

The Effect of Different Neutral Ligands on Photoluminescence and Electroluminescence Properties of Ternary Terbium Complexes

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Three terbium complexes Tb(tba-PMP)₃(TPPO) (**A**), Tb(tba-PMP)₃(H₂O) (**B**), and Tb(tba-PMP)₃(Phen) (**C**) (where tba-PMP, TPPO, and Phen stand for β -diketone 1-phenyl-3-methyl-4-(*tert*-butylacetyl)-5-pyrazolone, triphenyl phosphine oxide, and 1,10-phenanthroline, respectively) with different neutral ligands were synthesized and characterized, and the mechanism of how the neutral ligands affect photoluminescence (PL) and electroluminescence (EL) properties of terbium complexes was studied. Experiments revealed neutral ligand TPPO and Phen strongly affect the terbium complex PL intensity, TPPO enhanced the PL intensity of complex **A**, while Phen reduced the PL intensity of complex **C** compared to that of complex **B**. Investigation indicated this is caused by the different excited energy levels between tba-PMP, TPPO, and Phen, which were obtained from their phosphorescence spectra measured with their corresponding gadolinium complexes Gd(tba-PMP)₃-(H₂O)(EtOH), Gd(TPPO)₂(NO₃)₃, and Gd(Phen)₂(NO₃)₃. Compared to complex **B**, the energy absorbed by TPPO can be efficiently transferred to tba-PMP and the central ion Tb³⁺ due to its excited singlet and triplet energy levels matching that of tba-PMP and the ⁵D₄ energy level of Tb³⁺, and consequently enhancing the PL intensity of **A**, while on the contrary, negative energy transfer occurred between Phen and tba-PMP or Tb³⁺ since the triplet energy level of Phen is lower than that of tba-PMP and the ⁵D₄ energy level of Tb³⁺ as well. Experimental results show terbium complex electroluminescence (EL) is greatly dependent on its PL intensity, the performance achieved based on complexes **A**, **B**, and **C** being 9540 cd/m² and 7.2 lm/W, 3230 cd/m² and 1.17 lm/W, and 690 cd/m² and 0.13 lm/W, respectively, with the power efficiency ratio **A**:**B**:**C** = 55:9:1, which was greatly enlarged compared to their PL intensity ratio **A**:**B**:**C** = 2.1:1.3:1.

Introduction

Lanthanide complexes, especially terbium and europium complexes,^{1–10} are of great interest in the field of electroluminescence (EL) because their emission is due to the electronic transitions of the central ions that give a sharp narrow spectral characteristic and 100% emission quantum efficiency.¹⁰ Recently, we reported¹¹ a new terbium complex Tb(eb-PMP)₃TPPO (eb-PMP and TPPO stand for 1-phenyl-3-methyl-4-(2-ethylbutyryl)-5-pyrazolone and triphenyl phosphine oxide, respectively), with experiments indicating that carrier transport was relatively balanced in this complex, which led to the exciton being easily confined in the emitting layer, and a performance of 8800 cd/m², 9.4 lm/W, and external quantum efficiency 21 cd/A was achieved in a device with the configuration of ITO/TPD (20 nm)/Tb(eb-PMP)₃TPPO (50 nm)/BCP (20 nm)/AlQ (30 nm)/Mg:Ag, which confirmed that a high-efficiency EL performance could be obtained from undoped lanthanide complex. However, our further experimental results¹² showed that balanced carrier injection is not the only factor that affects terbium complex EL performance, another key aspect being the complex PL intensity. Complexes with higher PL intensity will achieve higher EL efficiency when the carrier injection is well-balanced. Our results also revealed that TPPO could strengthen terbium complex PL intensity while Phen gave the negative effect.^{12,13} However, the

mechanism of how the neutral ligand affects the lanthanide complex PL intensity is still not clear, and in addition, β -diketone eb-PMP is a liquid, which not only leads to difficult purification (by chromatograph) during the synthesis of ligand, but also makes the complex melting point relatively low (159.4 °C), which is a disadvantage for practical application. In this work, a new ligand 1-phenyl-3-methyl-4-(*tert*-butylacetyl)-5-pyrazolone (tba-PMP) with a higher melting point (89–90 °C) was synthesized, which is easily purified through recrystallization with a yield higher than 80%. By using tba-PMP as an anionic ligand together with different neutral ligand, three terbium complexes Tb(tba-PMP)₃(TPPO) (**A**, mp 211.7 °C), Tb(tba-PMP)₃(H₂O) (**B**, mp 249.1 °C), and Tb(tba-PMP)₃(Phen) (**C**, mp 298.2 °C) were synthesized and their PL and EL properties are investigated and compared. By measuring the excited energy level of tba-PMP, TPPO, and Phen from the phosphorescence spectra of their corresponding gadolinium complexes Gd(tba-PMP)₃(H₂O)(EtOH), Gd(TPPO)₂(NO₃)₃, and Gd(Phen)₂(NO₃)₃, the energy transfer mechanism between different ligands and the central terbium ion is suggested, which is the reason for the different PL intensities of the three complexes.

Experimental Section

Materials. 2,9-Dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP, 98%) and *tert*-butylacetyl chloride (99%) were obtained from Acros; *N,N'*-diphenyl-*N,N'*-bis(3-methylphenyl)-1,1'-biphenyl-4,4'-diamine (TPD, 99%) was purchased from Aldrich;

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N,N'-diphenyl-*N,N'*-bis(1-naphthyl)-1,1'-diphenyl-4,4'-diamine (NPB) was kindly supplied by Technical Institute of Physics and Chemistry, Chinese Academy of Science as a gift. All were used as supplied. Tris(8-hydroxyquinolino)aluminum (AlQ) was synthesized in our lab and sublimated two times before use. Indium tin oxide (ITO) glass substrate with a sheet resistance of 15 Ω/\square was kindly supplied by China Southern Glass Holding Co. Ltd.

Apparatus. NMR spectra were recorded on a Bruker DRX300 instrument. The crystal was mounted on a glass fiber and transferred to a RIGAKU RAXIS RAPID imaging plate diffractometer with graphite-monochromatized Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å). The structure was solved by the Patterson methods (SHELXS-97) and refined by the full-matrix least-squares method, using the program SHELXL-97. TG analysis was measured on a SDT 2960 simultaneous TG-DTA (Thermal Analysis, U.S.A) under N_2 with a temperature rising rate 10 deg/min. The photoluminescence (PL) and electroluminescence (EL) spectra were measured with a Hitachi F-4500 fluorescence spectrophotometer. Luminance-voltage ($L-V$) characteristics were measured with a computer-controlled Keithley 2400 Sourceceter unit with a calibrated silicon diode. FT-IR spectra were taken on a Nicolet MAGNA-IR spectrometer. UV-visible absorption spectra were recorded with a Shimadzu 3100 UV-vis-NIR spectrophotometer. In the phosphorescence measurement, the fourth harmonic 266 nm of the pulsed GCR-4 Nd:YAG Laser (Spectra-Physics, USA) with 30 Hz repetition rate and 6 ns pulse width was used as the excitation source, which is close to the peak wavelength of the excitation band of the terbium complexes. The emission from the samples was collected by a set of focus lenses, dispersed by a Spectra-pro-500 mm focal length monochromator (ARC) with a 2400 grooves/mm grating and detected by the PD 493 photomultiplier tube (ARC). To reduce the laser scattering light, a BG-24 filter (Schott) was placed in front of the monochromator. The output of the photomultiplier was sent to the SD 2000 boxcar system (Ocean Optics) for averaging and then transferred to the computer. All the experiments are completed at room temperature.¹⁴

Synthesis of tba-PMP. 1-Phenyl-3-methyl-pyrazolone-5 (PMP) (7.5 g, 0.05 mol) was dissolved in 150 mL of dried 1,4-dioxane and the solution was heated to 70 °C under stirring for 10 min. After calcium hydroxide (9 g, 0.18 mol) and barium hydroxide (1 g, 0.03 mol) were added in small portions, *tert*-butylacetyl chloride (8 mL, 0.058 mol) was added dropwise. The resulting mixture was refluxed for 24 h. The cloudy pinkish mixture was cooled to room temperature and then poured into a stirred solution of ice-cold hydrochloric acid (350 mL of a 3 mol L^{-1} solution) and yellow product precipitated. The product was purified by recrystallization from ethanol solution and a yellow needle crystal was obtained with a yield of 80%. Mp 89–90 °C. Anal. Calcd for $C_{16}H_{20}N_2O_2$: C 70.23; H 7.38; N 10.24. Found: C 70.66; H 7.65; N 10.07. 1H NMR (200 Hz, $CDCl_3$) δ : 7.87 (2H), 7.45 (2H), 7.28 (1H), 2.62 (2H), 2.48 (3H), 1.86 (4H), 1.12 (9H).

Synthesis of Terbium Complexes. Complexes **A**, **B**, and **C** were synthesized according to the method reported previously.⁸ For complexes **A** and **B**, the reaction was carried out in ethanol solution, while for complex **C**, the solvent was a mixture of ethanol and $CHCl_3$ ((v/v) 1:1). The complexes were all purified by recrystallization from the same solvent as the reaction with a yield no less than 80%. Tb(tab-PMP)₃(TPPO) (**A**): Anal. Calcd for $C_{66}H_{72}N_6O_7PtB$: C, 63.14; H, 5.74; N, 6.70. Found: C, 63.32; H, 5.78; N, 6.76. Tb(tab-PMP)₃(H₂O) (**B**):

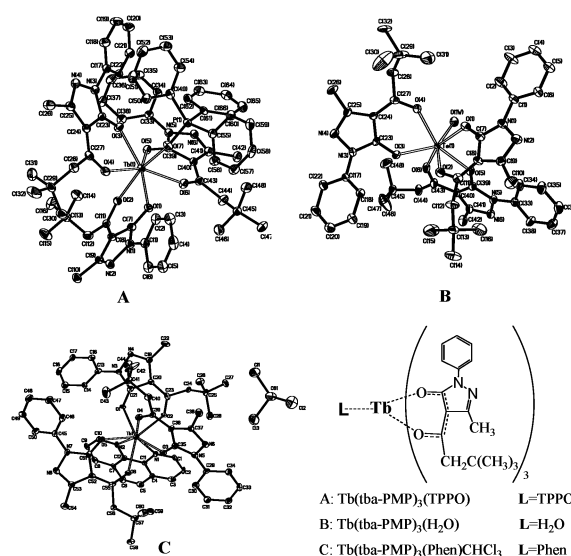


Figure 1. Chemical and crystal structures of complexes **A**, **B**, and **C**. Ellipsoids are drawn at the 30% probability level and hydrogen atoms were omitted for clarity.

Anal. Calcd for $C_{50}H_{65}N_6O_8Tb$: C, 57.91; H, 6.32; N, 8.36. Found: C, 57.47; H, 5.88; N, 8.36. Tb(tab-PMP)₃(Phen) (**C**): Anal. Calcd for $C_{61}H_{66}N_8O_6Cl_3Tb$: C, 57.53; H, 5.19; N, 8.80. Found: C, 58.01; H, 5.49; N, 8.86.

Synthesis of Gadolinium Complexes. Gadolinium complexes comprising solely neutral ligands without anionic ligands or comprising only tab-PMP ligand without neutral ligand were also synthesized for triplet energy level measurement. Gd(tba-PMP)₃(H₂O)₂: To a 50-mL ethanol solution containing 1 mmol of Gd(NO₃)₃(H₂O)₆ and 3 mmol of 1-phenyl-3-methyl-4-(*tert*-butylacetyl)-5-pyrazolone (tba-PMP) was added 3 mL of 1.0 mol L^{-1} NaOH dropwise under stirring and the solution was heated to refluxing for 5 h. The resulting solution was filtered and the colorless crystal was obtained after 2 days. The crystal was then purified by recrystallization from ethanol solution. Gd(TPPO)₂(NO₃)₃: To a 50-mL ethanol solution containing 2 mmol of TPPO was added 1 mmol of Gd(NO₃)₃(H₂O)₆ dropwise under stirring and the solution was heated to refluxing for 2 h. The resulting solution was filtered and a white powder was obtained. Gd(Phen)₂(NO₃)₃: The synthesis of Gd(phen)₂(NO₃)₃ was the same as that for complex Gd(TPPO)₂(NO₃)₃.

Results and Discussion

Crystallography. Single crystals of complexes **A** and **B** were obtained by recrystallization from their ethanol solution and complex **C** was obtained from its $CHCl_3$ solution. Complex **B** lost the ethanol molecule in the single crystal. Their chemical and crystal structures are shown in Figure 1. For complexes **A** and **B**, the central Tb(III) ions are surrounded by seven oxygen atoms, six of which are from three β -diketonates, with the other being respectively from triphenyl phosphine oxide and the water molecule; for complex **C**, the central Tb(III) ion is surrounded by six oxygen and two nitrogen atoms, respectively from β -diketonates and 1,10-phenanthroline, and in addition, there exists a $CHCl_3$ molecule in the crystal of complex **C**. The average Tb–O distance is 2.323 (range 2.281(2)–2.399(4) Å), 2.255 (range 2.282(4)–2.404(4) Å), and 2.341 Å (range 2.287(4)–2.396(4) Å) for complexes **A**, **B**, and **C**, respectively, which is reasonable and coincides with the standard bond length for different coordination numbers in terbium complexes.¹⁵

TG Analysis. The TG curves of complexes **A**, **B**, and **C** are shown in Figure 2. It is clear that complex **A** is very stable at

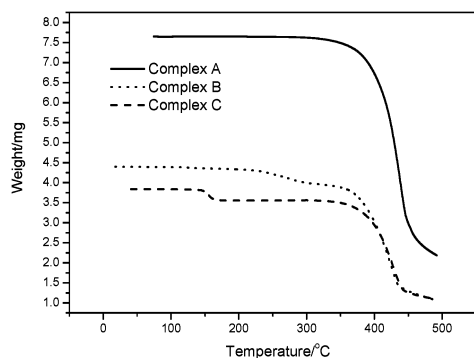


Figure 2. TG curves of complexes **A**, **B**, and **C**.

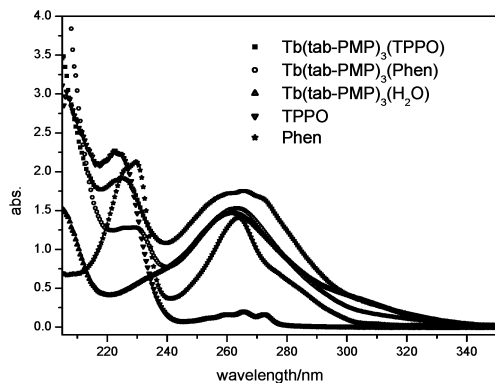


Figure 3. UV-vis spectra of the three complexes and neutral ligands.

temperatures below 300 °C while complexes **B** and **C** lost their water, ethanol, and CHCl_3 molecules, the lost weight ratio being 7.4% and 8.2% for complexes **B** and **C**, respectively, which match the weight percent (6.18% and 9.30%) of the corresponding lost molecules within experimental error.

UV-Vis. UV-vis absorbance spectra of the three complexes and the ligands measured from their CHCl_3 solutions are shown in Figure 3. Complexes **A** and **C** had similar UV-Vis characteristics with one main peak at around 265 nm, originating from tab-PMP^{1-} (the same as complex **B**), and the other absorbance at lower wavelength contributed by the neutral ligand TPPO and Phen, respectively; the absorbance of Phen became blue-shifted in complex **C** due to the coordination of the nitrogen atoms.

Phosphorescence Spectra. The phosphorescence spectra of complexes $\text{Gd}(\text{tba-PMP})_3(\text{H}_2\text{O})_2$, $\text{Gd}(\text{TPPO})_2(\text{NO}_3)_3$, and $\text{Gd}(\text{Phen})_2(\text{NO}_3)_3$ are shown in Figure 4. From the phosphorescence spectra, the triplet energy levels, which correspond to their peak emission wavelength, are 2.51 (465 nm), 2.35 (530 nm), and 2.09 eV (595 nm) respectively for $\text{Gd}(\text{tba-PMP})_3(\text{H}_2\text{O})_2$, $\text{Gd}(\text{TPPO})_2(\text{NO}_3)_3$, and $\text{Gd}(\text{Phen})_2(\text{NO}_3)_3$.

Photoluminescence. PL spectra (excitation and emission) of the three complexes measured from their 80-nm evaporated films are given in Figure 5. Since during evaporation complexes **B** and **C** lost their water and ethanol or CHCl_3 molecules, respectively, confirmed by TG, the emitting species were respectively $\text{Tb}(\text{tba-PMP})_3$ and $\text{Tb}(\text{tba-PMP})_3(\text{Phen})$ for complexes **B** and **C** (here and after) in the evaporated films. All three complexes had the same excitation spectra and emitted the characteristic bands of the central Tb^{3+} ion with the main peak at around 545 nm, assigned to the $\text{Tb}^{3+} f-f$ transition of $^5\text{D}_4 \rightarrow ^7\text{F}_5$. However, the emission intensity (integral area) is quite different for each complex with a ratio of **A**:**B**:**C** = 2.1:1.3:1. Obviously, this difference no doubt originated from the different coordination environments caused by the different

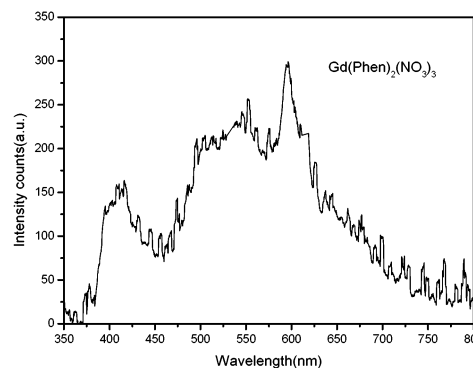
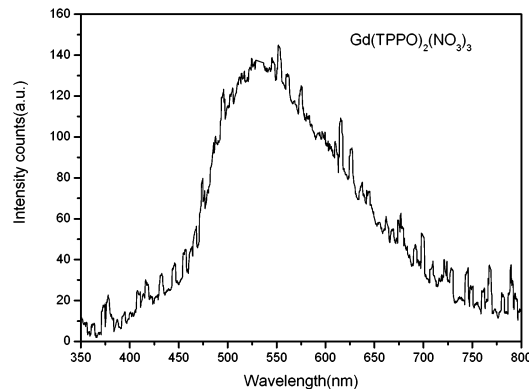
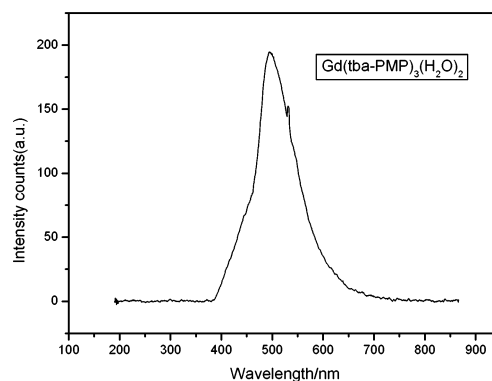


Figure 4. Phosphorus spectra of complexes $\text{Gd}(\text{tba-PMP})_3(\text{H}_2\text{O})_2$, $\text{Gd}(\text{TPPO})_2(\text{NO}_3)_3$, and $\text{Gd}(\text{Phen})_2(\text{NO}_3)_3$.

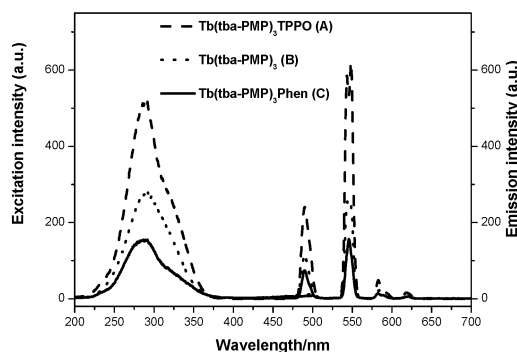


Figure 5. Photoluminescence spectra (excitation and emission) of complex **A**, **B**, and **C** measured from their 80 nm vacuum evaporated films on quartz substrates.

neutral ligands. Compared to complex **B** without neutral ligand, TPPO strengthened the PL intensity of complex **A**, while on the contrary, Phen made the PL intensity of complex **B** decrease.

This phenomenon could be explained by the energy transfer between ligands and the central metal ion. The singlet state energy levels of tab-PMP , TPPO, and Phen are estimated by

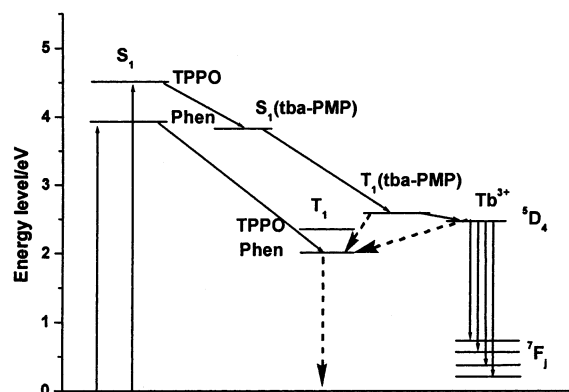


Figure 6. Schematic energy level diagram and the energy transfer process: S_1 , first excited singlet state; T_1 , first excited triplet state.

TABLE 1: The Singlet and Triplet State Energy Level of the Ligands

complexes	singlet energy level/eV	triplet energy level/eV
tab-PMP	3.81	2.51
TPPO	4.51	2.35
Phen	3.87	2.09

referencing their absorbance edge; they are 3.81 (325 nm), 4.51 (275 nm), and 3.87 eV (320 nm), respectively. For comparison and clarity, the singlet and triplet energy levels of the ligands are summarized in Table 1 and illustrated in Figure 6. In complex **A**, the S_1 energy level of TPPO matches that of tba-PMP and the 5D_4 energy level of Tb^{3+} , so the energy absorbed by TPPO could be transferred to tba-PMP or Tb^{3+} ion directly, leading to the enhancement of the PL intensity of complex **A**. For complex **C**, as the S_1 state of phen is in the same energy level as tba-PMP, it is difficult for the positive energy transfer to occur, while at the same time, since the T_1 energy level of Phen is much lower than that of tba-PMP and 5D_4 of Tb^{3+} , the reverse energy transfer occurred, resulting in a PL decrease of complex **C** compared to complex **B**. In addition, the main emission of complexes **B** and **C** peaked at 545 nm and split into two peaks at 542 and 548 nm and the half-width became wider compared to complex **C**; this may be caused by the different coordination environments of the central ions as the polymerization may occur because of their unsaturated coordination number.¹³

Electroluminescence. Our previous report has confirmed that balanced carrier injection and a well-confined recombination zone in the emitting layer are crucial for lanthanide complex EL performance enhancement.¹³ As complex **A** has a similar structure to complex $Tb(eb-PMP)_3(TPPO)$, it shows the same EL properties. In device A1 with the configuration of ITO/TPD (20 nm)/complex **A** (50 nm)/BCP (20 nm)/AIQ (30 nm)/ $Mg_{0.9}Ag_{0.1}$, the recombination zone was well confined in the complex layer (EL spectrum shown in Figure 7) and a performance of brightness 9540 cd/m^2 , power efficiency 7.12 lm/W , and peak external quantum efficiency 18.1 cd/A was achieved from this device, and the peak power efficiency occurred at a luminance of 447 cd/m^2 and it was still higher than 2.0 lm/W at a brightness 4000 cd/m^2 , similar to complex $Tb(eb-PMP)_3(TPPO)$.¹¹

Although complex **B** has as good hole-transport properties as complex $Tb(PMIP)$,^{11,12} after introducing the hole-blocking layer BCP and altering the thickness of different layers to adjust the injection ratio of electron and hole, device B1 with the configuration of ITO/TPD (30 nm)/complex **B** (30 nm)/BCP (30 nm)/AIQ (20 nm)/ $Mg_{0.9}Ag_{0.1}$ emitted pure green light originating from complex **B** (Figure 7), and the performance

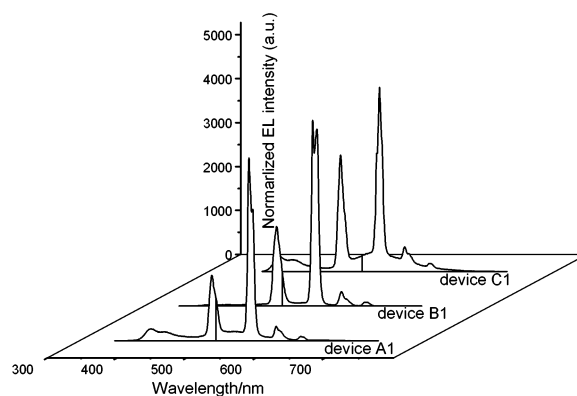


Figure 7. Normalized EL spectra of device A1 (ITO/TPD (20 nm)/A (50 nm)/BCP (20 nm)/AIQ (30 nm)/ $Mg_{0.9}Ag_{0.1}$), device B1 (ITO/TPD (30 nm)/B (30 nm)/BCP (30 nm)/AIQ (20 nm)/ $Mg_{0.9}Ag_{0.1}$), and device C1 (ITO/TPD (20 nm)/C (50 nm)/BCP (20 nm)/AIQ (30 nm)/ $Ag_{0.9}Ag_{0.1}$) at an applied voltage of 10 V.

TABLE 2: PL and EL Property Comparison of the Three Complexes A, B, and C

complexes	rel PL intensity	brightness (cd/m^2)	power eff (lm/W)
A	2.1	9540	7.12
B	1.3	3230	1.17
C	1	690	0.13

obtained from device B1 was 3230 cd/m^2 (18 V) and 1.17 lm/W , similar to that of its analogue complex $Tb(PMIP)_3$ (2800 cd/m^2 , 2.61 lm/W). The best EL (Figure 7) presentation obtained from complex **C** was 690 cd/m^2 and 0.13 lm/W in a device (device C1) having a structure of (ITO/TPD (20 nm)/C (50 nm)/BCP (20 nm)/AIQ (30 nm)/ $Mg_{0.9}Ag_{0.1}$), presenting the same magnitude to its analogue complex $Tb(PMIP)_3(Phen)$.¹⁶

The PL properties and the best EL performance of the three complexes obtained from their corresponding multilayer devices are summarized in Table 2. The PL intensity of complex **A** was twice that of complex **B**, while the EL efficiency achieved from complex **A** was more than 6 times higher than that from complex **B**. Similarly, the PL intensity of complex **C** decreased to half that of complex **B** and the EL efficiency obtained from complex **C** decreased by nearly one magnitude. This result indicated the terbium complex PL intensity greatly affects its EL performance.

Conclusions

In summary, we report the effect of the neutral ligands (TPPO, Phen) on the PL and EL properties of the terbium complexes. Our experimental results revealed that neutral ligands strongly affect the terbium complexes PL quantum yield due to their different excited singlet and triplet energy levels. Compared to complex **B**, if the energy absorbed by the neutral ligand (TPPO) can be efficiently transferred to negative-charged ligand (tba-PMP) or the central Tb^{3+} ion, the PL of the complex is enhanced, but if the reverse energy transfer occurs, the complex PL intensity decreases. Our experiments further confirmed that high PL yield and well-balanced carrier injection are both important for terbium complexes EL performance. High PL intensity complexes can be synthesized by utilizing more suitable ligands (both negatively charged and neutral ligands); the second issue can be satisfied by both ligand modification and device optimization. The performance of 9640 cd/m^2 , 7.12 lm/W , and external quantum efficiency 18.1 cd/A achieved from complex $Tb(tab-PMP)_3(TPPO)$ (**A**) was one of the best performances of terbium complexes. Our experimental results provide

a useful guide for future work in lanthanide complex EL performance enhancement.

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Supporting Information Available: X-ray crystallographic data for complexes **A**, **B**, and **C** (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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