, and $^5F_5 \rightarrow ^5I_6$ transitions, respectively. Figure 2 presents the emission spectrum in the visible region under the same wavelength excitation. Two peaks at 580 nm [$(^5S_2, ^5F_4) \rightarrow ^5I_8$], 660 nm ($^5F_5 \rightarrow ^5I_8$) appeared. Basically, T_1 of DBM may sensitize the levels of Ho³⁺ below 20 300 cm⁻¹ via energy transfer, and the probability of energy transfer was strongly influenced by the energy difference between the energy donor and acceptor.¹⁷ Shown in the inset of Fig. 1(a) are the 5S_2 , 5F_4 , 5F_5 , 5I_6 , and 5I_7 levels populated while the $^5I_7 \rightarrow ^5I_8$ transition (>1900 nm) exceeded the measurement range of the Ge detector. Since the optimum energy difference favors efficient ligand-to-ion energy transfer, it was supposed that the

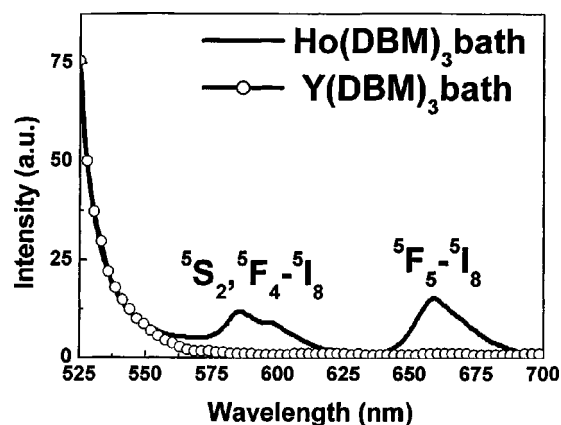


FIG. 2. The PL spectra of Ho(DBM)₃ bath and Y(DBM)₃bath films in the visible range under the 514 nm excitation.

5S_2 , 5F_4 , and 5F_5 levels were the main acceptor levels and the excited electrons on the 5F_5 and 5I_6 levels could partially come from the relaxation of the upper levels.

The NIR emissions from the device ITO/TPD (50 nm)/Ho(DBM)₃bath (50 nm)/Mg:Ag(10:1, 150 nm) were also observed. As shown in Fig. 1(b), the EL spectrum was consistent with PL, indicating that the same electronic transitions took place in both cases and that DBM only sensitized the levels below its T_1 . Integrated values of individual peaks of the NIR EL spectra versus driving voltage are plotted in the inset of Fig. 1(b). Similar to typical OLEDs, the NIR emissions were detectable at 9 V and drastically increased with increasing voltage. We noted that the spectra were voltage independent, indicating that the branching ratio of down-conversion transitions from radiative levels of the Ho³⁺ ions was not effected by the electric field and current injection. Although the full width at half maximum (FWHM) of 1500 nm emissions in the PL and EL cases was ~ 55 nm, the broadband IR emission covering the 1400–1700 nm range can be observed, providing a satisfied waveband for the wavelength division multiplexing technology in optical communications. This broad coverage should be ascribed to Stark splitting of the 5F_5 and 5I_6 levels, and further investigations are being carried out to seek a better understanding.

The visible EL spectra of the TPD/Ho(DBM)₃bath device under different biases are shown in Fig. 3. A structureless broadband (FWHM ~ 100 nm) peaking at 560 nm and a narrower peak (FWHM ~ 20 nm) at 660 nm were observed. To identify the origin of the two bands, a nonluminescent complex, Y(DBM)₃ bath, was used as comparison. The two complexes were very similar to each other in many aspects except for luminescent properties. That is, the inert electronic configuration of the Y³⁺ ion cannot be excited by the T_1 of ligands so that there is no emission from the Y³⁺ ion. According to Fig. 2, under 514 nm excitation, while the Y(DBM)₃ bath film showed no PL emission, the Ho(DBM)₃bath film exhibited two peaks (FWHM ~ 20 nm) at 580 nm and 660 nm, confirming that the two peaks should originate from the $(^5S_2, ^5F_4) \rightarrow ^5I_8$ and $^5F_5 \rightarrow ^5I_8$ transitions, respectively. On the other hand, a broadband emission with FWHM of 100 nm was observed from the TPD/Y(DBM)₃ bath device, which has been proven to be the exciplex emission at TPD/RE-complex interface.¹⁸ It was noted that the two broadband emissions from TPD/RE-complex devices

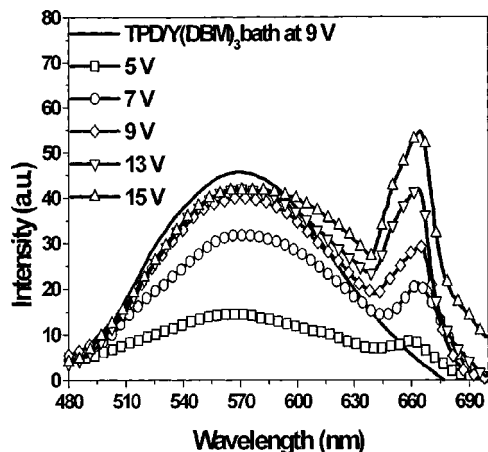


FIG. 3. The EL spectra of TPD/Ho(DBM)₃ bath device at different driving voltage and a typical EL emission of exciplex from TPD/Y(DBM)₃ bath device.

were much broader than the 580 nm PL emission of the Ho(DBM)₃bath film and almost identical to each other as shown in Fig. 3. Therefore the broadband emission at 560 nm and a sharp peak at 660 nm were attributed to the interfacial exciplex and the $^5F_5 \rightarrow ^5I_8$ transition of the Ho³⁺ ions, respectively. The absence of the $(^5S_2, ^5F_4) \rightarrow ^5I_8$ transition at 580 nm in the EL spectra could be due to its intrinsic weakness.

It was of interest that the EL spectra of TPD/Ho(DBM)₃ bath device in Fig. 3 varied; i.e., the 660 nm peak from Ho³⁺ ions grew faster than that of exciplex with increasing voltage. It should be pointed out that the series EL spectra were recorded under the same experimental condition and therefore the spectra represented the real EL intensity. As shown in Fig. 3, at a low driving voltage such as 5 V, the exciplex emission dominated the EL spectra due to a charge accumulation at TPD/Ho(DBM)₃ bath interface where charge recombination took place.¹⁸ As the bias increased, the exciplex emission tended to saturate above 9 V. Nevertheless, the 660 nm peak kept growing and became almost comparable with the exciplex beyond 13 V. This phenomenon could be attributed to the diffusion of more holes and the extension of the recombination zone into the RE-complex bulk layer.

Therefore, the Ho³⁺ emissions were enhanced.

In conclusion, the attractive 1500-nm-PL and -EL emissions were observed from the Ho(DBM)₃ bath film. The mechanism of luminescence from the complex was established and confirmed by further comparison. The broadband emission at 1500 nm of Ho complexes could be a suitable candidate for optoelectronics.

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