Inorg. Chem. **2005**, *44*, 8929–8936

Tuning the Triplet Energy Levels of Pyrazolone Ligands to Match the $^5D_0$ Level of Europium(III)

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Received May 25, 2005

Three pyrazolone-based ligands, namely 1-phenyl-3-methyl-4-(1-naphthoyl)-5-pyrazolone (**HL1**), 1-phenyl-3-methyl-4-(4-dimethylaminobenzoyl)-5-pyrazolone (**HL2**), and 1-phenyl-3-methyl-4-(4-cyanobenzoyl)-5-pyrazolone (**HL3**), were synthesized by introducing electron-poor or electron-rich aryl substituents at the 4-position of the pyrazolone ring. Their corresponding europium complexes Eu(**L*X***)$_3$(H$_2$O)$_2$ and Eu(**L*X***)$_3$(TPPO)(H$_2$O) (***X*** = 1–3) were characterized by photophysical studies. The characteristic Eu(III) emission of these complexes with at most 9.2×10^{-3} of fluorescent quantum yield was observed at room temperature. The results show that the modification of ligands tunes the triplet energy levels of three pyrazolone-based ligands to match the $^5D_0$ energy level of Eu^{3+} properly and improves the energy transfer efficiency from antenna to Eu^{3+}, therefore enhancing the Eu(III) emission intensity. The highest energy transfer efficiency and probability of lanthanide emission of Eu(**L1**)$_3$(H$_2$O)$_2$ are 35.1% and 2.6%, respectively, which opens up broad prospects for improving luminescent properties of Eu(III) complexes by the modification of ligands. Furthermore, the electroluminescent properties of Eu(**L1**)$_3$(TPPO)(H$_2$O) were also investigated.

Introduction

On the basis of the unique photophysical properties of lanthanide cations (long luminescence lifetime and very sharp emission band),[1] rare earth metal complexes, especially europium(III) complexes, as luminescent materials have received increasing attention for application in bioassays[2] and sensor systems.[3] It is well-known that the application of the strong absorbing "antennae" for light harvesting is required for the low extinction coefficients of the lanthanide ions. The β-diketone ligand is one kind of important "antenna", from which the energy can be effectively transferred to Eu(III) and Tb(III) ions for high harvest emissions.[4–6] For example, the terbium complexes based on the pyrazolone-based ligands 1-phenyl-3-methyl-4-isobutyryl-5-pyrazolone (**HL4**)[7] and 1-phenyl-3-methyl-4-(2-ethylbutyryl)-5-pyrazolone (**HL5**)[8] (see Chart 1) can emit characteristic Tb(III) photoluminescence with high quantum yield.

Recently, europium complexes have attracted more interest in organic light-emitting diodes (OLED) for their saturated red-emission.[5,9–17] Although several europium complexes have been applied as red emitters in electroluminescent (EL) devices, their ligands are mainly limited to 1,3-diphenyl-

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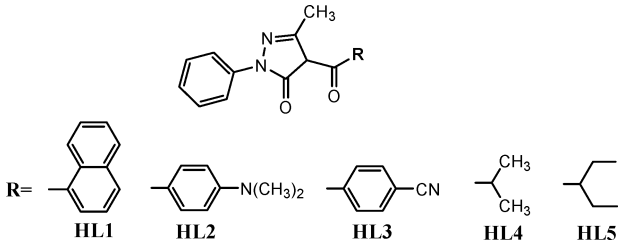
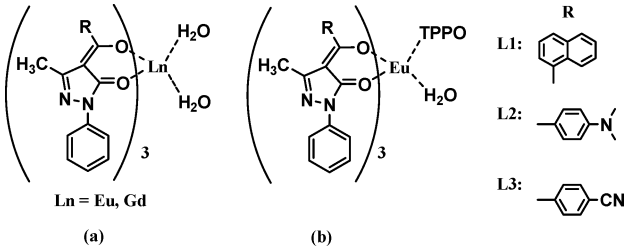
10.1021/ic050844p CCC: $30.25
Published on Web 11/02/2005

Chart 1. Molecular Structures of the Pyrazolone-Based Ligands

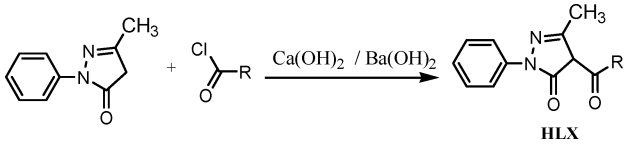


1,3-propanedione (HDBM) and α-thenoyltrifluoroacetone (HTTA).[9−14] However, the electroluminescent properties of these europium complexes[13] have not been as satisfactory as those of the terbium complexes[8] up to now. One of the important reasons is the poor carrier transporting property of these europium complexes.[5,8,18] In our previous study, we noticed that the pyrazolone-based ligands (**HL4**)[7] and (**HL5**)[8] with an alkyl group at the 4-position of pyrazolone ring not only have suitable triplet energy levels matching $^5D_4$ (20 400 cm^{-1}) of Tb^{3+} but also have good carrier transporting properties. The OLED device based on tris[1-phenyl-3-methyl-4-(2-ethylbutyryl)-5-pyrazolonato](triphenylphosphine oxide)terbium [Tb(**L5**)$_3$(TPPO)] exhibited good electroluminescent properties (11 lm W^{-1}).[8] However, the triplet energy level of **HL5** is too high for the $^5D_0$ (17 500 cm^{-1}) energy level of Eu^{3+}, so that this ligand is not suitable to be used as a sensitizer for europium(III) ion. To reduce the triplet energy level of the pyrazolone-based ligand, herein, 1-phenyl-3-methyl-4-(1-naphthoyl)-5-pyrazolone (**HL1**), 1-phenyl-3-methyl-4-(4-(dimethylamino)benzoyl)-5-pyrazolone (**HL2**) and 1-phenyl-3-methyl-4-(4-cyanobenzoyl)-5-pyrazolone (**HL3**) (see Chart 1) were synthesized by introducing electron-poor or electron-rich aryl substituents into the 4-position of the pyrazolone ring. Their corresponding lanthanide (Ln = Eu, Gd) complexes (see Chart 2) were obtained and investigated by measuring their photophysical properties.

Chart 2. Molecular Structures of the Eu(III) Complexes with the Pyrazolone-Based Ligands (**L1**−**L3**)



Scheme 1. Synthesis Route of the Pyrazolone Ligands



Experimental Section

Materials and Apparatus. 2,9-Dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP), 1-phenyl-3-methyl-5-pyrazolone, 4-*N*,*N*-dimethylaminobenzoyl chloride, 4-cyanobenzoyl chloride, and 1-naphthoyl chloride were obtained from Acros. *N*,*N*′-Diphenyl-*N*,*N*′-bis(1-naphthyl)-1,1′-diphenyl-4,4′-diamine (NPB) was purchased from Aldrich. Tris(8-hydroxyquinolinato)aluminum (AlQ) was synthesized in our laboratory and sublimed twice before use. The lanthanide oxides were purchased from Shanghai Yuelong Co., Ltd., and the lanthanide nitrate hexahydrates were synthesized in our laboratory. Indium tin oxide (ITO) glass substrate with a sheet resistance of 15 Ω/□ was kindly supplied by China Southern Glass Holding Co. Ltd.

The photoluminescence spectra were measured on an Edinburgh LFS920 fluorescence spectrophotometer. UV−visible absorption spectra were recorded using a Shimadzu 3000 UV−vis−NIR spectrophotometer. NMR spectra were recorded on Mercury Plus 400NB NMR spectrometer. The luminance−current−voltage (*B*−*I*−*V*) curves were measured with a computer-controlled Keithley 2400 sourcemeter unit with a calibrated silicon diode. The EL luminescence and chromaticity values were measured using a Photo Research PR-650 spectrophotometer. The element analyses were performed with VarioEL III O-Element analyzing system. Fluorescence lifetime was recorded on a single photon counting spectrometer from Edinburgh Instruments (FLS920) with microsecond pulse lamp as the excitation source. The data were analyzed by iterative convolution of the luminescence decay profile with the instrument response function using a software package provided by Edinburgh Instruments.

General Procedure for Synthesis of the Ligands. The ligands (**HL1**−**HL3**) were synthesized according to the method reported previously[19] (see Scheme 1). 1-Phenyl-3-methyl-5-pyrazolone (0.05 mol) and 150 mL of dried 1,4-dioxane were placed in a 50 mL flask with a magnetic stirrer and heated at 70 °C for 10 min. To the resulting yellow solution, calcium hydroxide (0.12 mol) and barium hydroxide (0.03 mol) in small portions were added, and then the corresponding acyl chloride (0.058 mol) was added dropwise. The resulting mixture was heated to reflux for 24 h. The cloudy yellowish mixture was cooled to room temperature and

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poured into a 350 mL solution of ice-cold hydrochloric acid (3 mol L^{-1}) under stirring. The yellow precipitate was filtered and recrystallized from acetone and water.

1-Phenyl-3-methyl-4-(1-naphthoyl)-5-pyrazolone (HL1). Yield: 62%. Mp: 167−169 °C. ^{1}H NMR (DMSO, 400 MHz, TMS): δ 8.039 (d, J = 7.2 Hz, 1H; ph-H), 8.002 (d, J = 6.8 Hz, 1H; ph-H), 7.953 (d, J = 7.2 Hz, 1H; ph-H), 7.661 (d, J = 7.2 Hz, 2H; ph-H), 7.583 (m, 4H; ph-H), 7.464 (t, J = 6.4 Hz, 2H; ph-H), 7.296 (t, J = 7.6 Hz, 1H; ph-H), 1.879 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$): δ 193.1, 161.2, 148.9, 137.4, 135.6, 133.7, 131.2, 129.9, 129.4, 128.8, 127.7, 127.0, 126.9, 125.6, 125.1, 125.0, 121.0, 105.6, 14.9.

1-Phenyl-3-methyl-4-(4-dimethylaminobenzoyl)-5-pyrazolone (HL2). Yield: 55%. Mp: 194−195 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ 7.911 (d, J = 8 Hz, 2H; ph-H), 7.656 (d, J = 8 Hz, 1H; ph-H), 7.456 (t, J = 6 Hz, 2H; ph-H), 7.268 (t, J = 5.2 Hz, 1H; ph-H), 6.740 (d, J = 7.6 Hz, 2H; ph-H), 3.088 (s, 6H; N−CH_3), 2.298 (s, 3H; CH_3). ^{13}C NMR ($CDCl_3$): δ 188.5, 163.5, 153.5, 147.8, 138.0, 131.3, 129.2, 126.3, 123.2, 120.6, 110.9, 103.1, 40.3, 17.0.

1-Phenyl-3-methyl-4-(4-cyanobenzoyl)-5-pyrazolone (HL3). Yield: 78%. Mp: 177−179 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ 7.835 (m, 4H; ph-H), 7.738 (d, J = 8 Hz, 2H; ph-H), 7.485 (t, J = 7.6 Hz, 2H; ph-H), 7.337 (t, J = 7.6 Hz, 1H; ph-H), 2.048 (s, 3H; CH_3). ^{13}C NMR ($CDCl_3$): δ 191.1, 160.9, 147.4, 142.1, 137.1, 132.6, 129.5, 128.5, 127.4, 121.2, 118.1, 110.0, 103.7, 15.9.

Synthesis of the Complexes. The Eu(III) and Gd(III) complexes with the ligands **HL1**−**HL3** were synthesized according to the method reported previously.[8]

Eu(L1)$_3$(H$_2$O)$_2$, Tris[1-phenyl-3-methyl-4-(1-naphthoyl)-5-pyrazolonato]europium Dihydrate. A 1.0 mmol amount of $Eu(NO_3)_3\cdot 6H_2O$ was added to an ethanol solution containing 3.0 mmol of **HL1** under stirring, and the pH was adjusted to ca. 5 by dropwise adding of 3.0 mmol NaOH. The solution was stirred for 5 h to obtain the yellow solid product, which was washed using deionized water and dried. Anal. Calcd for $C_{63}H_{49}EuN_6O_8$: C, 64.67; H, 4.22; N, 7.18. Found: C, 64.85; H, 4.20; N, 7.25.

The other complexes were prepared and purified by the same procedure.

Eu(L2)$_3$(H$_2$O)$_2$, Tris[1-phenyl-3-methyl-4-(4-(dimethylamino)-benzoyl)-5-pyrazolonato]europium Dihydrate. Anal. Calcd for $C_{57}H_{58}EuN_9O_8$: C, 59.58; H, 5.09; N, 10.97. Found: C, 59.33; H, 5.34; N, 10.52.

Eu(L3)$_3$(H$_2$O)$_2$, Tris[1-phenyl-3-methyl-4-(4-cyanobenzoyl)-5-pyrazolonato]europium Dihydrate. Anal. Calcd for $C_{54}H_{40}EuN_9O_8$: C, 59.24; H, 3.68; N, 11.51. Found: C, 58.57; H, 3.82; N, 11.43.

Gd(L1)$_3$(H$_2$O)$_2$, Tris[1-phenyl-3-methyl-4-(1-naphthoyl)-5-pyrazolonato]gadolinium Dihydrate. Anal. Calcd for $C_{63}H_{49}GdN_6O_8$: C, 64.38; H, 4.20; N, 7.15. Found: C, 64.75; H, 4.18; N, 7.11.

Gd(L2)$_3$(H$_2$O)$_2$, Tris[1-phenyl-3-methyl-4-(4-(dimethylamino)benzoyl)-5-pyrazolonato]gadolinium Dihydrate. Anal. Calcd for $C_{57}H_{58}GdN_9O_8$: C, 59.31; H, 5.06; N, 10.92. Found: C, 59.82; H, 4.93; N, 11.45.

Gd(L3)$_3$(H$_2$O)$_2$, Tris[1-phenyl-3-methyl-4-(4-cyanobenzoyl)-5-pyrazolonato]gadolinium Dihydrate. Anal. Calcd for $C_{54}H_{40}GdN_9O_8$: C, 58.95; H, 3.66; N, 11.46. Found: C, 58.34; H, 3.74; N, 11.03.

Eu(L1)$_3$(TPPO)(H$_2$O), Tris[1-phenyl-3-methyl-4-(1-naphthoyl)-5-pyrazolonato](triphenylphosphine oxide)europium Hydrate. A 1.0 mmol amount of $Eu(NO_3)_3\cdot 6H_2O$ was added to an ethanol solution containing 3.0 mmol of HL1 and 1.0 mmol of triphenylphosphine oxide, and after stirring, 3.0 mmol of NaOH was added dropwise with the pH being about 5. The solution was stirred for 5 h to obtain the yellowish solid product. The product was washed using deionized water and dried. Anal. Calcd for $C_{81}H_{62}EuN_6O_8P$: C, 68.02; H, 4.37; N, 5.88. Found: C, 68.69; H, 4.75; N, 5.33.

Eu(L2)$_3$(TPPO)(H$_2$O), Tris[1-phenyl-3-methyl-4-(4-(dimethylamino)benzoyl)-5-pyrazolonato](triphenylphosphine oxide)europium Hydrate. Anal. Calcd for $C_{75}H_{71}EuN_9O_8P$: C, 63.92; H, 5.08; N, 8.94. Found: C, 64.10; H, 5.34; N, 8.58.

Eu(L3)$_3$(TPPO)(H$_2$O), Tris[1-phenyl-3-methyl-4-(4-cyanobenzoyl)-5-pyrazolonato](triphenylphosphine oxide)europium Hydrate. Anal. Calcd for $C_{72}H_{53}EuN_9O_8P$: C, 63.81; H, 3.94; N, 9.30. Found: C, 64.23; H, 3.94; N, 8.99.

Crystallography. The crystals of **HL2** and Eu(**L3**)$_3$(TPPO)(H$_2$O) were mounted on glass fibers and transferred to a Bruker SMART CCD area detector. Crystallographic measurements were carried out using a Bruker SMART CCD diffractometer, with σ scans and graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å), at room temperature. The structures were solved by direct methods and refined by full-matrix least-squares on F^2 values using the program SHELXS-97.[20] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were calculated in ideal geometries. For the full-matrix least-squares refinements [$I > 2\sigma(I)$], the unweighted and weighted agreement factors of $R1 = \Sigma(F_o - F_c)/\Sigma F_o$ and $wR2 = [\Sigma w(F_o^2 - F_c^2)_2/\Sigma w F_o^4]^{1/2}$ were used. The crystal data and details of the structure determinations are summarized in Table 1. CCDC reference nos.: 225972 for **HL2** and 271332 for Eu(**L3**)$_3$(TPPO)(H$_2$O).

Table 1. Crystal Data, Collection, and Structure Refinement Parameters

param	**HL2**	Eu(**L3**)$_3$(tppo)(H$_2$O)
empirical formula	$C_{19}H_{18}N_3O_2$	$C_{72}H_{53}EuN_9O_8P$
fw	320.36	1355.16
cryst system	monoclinic	triclinic
space group	$P2_1/c$	$P\bar{1}$
cryst size	0.20 × 0.10 × 0.05	0.20 × 0.18 × 0.12
a/Å	7.625(2)	14.161(3)
b/Å	17.919(6)	15.122(3)
c/Å	12.219(4)	17.272(4)
α (deg)	90	100.72(3)
β (deg)	106.286	111.64(3)
γ (deg)	90	106.88(3)
V/Å^3	1602.5(9)	3106.0(11)
Z	4	2
ρ_{calcd}/g cm^{-3}	1.328	1.449
μ/mm^{-1}	0.088	1.102
F(000)	676	1380
R1 [$I > 2\sigma(I)$]	0.0587	0.0499
wR2 [$I > 2\sigma(I)$]	0.1676	0.1053
R1 (all data)	0.0884	0.0990
wR2 (all data)	0.1863	0.1195
GOF	0.949	0.908

Preparation of EL Devices. Electroluminescent devices based on the europium complex were fabricated through vacuum deposition of the materials onto clean glass precoated with a layer of indium tin oxide at 10^{-5} Pa. The rates of deposition of each organic compound were 1−2 Å s^{-1} and for the europium complex were 0.1−0.2 Å s^{-1}. The cathode was formed through coevaporation of Mg and Ag with Mg:Ag ratio of 10:1, followed by vacuum deposition of Ag (80 nm). The emitting diode has an effective area of 4.0 mm^2. The thickness of the deposited layer and the evaporation

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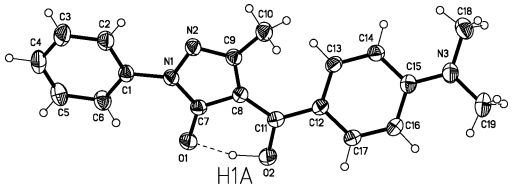

Figure 1. ORTEP diagram of **HL2** with the thermal ellipsoids drawn at the 30% probability level.

speed of the individual materials were monitored in a vacuum with quartz crystal monitors.

Results and Discussion

Synthesis and Characterization of the Ligands. 1-Phenyl-3-methyl-4-(*R*)-5-pyrazolone ligands (**HL*X***, ***X*** = 1−3) were prepared according to Scheme 1 and characterized by NMR. The resulting compounds are soluble in ethanol, chloroform, acetonitrile, and dimethyl sulfoxide. No obvious ^{1}H NMR signals of the hydrogen atom linked to the carbon atom of the pyrazolone ring were observed for all ligands, indicating that the enol configuration of β-diketonate formed.[1b] This conclusion was confirmed further by the crystallographic data for the ligand **HL2**.

The crystallographic data for **HL2** are listed in Table 1. An ORTEP diagram for the common repeating unit is shown in Figure 1. The molecular structure of **HL2** reveals a planar arrangement of non-hydrogen atoms (O2, C11, C8, C7, O1, mean deviation of 0.0362 Å), and H1A lies 0.0318 Å from this plane. The carbonyl bond lengths for C11−O2 and C7−O1 are 1.30(5) and 1.28(7) Å, respectively. There is an intramolecular hydrogen bond between the atoms O1 and O2 (O2−H1A···O1, 2.529 Å, 160.3°). These data suggest that, in the ring consisting of O1/O2, the enolic proton is not shared symmetrically with the carbonyl oxygens; that is, **HL2** exists in the enol form in the solid state. Although the phenyl plane consisting of C1−C6 and the pyrazolone ring (mean deviation of 0.0632 Å) are almost in a plane, in which the dihedral angle is 5.2°, the whole molecule is not coplanar, and the dihedral angle between the pyrazolone ring and the phenyl plane consisting of C12−C17 is 42.5°.

Structure Characterization of Eu(L3)$_3$(TPPO)(H$_2$O). The structure of Eu(**L3**)$_3$(TPPO)(H$_2$O) was characterized by X-ray crystallography. Details of the crystal data and data collection parameters for Eu(**L3**)$_3$(TPPO)(H$_2$O) are given in Table 1. An ORTEP diagram for the asymmetric unit of Eu(**L3**)$_3$(TPPO)(H$_2$O) is shown in Figure 2. The coordination geometry of the metal center is best described as a distorted bicapped trigonal prism with the trigonal prism being composed of six oxygen atoms (O1, O2, O3, O5, O6, O8). Among them, O1, O2 and O5, O6 are from two β-diketones, and O3 and O8 are from the third diketone and a water molecule, respectively. Another two oxygen atoms (O4, O7) cap the two quadrilateral faces O3−O5−O8−O1 and O2−O6−O3−O1, respectively. The average Eu−O distance is 2.39(6) Å [2.34(4)−2.49(0) Å], which is little smaller than the sum of the radii of Eu^{3+} (1.07 Å, eight coordinated) and O^{2-} (1.42 Å).[1b] It is noted that, in this complex, the bischelate rings are coplanar. The band lengths between the oxygen

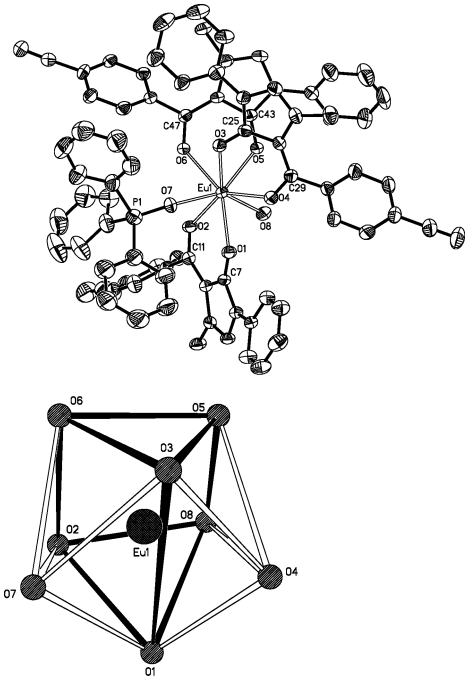

Figure 2. ORTEP diagram of Eu(**L3**)$_3$(TPPO)(H$_2$O) with the thermal ellipsoids drawn at the 30% probability level and the H atoms removed for clarity.

and the carbon atoms of the β-diketonato anions are almost unified (1.26(3), 1.24(8), 1.26(5), 1.26(6), 1.26(9), and 1.26(2) Å corresponding to O1−C7, O2−C11, O3−C25, O4−C29, O5−C43, and O6−C47, respectively), implying that strong conjugation exists in the chelate rings.

UV−Vis Spectra. UV−vis absorption spectra of the ligands (**HL1**−**HL3**) and their corresponding Eu(III) complexes are shown in Figure 3. The maximum absorption bands at 282, 350, and 293 nm for the ligands **HL1**−**HL3**, respectively, are attributed to singlet−singlet $\pi-\pi^*$ enol absorption of β-diketonates. Compared with the ligand **HL4** (λ_{max} = 262 nm), the absorption peaks are red-shifted 20, 88, and 31 nm for **HL1**−**HL3**, respectively. Interestingly, the UV−vis maximum band is red-shifted to 350 nm for **HL2**, indicating that the conjugation degree enlarges and the $\pi-\pi^*$ energy level is lowered by introduction of the *N*,*N*-dimethylaminobenzoyl group. Furthermore, compared with the spectra of the ligands **HL1**−**HL3**, the first absorption bands of the corresponding europium complexes are all red-shifted 6−10 nm, which is a consequence of the enlargement of the conjugate structure of ligands after coordinating to the lanthanide ion. The spectral shapes of the Eu(III) complexes in $CHCl_3$ are similar to those of the corresponding ligands, indicating that the coordination of the europium ion does not significantly influence the energy of the singlet state of the β-diketone ligands. The molar absorption coefficients (ϵ) of **HL1**−**HL3** are calculated as 1.8×10^4 (282 nm), 1.9×10^4 (350 nm), and 1.3×10^4 (293 nm) L·mol^{-1}·cm^{-1}, respectively, revealing that these ligands have a strong ability of absorbing light. Similarly, the determined molar absorption coefficients (ϵ) of the complexes Eu(**L*X***)$_3$(H$_2$O)$_2$ (***X*** = 1−3) were 6.1×10^4 (288 nm), 5.5×10^4 (360 nm), and 3.5×10^4 (301 nm) L·mol^{-1}·cm^{-1}, respectively, which are about

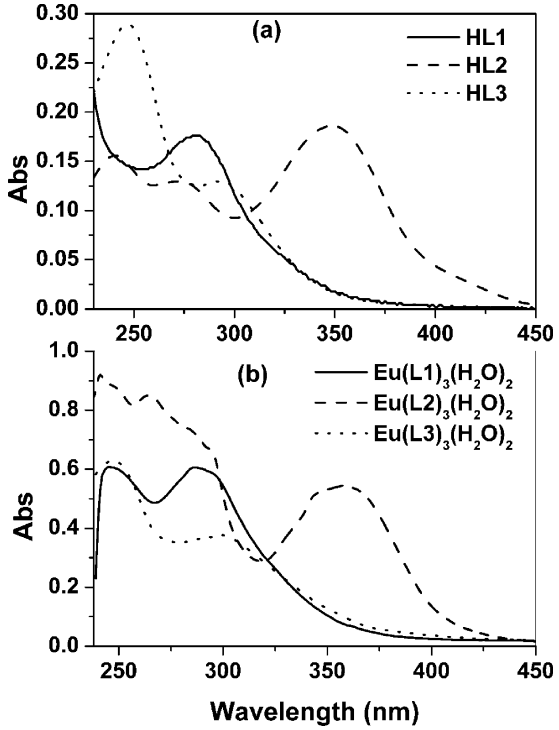

Figure 3. Absorption spectra of the ligands (a) and their Eu(III) complexes (b) in $CHCl_3$ solution ($c = 1.0 \times 10^{-5}$ M).

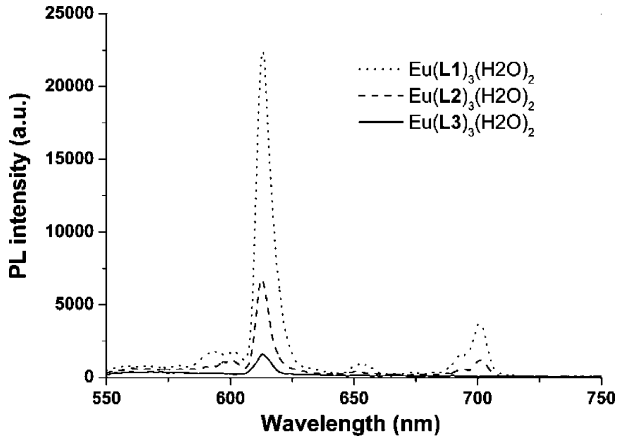

Figure 4. Luminescence spectra of Eu(**L*X***)$_3$(H_2O)$_2$ (***X*** = 1−3) at 298 K. The intensities are relative to the fluorescence intensity of Eu(**L1**)$_3$(H_2O)$_2$.

three times of those of the corresponding ligands, indicating the presence of three ligands/complex molecule.

Fluorescence Spectra. The red luminescence, characteristic of $^5D_0 \rightarrow {}^7F_J$ ($J = 0-4$) emission bands of Eu^{3+} was observed when Eu(**L*X***)$_3$(H_2O)$_2$ (***X*** = 1−3) were excited at 290 nm (see Figure 4). However, the fluorescent intensities of these complexes are different. The excitation spectra of Eu(**L1**)$_3$(H_2O)$_2$, Eu(**L2**)$_3$(H_2O)$_2$, and Eu(**L3**)$_3$(H_2O)$_2$ with band maxima at 284, 349, and 295 nm, respectively, match the corresponding absorption spectra, confirming that energy transfer takes place from the ligands to Eu^{3+} ion. We also investigated the emission spectra of the complexes Eu(**L*X***)$_3$(H_2O)$_2$ (***X*** = 1−3) in the different solvents, such as CH_3CN, $CHCl_3$, DMF, and DMSO. The similarity of the emission patterns in these solvents suggests that there are no solvent-dependent structural changes in the complexes.

Photophysical Properties of the Complexes. The data for photophysical properties for Eu(**L*X***)$_3$(H_2O)$_2$ (***X*** = 1−3) are shown in Table 2. The overall luminescent quantum yields ($\phi_{overall}$) of these europium complexes were measured using Rhodamine B in ethanol (2.0×10^{-5} mol/L, $\phi_{ref} = 0.69$)[21] as a reference and were calculated according to the well-known method given

$$\phi_{overall} = \frac{n^2 A_{ref} I}{n_{ref}{}^2 A I_{ref}} \phi_{ref} \quad (1)$$

Here n, A, and I denote the refractive index of solvent, the area of the emission spectrum, and the absorbance at the excitation wavelength, respectively. Subscript ref denotes the reference, and no subscript denotes the unknown sample. The refractive index is assumed to be equivalent to that of the pure solvent: 1.361 for ethanol and 1.344 for CH_3CN at room temperature. The overall fluorescent quantum yields ($\phi_{overall}$) of Eu(**L1**)$_3$(H_2O)$_2$, Eu(**L2**)$_3$(H_2O)$_2$, and Eu(**L3**)$_3$(H_2O)$_2$ were calculated as 9.2×10^{-3}, 3.1×10^{-3}, and 4.0×10^{-4}, respectively, revealing that the structural change of the ligands affects the fluorescent quantum yields of the Eu(III) complexes.

The luminescence lifetimes (τ) were also investigated for these complexes except for Eu(**L3**)$_3$(H_2O)$_2$ due to its very weak fluorescent intensity. The measured luminescent decays (see ESI) of Eu(**L1**)$_3$(H_2O)$_2$ and Eu(**L2**)$_3$(H_2O)$_2$ can be described by monoexponential kinetics, which suggests that in these complexes only one species exists in the excited state. In combination with the data for the fluorescent intensities, the data for the fluorescent lifetimes show that the higher the fluorescent intensities, the longer the fluorescent lifetimes are for the complexes (see Table 2). According to the above results of fluorescence and phosphorescence properties of the europium complexes, we can conclude that the modification of the ligands is effective.

To understand the effect of the ligand modification on the fluorescence properties of Eu(**L*X***)$_3$(H_2O)$_2$ (***X*** = 1−3), the efficiency of energy transfer ($\phi_{transfer}$) from the ligand to Eu^{3+} and the probability of the europium emission (ϕ_{Ln}) were investigated on the basis of the method developed by Selvin et al.[22] The overall quantum yield ($\phi_{overall}$) of the europium complex treats the complex as a "black box" where internal processes are not explicitly considered: given that complex absorbs a photon (i.e. the antenna is excited), the overall quantum yield can be defined as

$$\phi_{overall} = \phi_{transfer}\phi_{Ln} \quad (2)$$

When a lanthanide chelate is mixed with an acceptor of known quantum yield and very short fluorescence lifetime (ns), the efficiency of energy transfer between them (ϕ_{ET}) and the probability of lanthanide emission (ϕ_{Ln}) are calculated from both fluorescence decay lifetime and intensity measure-

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Table 2. Photophyscical Properties of Eu(**L*X***)$_3$(H$_2$O)$_2$ (***X*** = 1−3) in Acetonitrile

compd	λ_{max}^{abs}/nm ($10^{-4}\epsilon$/dm^3 mol^{-1} cm^{-1})	S_1/cm^{-1}	λ_{max}^{phos}/nm[b]	T_1/cm^{-1}	λ_{max}^{PL}/nm[c]	τ/μs (χ^2)[c]	$\phi_{overall}$ ($\times 10^3$)	ϕ_{Ln}/%	$\phi_{transfer}$/%	k_{rad}/s^{-1}	$10^{-4}k_{nr}$/s^{-1}
Eu(**L1**)$_3$(H$_2$O)$_2$	288 (6.1)	∼28 900	554	∼19 600	614	31.50 (1.10)	9.2	2.6	35.1	835	3.13
Eu(**L2**)$_3$(H$_2$O)$_2$	360 (5.5)	∼24 450	525	∼19 900	614	18.57 (1.12)	3.1	1.9	16.1	1050	5.28
Eu(**L3**)$_3$(H$_2$O)$_2$	301 (3.5)	∼27 027	593	∼18 200	614		0.4				
Eu(**L4**)$_3$(H$_2$O)$_2$	265 (3.5)	∼32 785	460	∼23 500							

[a] S_1: singlet energy level. T_1: triplet energy level. χ^2 is called the "reduced chi-square". [b] Emission band maximum at 77 K. [c] Emission band maximum and decay lifetimes in CH_3CN solution at room temperature.

ments as the following:

$$\phi_{ET} = 1 - (\tau_{da}/\tau_d) \quad (3)$$

$$\phi_{Ln} = \phi_a(I_{da}/I_{ad})/(1/\phi_{ET} - 1) = \phi_a I_{da}(\tau_d - \tau_{ad})/(I_{ad}\tau_{ad}) \quad (4)$$

Here ϕ_a is the fluorescence quantum yield of the acceptor, τ_{ad} and τ_d are the lanthanide complex's excited-state lifetime in the presence and absence of the acceptor respectively, I_{da} is the area under the residual lanthanide emission in the presence of the acceptor, and I_{ad} is the area of the fluorescent emission part of the acceptor.

Here, the acceptor was Rhodamine B in acetonitrile, $\phi = 0.52$ and $\tau < 10$ ns. For example, in a mixture solution consisted of 10 μM Eu(**L1**)$_3$(H$_2$O)$_2$ and 1 μM Rhodamine B, the emission lifetime of the Eu(III) complex ($\lambda_{em} = 614$ nm) decreased from 31.50 to 29.4 μs, indicating that 6.7% of energy transferred to Rhodamine B. From these measurements and eq 4, the quantum yield (ϕ_{Ln}) of Eu^{3+} in Eu(**L1**)$_3$(H$_2$O)$_2$ was determined to be 2.6% (in Table 2). Similarly, the other quantum yield (ϕ_{Ln}) of Eu^{3+} was 1.9% for Eu(**L2**)$_3$(H$_2$O)$_2$ (in Table 2). In combination with the overall quantum yields ($\phi_{overall}$) of Eu(**L1**)$_3$(H$_2$O)$_2$ and Eu(**L2**)$_3$(H$_2$O)$_2$, we can calculate the efficiency ($\phi_{transfer}$) of energy transfer from the ligand to Eu^{3+} according to eq 2. It can be seen from Table 2 that $\phi_{transfer}$ values of the complexes Eu(**L1**)$_3$(H$_2$O)$_2$ and Eu(**L2**)$_3$(H$_2$O)$_2$ were 35.1% and 16.1%, respectively. However, for its very weak fluorescence emission, we did not obtain the quantum yield (ϕ_{Ln}) and the energy transfer efficiency ($\phi_{transfer}$) for Eu(**L3**)$_3$(H$_2$O)$_2$.

With ϕ_{Ln} and τ_d determined in acetonitrile, radiative and nonradiative decay rates for the Eu(III) complexes were calculated via the following:

$$k_{rad} = \phi_{Ln}/\tau_d \quad k_{nr} = (1 - \phi_{Ln})/\tau_d \quad (5)$$

Taking 2.6% of ϕ_{Ln} and 31.50 μs of τ_d into account, the radiative and nonradiative decay rates of Eu(**L1**)$_3$(H$_2$O)$_2$ were 835 and 3.13×10^4 s^{-1}, respectively. Similarly, the radiative and nonradiative decay rates of Eu(**L2**)$_3$(H$_2$O)$_2$ were 1050 and 5.28×10^4 s^{-1} (in Table 2), respectively.

To elucidate the energy transfer process of the europium complexes, the energy levels of the relevant electronic states should be estimated. The singlet and triplet energy levels of **L1**−**L3** were estimated by referring to their wavelengths of UV−Vis absorbance edges and the lower wavelength emission edges of the corresponding phosphorescence spectra. It can be seen from Figure 3 that the wavelengths of absorbance

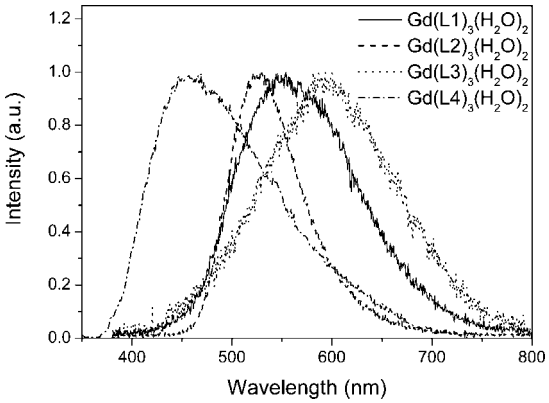

Figure 5. Phosphorescent spectra of Gd(**L*X***)$_3$(H$_2$O)$_2$ (***X*** = 1−4) at 77 K.

edge of the ligands **HL1**−**HL3** are 346, 409, and 370 nm, respectively, indicating that their singlet energy levels are ∼28 900, 24 450, and 27 027 cm^{-1}, respectively (see Table 2). The triplet energy level of the ligand was not affected significantly by the lanthanide ion, and the lowest lying excited level ($^6P_{7/2} \rightarrow {}^8S_{7/2}$) of Gd(III) is located at 32 150 cm^{-1}.[23] On this basis, the phosphorescence spectra of Gd(**L*X***)$_3$(H$_2$O)$_2$ (***X*** = 1−3) allow one to evaluate the $^3\pi\pi^*$ energy levels corresponding ligand anions **L*X*** (***X*** = 1−3) for all the lanthanide chelates. The phosphorescence spectra of Gd(**L1**)$_3$(H$_2$O)$_2$, Gd(**L2**)$_3$(H$_2$O)$_2$, and Gd(**L3**)$_3$(H$_2$O)$_3$ at 77 K present their bands with maxima at ca. 554 nm (18 050 cm^{-1}), 525 nm (19 048 cm^{-1}), and 593 nm (16 863 cm^{-1}), respectively, and their energies of zero-phonon transition of the triplet states ($^3\pi\pi^*$)[24] at about 19 600, 19 900 and 18 200 cm^{-1}, respectively (see Figure 5). Consequently, compared with the triplet energy level (23 500 cm^{-1}) of the ligand **L4** (see Figure 5), the triplet state levels were successfully lowered for the ligands (**L1**−**L3**) with electron-poor or electron-rich aryl substituents at the 4-position of the pyrazolone ring.

Generally, the sensitization pathway in luminescent europium complexes consists of excitation of the ligands into their excited singlet states, subsequent intersystem crossing of the ligands to their triplet states, and energy transfer from the triplet state to the ^5D_J manifold of the Eu^{3+} ion, following by internal conversion to the emitting $^5D_0$ state; finally, the

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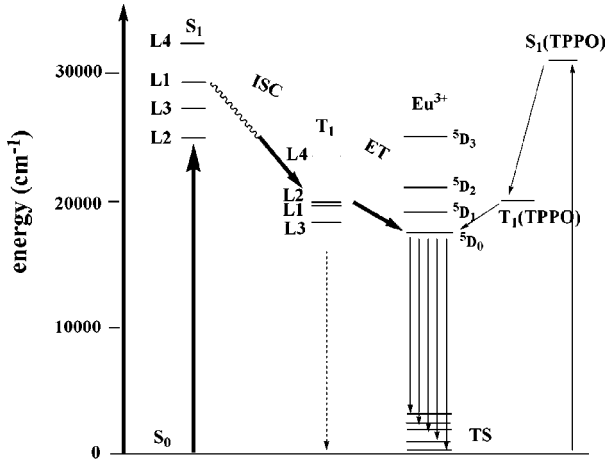

Figure 6. Schematic energy level diagram and the energy transfer process in the systems of Eu(**L*X***)$_3$·2H$_2$O (***X*** = 1−3). S_1: the first excited singlet state. T_1: the first excited triplet state.

Eu^{3+} ion emits when transition to the ground state occurs.[1,25] Moreover, the electron transition from the higher excited states, such as $^5D_3$ (24 800 cm^{-1}), $^5D_2$ (21 200 cm^{-1}), and $^5D_1$ (19 000 cm^{-1}), to $^5D_0$ (17 500 cm^{-1}) becomes feasible by internal conversion, and most of the photophysical processes take place in this orbital. Consequently, most europium complexes give rise to typical Eu(III) emission bands at ∼581, 593, 614, 654, and 702 nm corresponding to the deactivation of the excited state $^5D_0$ to the ground states ^7F_J (J = 0−4). Therefore, the energy level's match of the triplet state of the ligands to $^5D_0$ of Eu^{3+} is one of the key factors which affects the luminescent properties of the europium complexes.

According to the above experimental results, the schematic energy level diagram and the energy transfer process are shown in Figure 6. The triplet energy levels of **L1** (∼19 600 cm^{-1}), and **L2** (∼19 900 cm^{-1}) are obviously higher than the $^5D_0$ level (17 500 cm^{-1}) of Eu^{3+}, and their energy gaps $\Delta E(^3\pi\pi^*-^5D_0)$ between ligand- and metal-centered levels are ΔE > 2000 cm^{-1}, too high to allow an effective back energy transfer. According to Latva's empirical rule,[26] an optimal ligand-to-metal transfer process for Eu(III) needs $\Delta E(^3\pi\pi^*-^5D_0)$ > 2500 cm^{-1}; therefore, the ligand-to-metal transfer processes are effective for Eu(**L1**)$_3$(H$_2$O)$_2$ and Eu(**L2**)$_3$(H$_2$O)$_2$. We also noticed that the energy gap between the $^1\pi\pi^*$ and $^3\pi\pi^*$ levels are 9300 and 4550 cm^{-1} for the anions **L1** and **L2**, respectively (see Table 2). According to Reinhoudt's empirical rule that the intersystem crossing process becomes effective when $\Delta E(^1\pi\pi^*-^3\pi\pi^*)$ is at least 5000 cm^{-1},[27] we believe that the anions **L1** and **L2** (especially **L1**) are suitable as sensitizers for Eu(III) and that the intersystem crossing process of Eu(**L1**)$_3$(H$_2$O)$_2$ is more effective than that of Eu(**L2**)$_3$(H$_2$O)$_2$. Therefore, it is easy

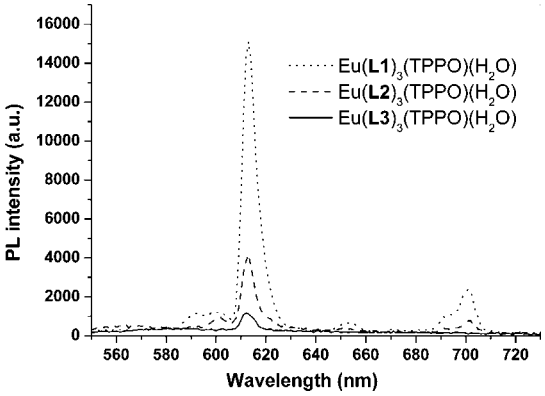

Figure 7. Luminescence spectra of Eu(**L*X***)$_3$(TPPO)(H$_2$O) (***X*** = 1−3) at room temperature. The intensities are relative to the fluorescence intensity of Eu(**L1**)$_3$(TPPO)(H$_2$O).

for us to understand that the fluorescent quantum yield of Eu(**L1**)$_3$(H$_2$O)$_2$ is higher than that of Eu(**L2**)$_3$(H$_2$O)$_2$ (see Table 2). On the contrary, the $^3\pi\pi^*$ state (∼18 200 cm^{-1}) of the anion **L3** is so close to $^5D_0$ (17 500 cm^{-1}) of Eu(III), giving $\Delta E(^3\pi\pi^*-^5D_0)$ = 700 cm^{-1}, too low to prevent thermally competitive back energy transfer from the Eu(III) excited state to the triplet state of **L3**, which predicts that little effective energy transfer takes place from the anion **L3** to Eu(III), resulting in a low fluorescence quantum yield (4.0 × 10^{-4}) of Eu(**L3**)$_3$(H$_2$O)$_2$.

Generally, the method of deoxygenating and reducing temperature becomes feasible to improve the quantum yield of the europium complexes.[28] Here, to improve the luminescence intensity, the stronger donor of triphenylphosphine oxide (TPPO)[29] with the triplet energy level of ∼20 000 cm^{-1} (see ESI) was introduced to exchange the coordinated water[30] and to form the ternary complexes Eu(**L*X***)$_3$(TPPO)(H$_2$O) (***X*** = 1−3). Figure 7 gives the luminescence spectra of Eu(**L*X***)$_3$(TPPO)(H$_2$O) (***X*** = 1−3). Compared to Eu(**L1**)$_3$(H$_2$O)$_2$, the quantum efficiency of Eu(**L1**)$_3$(TPPO)(H$_2$O) increases about 18%. Similarly, an increase of 24% was obtained for Eu(**L2**)$_3$(TPPO)(H$_2$O). Moreover, the fluorescence lifetime was increased to 33.7 μs for Eu(**L1**)$_3$(TPPO)(H$_2$O). Since the triplet energy level of TPPO matches the $^5D_0$ energy level of Eu^{3+}, the energy absorbed by TPPO could be transferred to Eu^{3+} ion directly (see Figure 6), leading to the enhancement of the emission quantum yields of the complexes Eu(**L*X***)$_3$(TPPO)(H$_2$O) (***X*** = 1, 2).

Electroluminescence Properties. For its good luminescent property, the complex Eu(**L1**)$_3$(TPPO)(H$_2$O) was used to fabricate the EL devices. No obvious light emission was obtained from the single-layer device A with the configuration of ITO/Eu(**L1**)$_3$(TPPO)(H$_2$O) (60 nm)/Mg:Ag$_{10:1}$ (200 nm)/Ag (80 nm). By using *N*,*N*′-diphenyl-*N*,*N*′-bis(1-naphthyl)-1,1′-diphenyl-4,4′-diamine (NPB) and tris(8-hydroxyquinolinato)aluminum (AlQ) as hole and electron trans-

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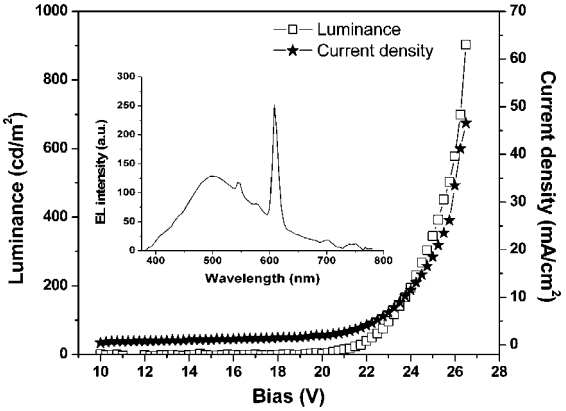

Figure 8. Current density−voltage (★) and luminance−voltage (□) curves of device B with the configuration of ITO/NPB (50 nm)/Eu(**L1**)$_3$(TPPO)-(H_2O):CBP (6%, 50 nm)/AlQ (40 nm)/Mg:$Ag_{10:1}$ (200 nm)/Ag (80 nm). Inset: EL spectrum (16 V).

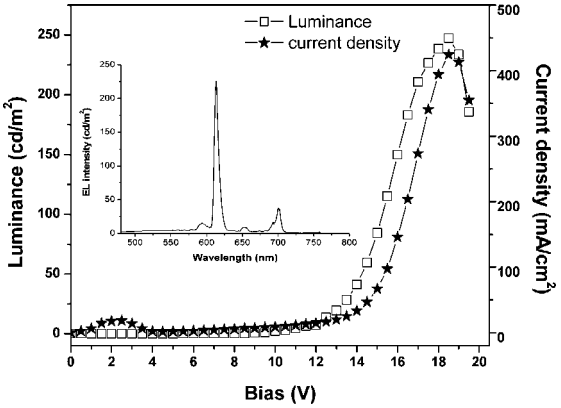

Figure 9. Current−voltage (★) and luminance−voltage (□) curves of device C with configuration of ITO/NPB (50 nm)/Eu(**L1**)$_3$(TPPO)(H_2O):CBP (15%, 50 nm)/BCP (20 nm)/AlQ (20 nm)/Mg:$Ag_{10:1}$ (200 nm)/Ag (80 nm). Inset: EL spectrum (18 V).

porting materials, respectively, and 4,4′-bis(carbazol-9-yl)biphenyl (CBP) as a host material, the three-layer device B with the configuration of ITO/NPB (50 nm)/Eu(**L1**)$_3$-(TPPO)(H_2O):CBP (6%, 50 nm)/AlQ (40 nm)/Mg:$Ag_{10:1}$ (200 nm)/Ag (80 nm) was fabricated. Figure 8 shows the EL spectrum of the device B. A broad EL emission peaked at 502 nm with a sharp emission peaked at 615 nm and the highest luminance of 920 cd·m^{-2} were observed, revealing that the emission of the device B was mainly from AlQ with a small amount of emission from the europium complex. After insertion of hole blocking material 2,9-dimethyl-4,7-diphenyl-1,10-phenyanthroline (BCP) between the europium complex and AlQ and improvement ofthe content of the Eu-(III) complex in CBP, device C with the configuration of ITO/NPB (50 nm)/Eu(**L1**)$_3$(TPPO)(H_2O):CBP (15%, 50 nm)/BCP (20 nm)/AlQ (20 nm)/Mg:$Ag_{10:1}$ (200 nm)/Ag (80 nm) was fabricated. Its EL spectrum is shown in Figure 9. Device C gave the characteristic emission of the central europium ion, indicating that the carrier recombination zone was well confined in the europium complex layer and their performance was 247 cd·m^{-2} at 18.5 V. Current−voltage ($I-V$) and luminance−voltage ($L-V$) curves of device C are also shown in Figure 9.

Conclusions

In conclusion, we have identified viable operating principles for the modulation of optical properties of the europium complexes by introducing electron-poor or electron-rich aryl substituents at 4-position of the pyrazolone ring. Three pyrazolone-based ligands **HL1**−**HL3** and their corresponding europium complexes Eu(**L*X***)$_3$(H_2O)$_2$ and Eu-(**L*X***)$_3$(TPPO)(H_2O) (***X*** = 1−3) were structurally and photophysically characterized. The experiment results prove that the modification of ligands not only alters the triplet state energy but also affects the quantum yield of Eu^{3+} emission and the energy transfer efficiency from the ligand to Eu^{3+}, finally resulting in the change of the overall emission quantum yield. The complex Eu(**L1**)$_3$(H_2O)$_2$ at room temperature exhibits 35.1% of energy transfer efficiency ($\phi_{transfer}$), 2.6% of probability of lanthanide emission (ϕ_{Ln}), and 9.2 × 10^{-3} of fluorescent quantum yield, which are the highest values in all europium complexes based on pyrazolone-based ligands up to now. Moreover, we used Eu(**L1**)$_3$(TPPO)(H_2O) as the emitter to fabricate successfully an OLED device with a saturated red electroluminescence of 247 cd·m^{-2}.

Acknowledgment. The authors thank the National Science Foundation of China (Grant 20490210), the NHTRDP (863 Program No. 2002AA302403), and Shanghai Sci. Tech. Comm. (Grants 03QB14006 and 03DZ12031) for financial support.

Supporting Information Available: Data for the crystal structure of **HL2** and Eu(**L3**)$_3$(TPPO)(H_2O) (CIF), decay lifetimes of Eu(**L1**)$_3$(H_2O)$_2$ and Eu(**L2**)$_3$(H_2O)$_2$, and the phosphorescent spectrum of Gd(NO_3)$_3$(TPPO)$_2$. This material is available free of charge via the Internet at http://pubs.acs.org.

IC050844P