Application of Chelate Phosphine Oxide Ligand in Eu^{III} Complex with Mezzo Triplet Energy Level, Highly Efficient Photoluminescent, and Electroluminescent Performances

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The chelate phosphine oxide ligand bis(2-(diphenylphosphino)phenyl) ether oxide (DPEPO) was used as a unit neutral ligand to prepare the complex Eu(TTA)$_3$(DPEPO) **1** (TTA = 2-thenoyltrifluoroacetonate). Compound **1** has a photoluminescence (PL) quantum yield of 55.3%, which is more than the twice of the PL quantum yield of Eu(TTA)$_3$(TPPO)$_2$ (TPPO = triphenylphosphine oxide). Investigation indicated that DPEPO in **1** has the mezzo first triplet excited energy level (T$_1$) between the first singlet excited energy level (S$_1$) and T$_1$ of TTA, which may support one more additional energy transfer routines from the T$_1$ energy level of DPEPO to that of TTA, and consequently results in the improvement of energy transfer in the Eu^{III} complex. DPEPO forms a complex with a more rigid and compact structure that can improve energy transfer between ligands and the center Eu^{III} ion, support the higher saturation level by the coordinating ability of the oxygen atom in the ether moiety, and consequently enhance the PL intensity and efficiency of the corresponding Eu^{III} complex. The multilayered electroluminescent (EL) device of **1** used as the red dopant exhibited an impressive brightness of 632 cd m^{-2} at 25 V. The device had the excellent voltage-independent spectral stability with an emission peak at 615 nm. To the best of our knowledge, this luminescence is the brightest emission among Eu complexes with phosphine oxide ligands. The maximum external quantum yield (η_{ext}) of 2.89% and the maximum current and power efficiency of 4.58 cd A^{-1} and 2.05 lm W^{-1} were achieved at a low turn-on voltage of 7 V and current density of 0.021 mA cm^{-2}. These properties demonstrate that the chelate phosphine oxides ligand DPEPO can not only be favorable to form the rigid and compact complex structure and increase the efficiency of devices, but also reduce the ability of the formation of exciplex. DPEPO shows much better performance compared with the ordinary phosphine oxide ligand triphenylphosphine oxide.

Introduction

As an important family of luminescent materials, lanthanide complexes have been studied as emitters for OLEDs because of their nearly monochromic characteristic emission, chemical environmental stability, and internal device quantum efficiency that approaches theoretically 100%.[1−5] It has been shown that the introduction of charge injection or transporting moieties into the ligands can improve the electroluminescent performance of organic lanthanide metal ion-based materials.[6] A group of Eu^{III} complexes with phenanthroline derivatives as the neutral ligands have been studied extensively.[7−14] The devices of these complexes showed a line emission from the Eu complex with maximum brightness values greater than 100 cd m^{-2},[5] and their device performance was much better than that of the complexes with another neutral ligand triphenylphosphine oxide (TPPO), of which devices have turn-on voltages more than 10 V and weak electroluminescence (EL).[13] The reason may be that the flat structure of the phenanthroline derivatives makes the charge injection and transport easier. As chelate ligands, phenanthroline derivatives could form more rigid and stable complexes than the single-coordinated phosphine oxide ligand TPPO. The stability of complexes in excited state will influence electroluminescent properties. However, the coordinating ability and the charge injection and transport ability may be greatly affected by the introduction of new substituents into the phenanthroline ring due to the high delocalization of their n electrons. This effect limits the modification of phenanthroline derivatives for further improving the device performances. In the phosphine oxide ligands, however, the coordinating ability of O atoms can be less influenced by the groups bonding to phosphorus atoms. The modification of TPPO would be much easier and more flexible than phenanthroline derivatives. With the aim of improving the coordinating ability and the carrier injection and transport ability of TPPO, in this work we tried to select out chelate phosphine oxide compounds as the unit neutral ligand. The application of the chelate phosphine oxide ligands in the luminescent rare earth (RE) complexes instead of single-coordinated TPPO can not only enhance the stability of the complexes but also improve the photoluminescent and electroluminescent properties of the lanthanide complexes. We chose bis(2-(diphenylphosphino)phenyl) ether oxides (DPEPO) as the neutral ligand to prepare the tertiary complex Eu(TTA)$_3$(DPEPO) **1**. The choice of bis(2-(diphenylphosphino)phenyl) ether oxides is based on its strong ability to coordinate lanthanide ions, its structure rigidity, and its good electron transporting ability. The chelate phosphine oxide ligand has the rigid structure, which not only can enforce the rigidity and form the more compact complexes so as to improve the triplet energy transporting from ligands to the center RE ion, but also can improve energy transfer between the two diphenyl phosphine oxide moieties through the bridge moieties to eliminate the

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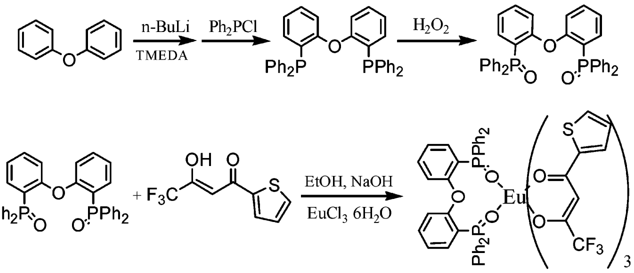
SCHEME 1: Molecular Structure and Synthetic Procedure of Eu(TTA)$_3$(DPEPO) 1



formation of the exciplex.[15] Furthermore, in DPEPO the O atom of the ether bridge is also capable of coordinating to the center metal.[15] This effect can improve the luminescent properties of the complex. The efficient and stable pure red emission from the multilayer organic light emitting diodes (OLEDs) based on **1** is demonstrated.

Experimental Section

Materials and Instruments. All the reagents and solvents used for the synthesis of **1** were purchased from Aldrich and Acros companies. Alq$_3$, BCP, CBP, and NPB used for EL device fabrication were purchased from Lumthec Corporation. All the reagents were used without further purification.

^{1}H NMR spectra were recorded using a Varian Mercury plus 400NB spectrometer relative to tetramethylsilane (TMS) as internal standard. Molecular masses were determined by a Shimadzu laser desorption/ionization time-of-flight mass spectrometer (LDI-TOF-MASS). Elemental analyses were performed on a Vario ELIII elemental analyzer. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed on Shimadzu DSC-60A and DTG-60A thermal analyzers under nitrogen atmosphere at a heating rate of 10 °C/min. Absorption and photoluminescence (PL) emission spectra of the target compound were measured in dichloromethane using a Shimadzu UV-3150 spectrophotometer and a Shimadzu RF-5301PC spectrophotometer, respectively. Phosphorescence spectra were measured in dichloromethane using an Edinburgh FLS 920 fluorescence spectrophotometer at 77 K cooling by liquid nitrogen.

Preparation of Eu(TTA)$_3$(DPEPO). *Bis(2-(diphenylphosphino)phenyl) ether*. Bis(2-(diphenylphosphino)phenyl) ether was prepared according to the process described in the literature (cf. ref 16) with some modifications (Scheme 1). A solution of 1.00 g of diphenyl ether (5.88 mmol) in 10 mL of THF, which was previously treated with sodium, was added dropwise to a stirred mixture of 8.1 mL of *n*-butyllithium (1.6 M in hexane, 12.96 mmol) and 2.08 mL of TMEDA (12.96 mmol) at room temperature. The reaction mixture was stirred overnight. Then a solution of 2.4 mL of chlorodiphenylphosphine (13.34 mmol) in 10 mL of hexanes was added dropwise to the reaction mixture during 30 min at 0 °C with an ice−water bath. The mixture reacted at 0 °C for another 1 h. A white precipitate, which was confirmed as LiCl, was formed. The mixture was then stirred at room-temperature overnight. Then 10 mL of water was added into the flask to stop the reaction. The mixture was extracted with 3 × 30 mL of dichloromethane. The organic layer was dried with MgSO$_4$. The solvent was removed in vacuo. The residue was purified by flash column chromatography using dichloromethane as eluent to yield (4-diphenylphosphanylphenyl) diphenylamine that is a white or sometimes straw yellow sticky solid in 92% yield. The sticky solid was washed with acetone and then dried in vacuo. Yield: 2.7 g of white powder (85%).

^{1}H NMR ($CDC1_3$, 400 MHz): δ (ppm) 7.350−7.155 (m, 22 H, Ph-H), 6.950 (tr, 2 H, $J = 7.2$), 6.800 (br, 2 H), 6.688 (q, $J_{H-H} = 8$, $J_{P-H} = 4$, Ph-H). LDI-TOP mass (*m*/*z*): 539.2 (M$^+$).

Bis(2-(diphenylphosphino)phenyl) ether oxides (DPEPO). A 2.69 g portion of bis(2-(diphenylphosphino)phenyl) ether (5 mmol) was dissolved in 10 mL of 1,4-dioxane at room temperature. 1 mL of 30% H$_2$O$_2$ (10.5 mmol) was added dropwise with vigorous stirring. The mixture was then stirred for another 2 h. Then 10 mL of water was added to stop the reaction. The mixture was extracted with 3 × 30 mL of dichloromethane. The oil phase was washed with 2 × 30 mL of water to remove 1,4-dioxane. The organic layer was dried with MgSO$_4$. The solvent was removed in vacuo. A white powder was obtained with yield 2.82 g (99%).

^{1}H NMR ($CDC1_3$, 400 MHz): δ (ppm) 7.751−7.558 (m, 9H, Phen-H); 7.544−7.194 (m, 13H, Phen-H); 7.153 (tr, 2H, $J = 8.4$, Phen-H); 7.079 (tr, 2H, $J = 7.6$, Phen-H); 6.040 (q, 2H, $J_{H-H} = 7.8$, $J_{P-H} = 5.6$). LDI-TOP mass (*m*/*z*): 571.5 (M$^+$).

Eu(TTA)$_3$(DPEPO) ***1***.[17] A 3.0 mmol sample of 2-thenoyltrifluoroacetone (TTA) was dissolved in ethanol, 3.0 mmol of NaOH in water solution was added to remove the H$^+$ in the TTA molecule, then 1.0 mmol of EuCl$_3$ 6H$_2$O in water solution was added dropwise and stirred at 60 °C for 30 min. Finally, 1.0 mmol of bis(2-(diphenylphosphino)phenyl) ether oxides (DPEPO) in ethanol was added in drops and stirred at 60−70 °C for 4 h. A white with pink hue precipitate was formed. The powder was washed with water and ethanol in reflux and yields 1.005 g of the complex with yield of 72.5%. Its melt point is 253 °C. ^{1}H NMR ($CDC1_3$, 400 MHz): δ (ppm) 9.117−8.781 (m, 9H, Phen-H); 7.752−7.432 (m, 17H, Phen-H and Th−H); 7.248−7.106 (m, 5H, Th−H); 6.929 (d, 2H, $J = 5.2$, Phen-H); 6.855 (d, 2H, $J = 2.8$, Phen-H); 6.653 (tr, 2H, $J = 4.2$, Phen-H); 4.059 (s, 3H, COCHCO). Anal. Calcd. for $C_{60}H_{40}EuF_9O_9P_2S_3$: C, 51.99; H, 2.91; Eu, 10.96; O, 10.39; S, 6.94; Found: C, 51.86; H, 2.95; Eu, 11.03; O, 10.52; S, 7.01. ESI/MS (*m*/*z*): 1386 (M$^+$, 56%), 757 (M^{2+} + 2 CH$_3$OH, 32%), 1166 (11%), 813 (11%), 571 (DPEPO$^+$, 100%).

Synthesis of Gadolinium Complexes. For triplet energy level measurement gadolinium complexes comprising neutral ligand DPEPO without TTAs and comprising TTAs without neutral ligand were also synthesized.

Gd(DPEPO)(NO$_3$)$_3$. A 1.0 mmol portion of DPEPO was dissolved in 50 mL of ethanol. A 1.0 mmol portion of Gd(NO$_3$)$_3$(H$_2$O)$_6$ in 0.1 mL of water was added in solution dropwise under stirring and the solution was heated to refluxing for 2 h. White precipitates were formed. The resulting solution was filtered and a white powder was obtained.

Gd(TTA)$_3$(H$_2$O)$_2$. A 3.0 mmol portion of HTTA was dissolved in 50 mL of ethanol. 3.0 mL of 1.0 mol L^{-1} NaOH was then added dropwise, and the mixture was stirred for 15 min. Then 1 mmol of Gd(NO$_3$)$_3$(H$_2$O)$_6$ in 0.1 mL of water was added in solution dropwise under stirring and the solution was heated to refluxing for 2 h. A yellow-with-pink powder was obtained by precipitating from a ethanol and water solution.

Fabrication and Testing of OLEDs. Four-layer OLEDs were fabricated by vacuum deposition with a configuration of ITO/NPB (30 nm)/**1**: CBP (30 nm, 10%)/BCP (40 nm)/Alq$_3$ (30 nm)/LiF (0.5 nm)/Al (100 nm), wherein NPB is *N*,*N*-bis(α-naphthylphenyl)-4,4′-biphenyldiamine as the hole-transporting layer, CBP is 4,4′-bis(carbazole-9-yl)biphenyl as host material, BCP is 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline as the electron transporting/hole blocking layer, Alq$_3$ was used as the electron transporting layer, and ITO and LiF/Al were used as the anode and cathode, respectively.[18] Before loading into a

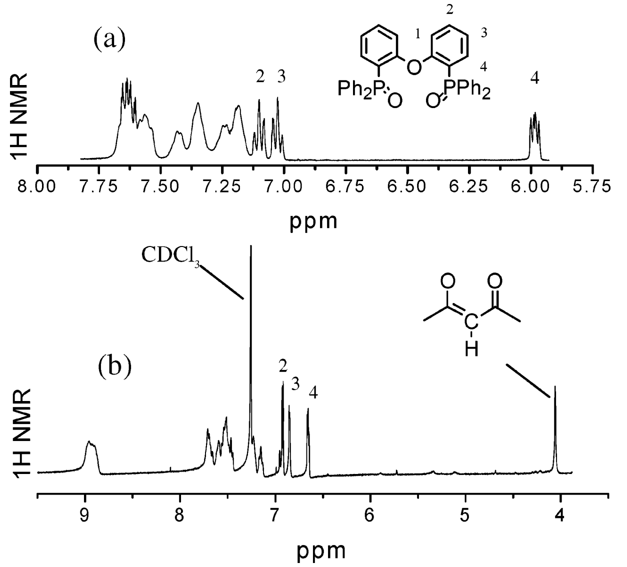


Figure 1. ^1H NMR (400 MHz) of (a) DPEPO and (b) **1** in $CDCl_3$. The different kinds of the protons bonding to the diphenyl ether group were marked with numbers and the corresponding peaks were marked with the same numbers.

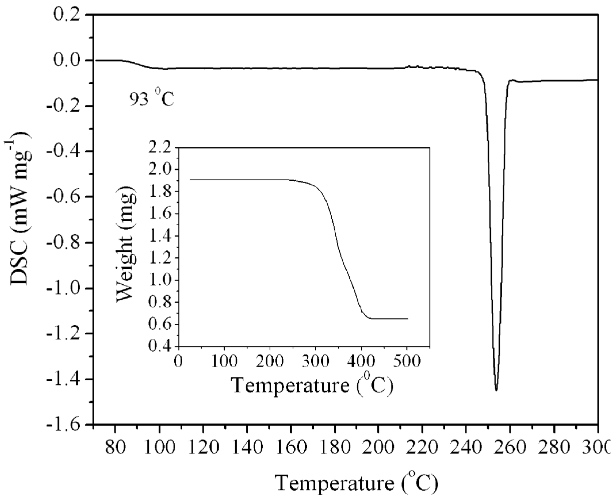


Figure 2. Thermal analysis curves: DSC curve and TGA curve (inset figure).

deposition chamber, the ITO substrate was cleaned with detergents and deionized water, dried in an oven at 120 °C for 4 h, and treated with UV-ozone for 25 min. Devices were fabricated by evaporating organic layers at a rate of 0.1−0.3 nm/s onto the ITO substrate sequentially at a pressure below 1×10^{-6} mbar. Onto the Alq_3 layer, a layer of LiF with 0.5 nm thickness was deposited at a rate of 0.1 nm/s to improve electron injection. Finally, a 100-nm-thick layer of Al was deposited at a rate of 0.6 nm s^{-1} as the cathode. The emission area of the devices was 0.12 cm^2 as determined by the overlap area of the anode and the cathode. The EL spectra and current−voltage luminescence characteristics were measured with a Spectrascan PR 650 photometer and a computer controlled DC power supply under ambient conditions.

Results and Discussions

Design, Synthesis, and Structure Analysis. With the purpose of designing chelate phosphine oxides with the unit structure using in Eu^{III} complexes, the phosphine oxide compounds should have not only the high coordinating ability but also should have the good carrier transporting ability. And the structure of the chelate ligands should improve the energy transfer between ligands and the center metal ion. Thanks to the pivotal work of McMillin, the comparison between bis(2-(diphenylphosphino)-phenyl) ether (DPEphos) and triphenylphosphine in their Cu^I complexes was discussed in detail.[15,20] DPEphos can reduce the distance between ligands and the center metal ions, and the O atom of the ether bridge has the coordinating ability, which could be inherited in its oxides. We thought the oxides of this ether should be suitable as the chelate ligand for luminescent Eu^{III} complexes. Simultaneously, the conjugated moiety in DPEPO could not only increase the rigidity of the complex, which will be very important to avoid the structure relaxation in the excited state, but also improve the thermal stability of the complex.

The ^1H NMR spectra of DPEPO and the complex **1** obtained at 400 MHz in *d*-chloroform solutions are shown in Figure 1a and b. The ^1H NMR spectrum of DPEPO consists of two mixed peaks with the chemical shifts in the ranges of 7.751−7.558 and 7.544−7.194 ppm, two triplicate peaks at 7.153 and 7.079 ppm, and one quadruplicate peak at 6.040. The mixed peaks are attributable to the protons in the four phenyl groups bonding to the phosphorus atoms and two protons at the 1 position of the diphenyl ether group. The triplicate peaks at 7.153 and 7.079 ppm are attributable to the protons at the 2 and 3 position of the diphenyl ether group with $J = 8.4$ and 7.6 Hz. The peak of the protons at 6.040 ppm at the 4 position is quadruplicate rather than duplicate because of the interaction between the phosphorus atom and the hydrogen atom. According to the spectrum J_{P-H} is 5.6 Hz and J_{H-H} is 7.8 Hz. The lanthanide-based complexes are well-known as shift reagents due to the paramagnetism of the lanthanide ion. Therefore, the peaks of DPEPO in the spectrum of **1** are much different with free DPEPO. One of the mixed peaks of the protons in the four phenyl groups shifts from about 7.60 ppm to nearly 9 ppm. The other mixed peak shifts from 7.544 to 7.750 with addition of peaks attributable to thiophyl groups from TTAs. The other mixed peaks attributable to thiophyl groups are found at the range of 7.248−7.106 ppm. The single peak at 4.059 ppm is attributable to the protons at the α position (COCHCO) of the three TTAs. The peak attributable to the protons at the 2 position of the diphenyl ether group shifts from 7.153 to 6.929 ppm. The peak attributable to the protons at the 3 position shifts from 7.079 to 6.855 ppm, and the peak of the protons at the 4 position is found at 6.653 ppm rather than 6.040 ppm former. The split states of the last three peaks are also changed. Both two former triplicate peaks change into duplicate peaks and the former quadruplicate peak changes into a triplicate peak, because $Eu(TTA)_3$ groups can affect the coupling constants of these peaks from DPEPO.

Thermal Properties. The thermal properties were analyzed by TGA and DSC (Figure 2). The decomposition temperature (T_d) of **1** is about 317 °C and the melt point (T_m) is 253 °C with the temperature of glass transition (T_g) found at 93 °C. It is shown that the thermal properties of **1** were better than that of $Eu(TTA)_3(TPPO)_2$ (T_d 300 °C, T_m 167 °C, and no T_g observed),[13] which originates from the more rigid structures of DPEPO. Furthermore, stronger intermolecular force is proved by higher T_m of **1**, which is about 86 °C more than that of $Eu(TTA)_3(TPPO)_2$. Higher T_d of **1** makes devices fabricated by vacuum evaporation more feasible. Simultaneously the structure of O bridge linkage, which limits the movement of diphenylphosphine oxide moieties, increases the rigidity of DPEPO and further of the whole complex. Compared with $Eu(TTA)_3(TPPO)_2$, in which TPPO has only one coordinating site so that

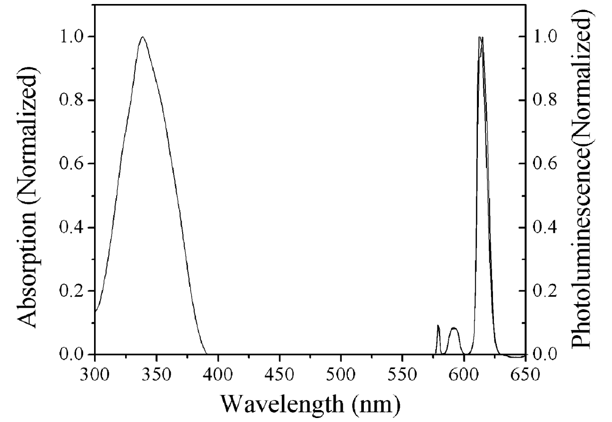


Figure 3. Absorption and emission spectra in CH_2Cl_2 solution (dash line and solid line) and emission spectrum in solid state (dot line).

it can move easier with little activating energy, **1** with the more rigid structure needs higher temperature to overcome the potential barriers when making its segments move, which should be the reason **1** has a relatively high T_g. High T_g is supposed to be good for increasing the device lifetime.

Optical Properties. Dilute CH_2Cl_2 solution of **1** (1×10^{-5} mol L^{-1}) absorbs at 338 nm (Figure 3). When **1** was excited with the appropriate radiations, the sharp characteristic emission at 612 nm of the Eu^{III} ion from $^5D_0 - {}^7F_2$ was observed accompanied by the weak emissions corresponding to $^5D_0 - {}^7F_j$ ($j \sim 0, 1, 3$). The solid-state emission of **1** was at 615 nm with 3 nm shifting red.

The PL quantum yield of **1** in CH_2Cl_2 solution (1×10^{-5} mol L^{-1}) was measured to be 55.3% using $Ru(bpy)_3Cl_2$ as the standard. This PL quantum yield, which is more than the twice of that of $Eu(TTA)_3(TPPO)_2$ (26.77%),[19] indicates that DPEPO is the better second ligand to improve the PL properties of the Eu complex than TPPO. Compared with the single coordinated ligand TPPO, the chelate phosphine oxide ligand has different effects on the PL properties of its complex. First, with the linkage of the two diphenylphosphine oxide groups by the ether bridge, the volume of single DPEPO is smaller than two TPPO and the O−Eu−O angle in **1** decreases compared with $Eu(TTA)_3(TPPO)_2$ because the bridge linkage restricts the movement of the two diphenylphosphine oxide groups. This compact structure makes the solvent molecule harder to get into the structure of **1** so as to reduce the solvent-induced quenching.[15] Simultaneously, the compact structure of **1** makes the three TTAs get closer to the center metal so as to improve the triplet energy transfer from TTAs to Eu^{III} ion. This rigid structure reduces the structure relaxation in the excited state as well.[20] Finally, the oxygen atom in the ether bridge also has the capability of coordinating to the center metal.[20] Higher coordinating saturation level is better to get a highly efficient luminescent Eu^{III} complex by increasing the interaction between DPEPO and Eu^{III}.

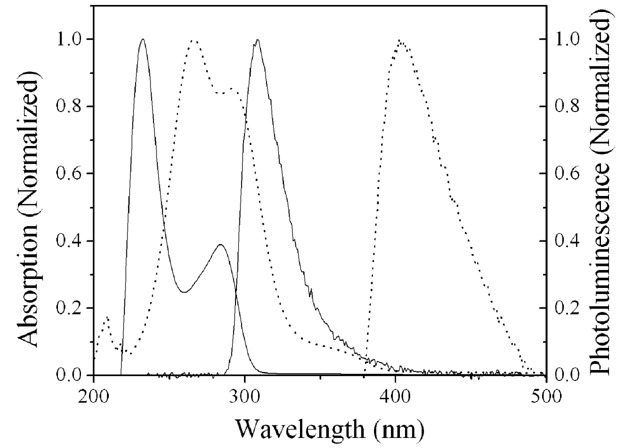


Figure 4. Absorption and photoluminescence spectra of DPEPO (solid lines) and TTA (dot lines) in CH_2Cl_2 solution.

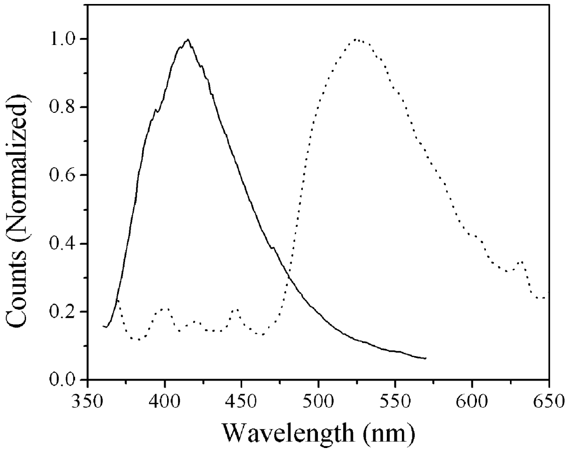


Figure 5. Phosphorescence spectra of complexes $Gd(DPEPO)(NO_3)_3$ (solid line) and $Gd(TTA)_3(H_2O)_2$ (dot line).

TABLE 1: Singlet and Triplet State Energy Levels of the Ligands

ligand	singlet energy level (eV)	triplet energy level (eV)
DPEPO	3.94	2.99
TPPO[21]	4.51	2.35
Phen[21]	3.87	2.09
TTA	3.12	2.35

Energy Transfer between Ligands and Eu^{III}. It is known that in the lanthanide complexes neutral ligands often play a role of absorbing and transporting energy to the other ligands or the center metal ions. According to absorption and photoluminescence spectra of DPEPO and TTA (Figure 4), it is found that there is a large area overlap between the emission peak of DPEPO and the absorption peak of TTA from 285 to 398 nm, which is almost equal to the range of the emission peak of DPEPO. It means that nearly all the radiations from DPEPO can be absorbed by TTA. This wide overlap shows the possibility of the highly efficient energy transfer from DPEPO to TTA.

To demonstrate the energy transfer process, the phosphorescence spectra of complexes $Gd(DPEPO)(NO_3)_3$ and $Gd(TTA)_3(H_2O)_2$ were measured for the triplet energy level data of the ligands (Figure 5). From the phosphorescence spectra, the triplet energy levels of $Gd(DPEPO)(NO_3)_3$ and $Gd(TTA)_3(H_2O)_2$, which correspond to their peak emission wavelengths, are 2.99 eV (415 nm) and 2.35 eV (527 nm), respectively. Because the lowest excited state $^6P_{7/2}$ of Gd^{III} is too high to accept energy from ligands, the data obtained from the phosphorescence spectra actually reveal the triplet energy levels of DPEPO and TTA in lanthanide complexes. The singlet state energy levels of DPEPO and TTA are estimated by referencing their absorbance edges, which are 3.94 eV (315 nm) and 3.12 eV (398 nm), respectively. For comparison, the singlet and triplet state energy levels are summarized in Table 1 and illustrated in Figure 6.

In Figure 6, the S_1 energy levels of all the ligands match that of TTA and the $^5D_0$ energy level of Eu^{III}. So the energy absorbed

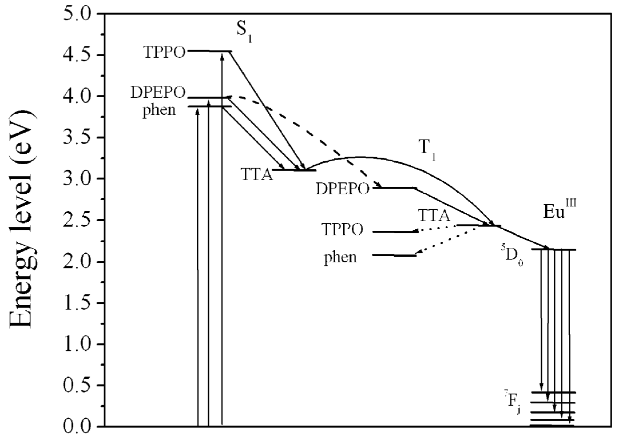


Figure 6. Schematic energy level diagram and the energy transfer process: S_1, first excited singlet state; T_1, first excited triplet state.

by the ligands could be transferred to the TTA or Eu^{III} ion directly. But it is known that the gap between two energy levels should be intermediate. Too big or small would decrease the efficiency of energy transfer. The energy gap between the S_1 energy levels of DPEPO and TTA is 0.82 eV, which is very close to the 0.75 eV between the S_1 energy levels of phen and TTA but much less than 1.29 eV between the S_1 energy levels of TPPO and TTA. Compared with TPPO, the energy gap between DPEPO and TTA is more appropriate to improve energy transfer from S_1 of DPEPO to that of TTA. At the same time the T_1 energy level of phen is much lower than that of TTA. So reverse energy transfer occurs.[21] The reverse energy transfer makes part of energy in T_1 state of TTA lose rather than transfer to Eu^{III}. As the T_1 state of phen is in the same energy level as $^5D_0$ of Eu^{III}, it is difficult to make the positive energy transfer occur. This effect results in the decrease of PL intensity of Eu(TTA)$_3$(phen). Similarly, the positive energy transfer from T_1 of TPPO to that of TTA is also very difficult due to their same T_1 energy levels. But the T_1 energy level of DPEPO is 0.64 eV higher than that of TTA, therefore the energy from the T_1 excited state of DPEPO can efficiently transfer to the T_1 excited state of TTA. Furthermore, part of S_1 excited states energy of DPEPO may transfer to its own T_1 states. So this part of energy can transfer to the T_1 excited state of TTA and further to Eu^{III} efficiently. The process can be summarized as five steps. Energy transfers from the S_1 excited state of DPEPO to that of TTA, then transfers from S_1 to T_1 excited state of TTA; or energy transfers from S_1 to T_1 excited state of DPEPO and then transfers from T_1 excited state of DPEPO to that of TTA. Finally energy transfers from T_1 excited state of TTA to $^5D_0$ of Eu^{III}. Obviously, different from phen and TPPO, DPEPO may have one more additonal energy transfer routine between T_1 excited states of DPEPO and TTA, which can improve the energy transfer from the ligands to the center ions.

EL Performances of Devices. Compound **1** was used as a dopant emitter to fabricate electroluminescent devices with the structure ITO/NPB (30 nm)/**1**:CBP (30 nm, 10%)/BCP (40 nm)/Alq$_3$ (30 nm)/LiF (0.5 nm)/Al (100 nm).

The current density−luminance−voltage ($I-L-V$) characteristics of devices are shown in Figure 7. The device gave off the pure characteristic emission of Eu^{III} ion at 616 nm and had a considerably low onset voltage of 7.0 V at a luminance of 1 cd m^{-2}, compared with 12 V of the device containing Eu(TTA)$_3$(phen) and 14 V of the device containing Eu(TTA)$_3$(TPPO)$_2$.[9,13] The lower turn-on voltage of the device may originate from the improvement of the carrier's injecting ability by introducing chelate phosphine oxide ligands with the more conjugated structure in **1**. Notably, the device has the maximum brightness reaching to 632 cd m^{-2} at 25 V. To the best of our knowledge, that is the highest brightness among the Eu complexes with phosphine oxide ligand to date. However, the devices with Eu(TTA)$_3$(TPPO)$_2$ serving as a dopant had much weaker EL emission intensity.[13]

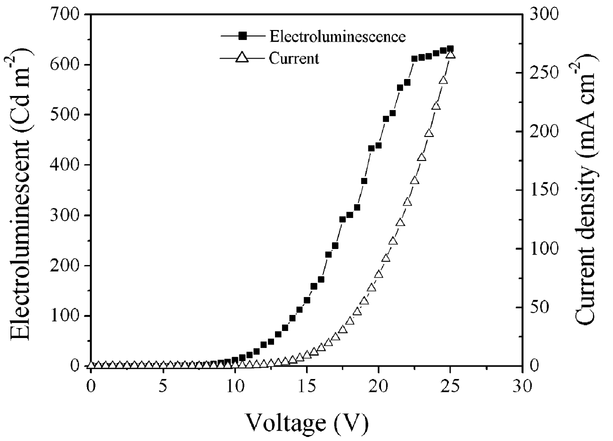


Figure 7. Current density−luminance−voltage characteristics.

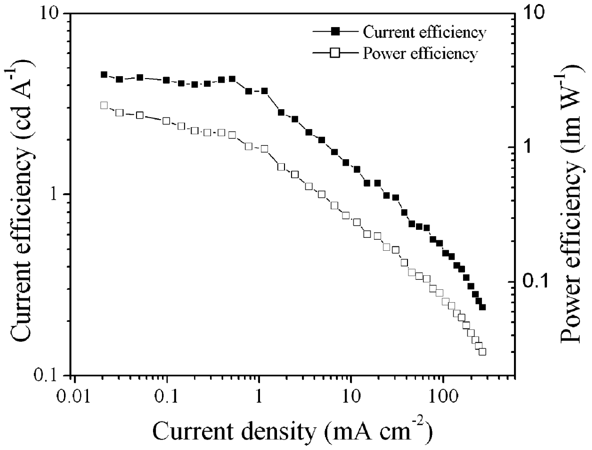


Figure 8. Current and power efficiency curves.

The current and power efficiency curves of the device are shown in Figure 8. The maximum external quantum yield (η_{ext}) of 2.89% and the maximum current and power efficiencies of 4.58 cd A^{-1} and 2.05 lm W^{-1} were achieved at a much lower current density of 0.021 mA cm^{-2} at 7 V. At the practical brightness of 100 cd m^{-2}, the current and power efficiency remained 1.98 cd A^{-1} and 0.445 lm W^{-1} (corresponding to η_{ext} of 1.25%) at a voltage of 14 V and a current density of 4.82 mA cm^{-2}. Compound **1** is among the highest efficient europium-based electroluminescent materials. The EL efficiency is much better than that of devices using Eu(TTA)$_3$(TPPO)$_2$ as a dopant, which originates from the introduction of the chelate phosphine oxide ligand. The structure of the O bridge linking the two diphenylphosphine oxide moieties increases the conjugated area of the neutral ligand, which can improve carrier injection and transport in **1**. In another aspect, the introduction of chelate phosphine oxide ligand also makes the complex more rigid, which reduces the structure relaxation in the excited state. Furthermore, the coordinating ability of the ether oxygen atom in DPEPO as mentioned above can not only saturate the coordination degree of the center RE ion to improve the electroluminescent properties of the complex,[11] but also makes the energy transfer from DPEPO to Eu^{III} ion easier and

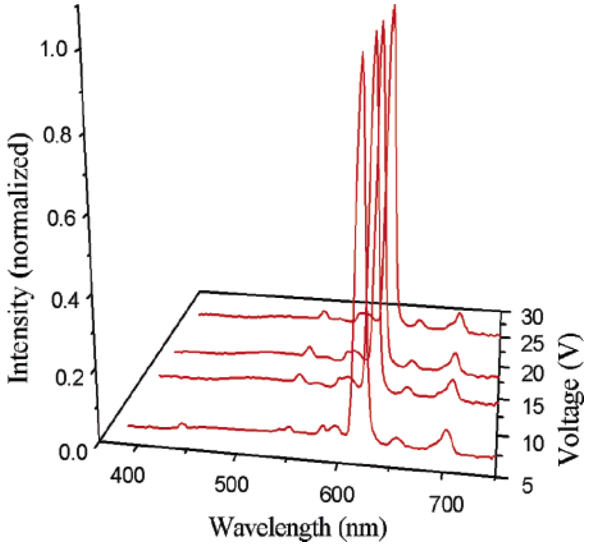


Figure 9. EL spectra of device at applied voltages of 7, 14, 18, and 25 V.

TABLE 2: EL Performances of the Europium Complexes

dopant	max. brightness (cd m^{-2})	turn-on voltage (V)	max. current efficiency (cd A^{-1})	max. energy efficiency (lm W^{-1})
[9]Eu(TTA)$_3$phen	505	12		
[13]Eu(TTA)$_3$(TPPO)$_2$	< 200	14		
Eu(TTA)$_3$(DPEPO)	634	7	4.58	2.05

more efficient. The existence of this oxygen atom supports another efficient channel of energy transfer between DPEPO and Eu^{III}.

The performances of OLEDs based on Eu(TTA)$_3$phen or Eu(TTA)$_3$(TPPO)$_2$ doped into CBP as the emitter in the literature are listed in Table 2 for comparison.[9,13] It is shown that the EL properties of Eu(TTA)$_3$(DPEPO) exceed these popular europium complexes in the brightness, turn-on voltage, and efficiency.

The electroluminescent spectra of the device at different voltages are also shown in Figure 9. All of the figures show the monochromatic light emission at 616 nm, which demonstrates that charge trapping is the dominating luminescence process.[22] The EL spectra remain very stable when increasing the voltage in the devices. It is not observed of any exciplex emission and the disturbance of the emission from CBP and Alq$_3$. This is distinct from those devices where the exciplex emission from the host materials doped with Eu(TTA)$_3$(TPPO)$_2$ could be observed clearly when the voltage increased.[23] Thus the present material and devices exhibited improved color stability, which should be also the consequence of using the chelate phosphine oxide ligand DPEPO instead of TPPO. The O bridge moiety in DPEPO can improve the energy transfer between two diphenylphosphine oxide groups to decrease the formation of exciplex. Almost the same electroluminescence spectra detected in a very wide voltage range from 7.0 to 25.0 V show that at high current density and voltage carriers were still caught in the emitting layer by CBP and **1** rather than entering into the NPB layer without recombination, and the absence of the emission from CBP shows us the efficient energy transfer between CBP and the complex at high voltages. It means that DPEPO can improve carrier injection and nearly all of the energy absorbed by DPEPO can be transferred efficiently to Eu^{III} ion.

Summary

In conclusion, a novel luminescent Eu^{III} complex with chelate phosphine oxide ligand, Eu(TTA)$_3$(DPEPO), was designed and synthesized. It is demonstrated that the chelate phosphine oxide ligand DPEPO can not only be favorable to form the rigid structure of the complex that is important to avoid the structure relaxation in excited state, but also can improve energy transfer between two diphenyl phosphine oxide moieties so as to reduce the formation of exciplex. Furthermore, the compact structure of DPEPO and the interaction between the O atom of ether moiety and Eu^{III} make the energy transfer from TTAs to Eu^{III} more efficient. In particular, DPEPO has the T$_1$ energy level between the S$_1$ and T$_1$ energy levels of TTA. This might enable energy transfer from the T$_1$ excited state of DPEPO to that of TTA, which cannot occur in the complexes containing TPPO or phen. These effects make the complex have the prominent PL efficiency of 55.3% and the EL maximum current efficiency of 4.58 cd A^{-1} (corresponding to η_{ext} of 2.89%). Eu(TTA)$_3$(DPEPO) seems attractive for practical applications due to the excellent spectral stability, high brightness, and high current and power efficiency at the brightness of 100 cd m^{-2}. It is shown that DPEPO could serve as an effective potential ligand to afford high performance organolanthanide-based electroluminescent materials. Most importantly, this compound shows the huge potential of the chelate phosphine oxide derivatives serving as ligands of the luminescent lanthanide complexes due to the easy modification and synthesis.

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