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# A Comparative Study of the Optical and Electroluminescent Properties of $Eu^{III}$ Complexes with TTA and 2-(2′-Pyridyl)azoles: The Crystal Structure of $[Eu(TTA)_3(PBO)]$

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Two $Eu^{III}$ mixed-ligand complexes, namely $[Eu(TTA)_3(PBO)]$ and $[Eu(TTA)_3(PBT)]$ [TTA = 1,1,1-trifluoro-3-(2-thenoyl)acetonato, PBO = 2-(2′-pyridyl)-1,3-benzoxazole, and PBT = 2-(2′-pyridyl)-1,3-benzothiazole], have been synthesized. $[Eu(TTA)_3(PBO)]$ has been structurally characterized by single-crystal X-ray diffraction analysis. The complex crystallizes in the monoclinic space group *C*2/*c*. The lattice parameters are $a = 41.346(4)$, $b = 10.0538(8)$, $c = 20.3793(16)$ Å, $\beta = 110.922(2)°$, Z = 8. The $Eu^{III}$ ion is eight-coordinate, with three bidentate $TTA^-$ anions and one bidentate N,O-chelated PBO molecule. A comparative study by UV and emission spectroscopy was carried out and electroluminescent properties of the related complexes $[Eu(TTA)_3(PBO)]$ and $[Eu(TTA)_3(PBT)]$ are reported as well.
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## Introduction

$Eu^{III}$ complexes have attracted tremendous interest due to their highly monochromic red emission with large Stokes shifts and long emission lifetimes of up to a few milliseconds.[1] These materials have found widespread applications in chemical and earth sciences as well as bioinorganic chemistry, ranging from DNA binding properties to antibody labels in immunoassays.[1–3] A particularly important class of complexes is that of lanthanide β-diketonates, which have recently attracted attention in the development of new materials based on red, near-infrared, and white-light photo-conversion and switching/sensing molecular devices,[4] sol–gel glasses,[5] liquid crystals,[6] red-emitting electroluminescent devices,[7–9] supramolecular assemblies,[10] polymers,[11] and Langmuir–Blodgett (LB) and self-assembled ultrathin films.[12–14]

As far as $Eu^{III}$ β-diketonates developed for electroluminescent devices are concerned, [Eu(β-diketonate)$_3$L]-type complexes (L = bidentate neutral heterocyclic ligand) have played a very important role. It has been demonstrated that the introduction of L to replace the two coordinated water molecules in [Eu(β-diketonate)$_3$($H_2O$)$_2$] is imperative to obtain vapor volatility for vacuum deposition film-based electroluminescent devices.[15] However, as almost all of the bidentate neutral heterocyclic ligands are α-diimines such as 2,2′-bipyridine (bpy), 1,10-phenanthroline (phen), or their substitutional derivatives, in addition to 2,2′-bipyridine *N*-oxide and 1,10-phenanthroline *N*-oxide,[16] novel types of complexes are limited.[1–8] We have reported a series of [Eu(β-diketonate)$_3$(α-diimine)]-type complexes for electroluminescent devices,[8] and introduced amphiphilic complexes of this kind into Langmuir–Blodgett films.[13] To promote rapid development of these research fields, it is important to develop novel examples of such complexes.

In addition to the great interest in functional metal complexes based on bpy and phen derivatives, structurally analogous 2-(2′-pyridyl)azoles such as 2-(2′-pyridyl)-1,3-benzoxazole (PBO), 2-(2′-pyridyl)-1,3-benzothiazole (PBT), and 2-(2′-pyridyl)benzimidazole (PBI), which are structurally similar to 2,2′-bipyridine or 1,10-phenanthroline *N*-oxide,[16] have attracted special attention for use in electroluminescent devices, as radiopharmaceuticals based on metal complexes of $[Re^{I}(CO)_3(L)X]$ (X = halide),[17] when attached to $Re^{V}O^{3+}$ and $Tc^{V}O^{3+}$ cores,[18] for complexation with $Ru^{II}$,[19] $Pt^{II}$,[20] $Rh^{III}$ and $Pd^{II}$,[20b] $Mo^{V}$,[21] $Sn^{II}$,[22] and $Co^{II}$, $Zn^{II}$ and $Cu^{II}$ etc.,[23] and because of their structural and physicochemical properties. We have reported the electroluminescence properties of $Eu^{III}$ complexes with PBI,[8c,8i] but so far little attention has been paid to lanthanide complexes with 2-(2′-pyridyl)azoles.[24] Here, we present a comparative study of the optical and electrolumines-

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cence properties of $Eu^{III}$ complexes of $[Eu(TTA)_3(L)]$ [TTA = 1,1,1-trifluoro-3-(2-thenoyl)acetonato; L = PBO, PBT, and PBI], and a single-crystal X-ray structural characterization of $[Eu(TTA)_3(PBO)]$.

## Results and Discussion

### Synthesis

2-(2′-Pyridyl)-1,3-benzoxazole (PBO), 2-(2′-pyridyl)-1,3-benzothiazole (PBT), and 2-(2′-pyridyl)benzimidazole (PBI), and their $Eu^{III}$ complexes $[Eu(TTA)_3(PBO)]$, $[Eu(TTA)_3(PBT)]$, and $[Eu(TTA)_3(PBI)]$ were prepared according to the reactions shown in Figure 1. The three 2-(2′-pyridyl)azoles were obtained by direct condensation of picolinic acid with 2-aminophenol, 2-aminothiophenol, and 1,2-phenylenediamine, respectively, in a 1:1 molar ratio in the presence of polyphosphoric acid,[25] although there have been reports of the synthesis of PBO based on the oxidation of the appropriate Schiff bases by $Ag_2O$[26a] and by the palladium-catalyzed carbonylation and condensation of aromatic halides and *o*-aminophenols.[27] Single crystals of PBT suitable for X-ray diffraction analysis were obtained by recrystallization from $CH_2Cl_2$/hexane; its structure and lattice parameters are consistent with those reported previously.[26b] The reaction of $[Eu(TTA)_3(H_2O)_2]$ with L (L = PBO, PBT and PBI) in a 1:1 molar ratio in refluxing ethanol for 1 h, and then washing of the filtered product with hot ethanol, yielded satisfactorily pure $[Eu(TTA)_3(L)]$. $[Eu(TTA)_3(PBO)]$ was also structurally characterized by single-crystal X-ray diffraction.

### Crystal Structure

A molecular view and the crystal packing of $[Eu(TTA)_3(PBO)]$ are shown in Figures 2 and 3, respectively; selected bond parameters are listed in Table 1. As expected, the PBO ligand coordinates to the $Eu^{III}$ ion in an unusual N,O-chelation mode. The complex crystallizes in the monoclinic space group *C*2/*c* with lattice parameters $a$ = 41.346(4), $b$ = 10.0538(8), $c$ = 20.3793(16) Å, $\beta$ = 110.922(2)°, and $Z$ = 8. The complex is mononuclear and the $Eu^{III}$ ion is eight-coordinate, with six oxygen atoms of three bidentate $TTA^-$

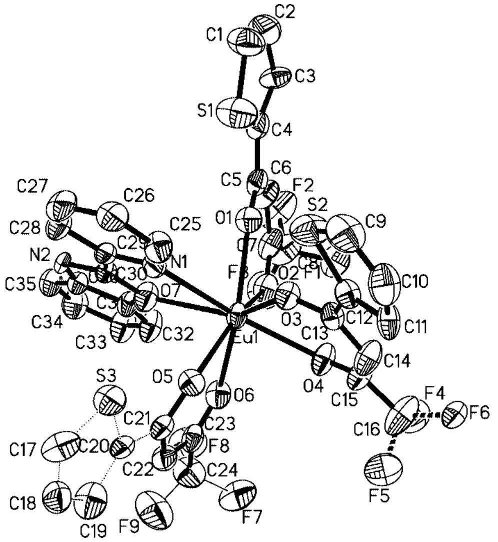

Figure 2. Asymmetric unit of $[Eu(TTA)_3(PBO)]$ with atom numbering scheme and thermal ellipsoids (30%).

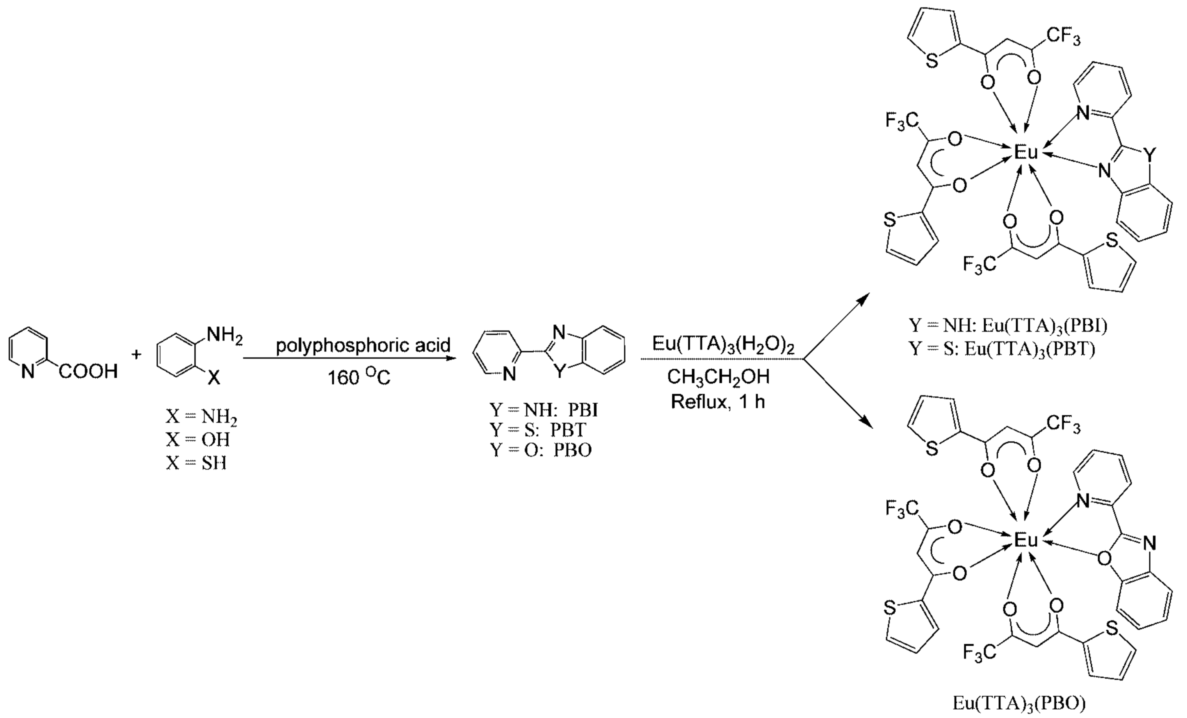

Figure 1. The synthetic routes to the $Eu^{III}$ complexes.

anions and one oxygen atom and one nitrogen atom of a bidentate PBO ligand. These atoms lie at the apices of a slightly distorted square antiprism. One of the two planes of the square antiprism is formed exclusively by oxygen atoms [O(1)–O(4)] and the other one by one nitrogen atom and three oxygen atoms [N(1) and O(5)–O(7)]. The two square planes are almost parallel to each other, as shown by the dihedral angle of 1.3°. The average bond lengths and angles of the TTA$^-$ ligands are similar to those reported for other TTA complexes.[28] The Eu–O bond lengths range from 2.33(2) to 2.58(2) Å, and the mean Eu–O(TTA) bond [2.36(2) Å] is 0.22 Å shorter than the average Eu–O(PBO) bond [2.58(2) Å], thus indicating that TTA has a stronger coordinating ability than PBO. The Eu−O bond in PBO of [Eu(TTA)$_3$(PBO)], however, is stronger than the Eu−N bonds found in [Eu(TTA)$_3$(PBO)], [Eu(DBM)$_3$(pip)] (DBM = dibenzoylmethanato; pip = 2-phenylimidazo[4,5-*f*]1,10-phenanthroline),[8h] and [Eu(DBM)$_3$(edapip)] {edapip = 3-ethyl-2-[4′-(dimethylamino)phenyl]imidazo[4,5-*f*]1,10-phenanthroline}.[8d] Interestingly, as shown in Figure 3, there is a π···π stacking interaction between two PBO molecular planes in two adjacent [Eu(TTA)$_3$(PBO)] molecules, with an interplanar distance of 3.354(1) Å and a dihedral angle of 0° between them.

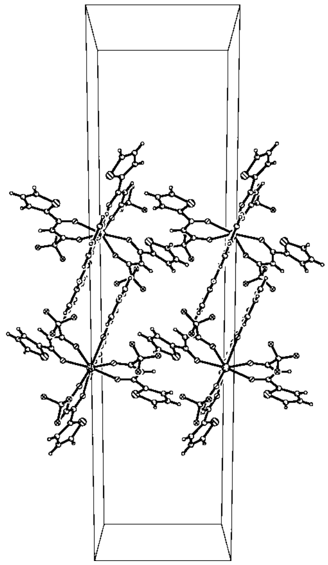

Figure 3. The molecular packing of [Eu(TTA)$_3$(PBO)] along the *a*-axis. Hydrogen atoms have been omitted for clarity.

Table 1. Selected bond lengths [Å] and angles [°] for [Eu(TTA)$_3$(PBO)].

| | | | |
|---|---|---|---|
| Eu(1)–O(1) | 2.33(2) | Eu(1)–O(2) | 2.38(2) |
| Eu(1)–O(3) | 2.38(2) | Eu(1)–O(4) | 2.33(2) |
| Eu(1)–O(5) | 2.36(2) | Eu(1)–O(6) | 2.38(2) |
| Eu(1)–O(7) | 2.58(2) | Eu(1)–N(1) | 2.68(2) |
| O(1)–Eu(1)–O(4) | 109.6(8) | O(1)–Eu(1)–O(5) | 135.2(7) |
| O(4)–Eu(1)–O(5) | 97.0(8) | O(1)–Eu(1)–O(6) | 147.3(8) |
| O(4)–Eu(1)–O(6) | 77.6(7) | O(5)–Eu(1)–O(6) | 72.1(8) |
| O(1)–Eu(1)–O(2) | 71.1(8) | O(4)–Eu(1)–O(2) | 80.0(8) |
| O(5)–Eu(1)–O(2) | 151.2(8) | O(6)–Eu(1)–O(2) | 79.3(8) |
| O(1)–Eu(1)–O(3) | 75.2(8) | O(4)–Eu(1)–O(3) | 71.4(7) |
| O(5)–Eu(1)–O(3) | 80.3(7) | O(6)–Eu(1)–O(3) | 135.2(8) |
| O(2)–Eu(1)–O(3) | 124.4(7) | O(1)–Eu(1)–O(7) | 85.9(8) |
| O(4)–Eu(1)–O(7) | 147.1(8) | O(5)–Eu(1)–O(7) | 90.7(8) |
| O(6)–Eu(1)–O(7) | 74.5(8) | O(2)–Eu(1)–O(7) | 78.1(8) |
| O(3)–Eu(1)–O(7) | 141.5(8) | O(1)–Eu(1)–N(1) | 69.4(7) |
| O(4)–Eu(1)–N(1) | 149.1(8) | O(5)–Eu(1)–N(1) | 69.3(8) |
| O(6)–Eu(1)–N(1) | 120.8(7) | O(2)–Eu(1)–N(1) | 125.4(8) |
| O(3)–Eu(1)–N(1) | 78.8(7) | O(7)–Eu(1)–N(1) | 63.0(8) |

## UV Spectra

The UV absorption spectrum of [Eu(TTA)$_3$(PBO)] is compared with those of [Eu(TTA)$_3$(H$_2$O)$_2$] and PBO in Figure 4. There is one principle π–π* absorption peak at 300 nm in the spectrum of PBO and two peaks at 266 and 338 nm in that of [Eu(TTA)$_3$(H$_2$O)$_2$], while a new shoulder centered at 318 nm appears in the spectrum of [Eu(TTA)$_3$(PBO)] in addition to one peak at 302 nm due to PBO and two peaks at 266 and 336 nm to [Eu(TTA)$_3$(H$_2$O)$_2$], thus indicating the complexation of PBO to the Eu(TTA)$_3$ moiety.

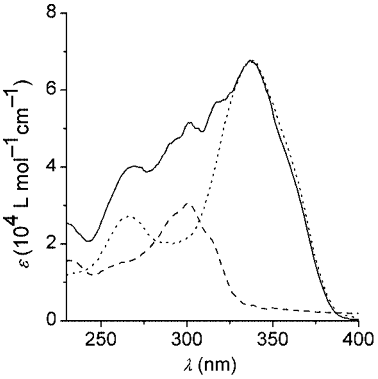

Figure 4. UV absorption spectra of PBO (dashed line), [Eu(TTA)$_3$(H$_2$O)$_2$] (dotted line), and [Eu(TTA)$_3$(PBO)] (solid line) in CH$_3$CN.

As shown in Figure 5, the complexation of PBT to Eu(TTA)$_3$ results in profound changes in the UV spectra: the π–π* absorption bands at 338 and 266 nm of [Eu(TTA)$_3$(H$_2$O)$_2$] are blue-shifted to 330 and 251 nm, respec-

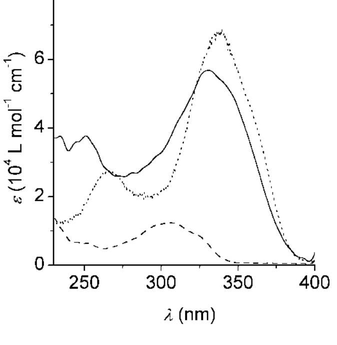

Figure 5. UV absorption spectra of PBT (dashed line), [Eu(TTA)$_3$(H$_2$O)$_2$] (dotted line), and [Eu(TTA)$_3$(PBT)] (solid line) in CH$_3$CN.

tively, for [Eu(TTA)$_3$(PBT)] and the molar extinction coefficient for the former is decreased as the coordination reaction takes place. Furthermore, the broad band at 305 nm for PBT disappears in the spectrum of [Eu(TTA)$_3$(PBT)].

In the spectrum of [Eu(TTA)$_3$(PBI)] (Figure 6), the dominant absorption feature for Eu(TTA)$_3$ is also blue-shifted to 323 nm relative to [Eu(TTA)$_3$(H$_2$O)$_2$]; no absorption feature for PBI is observed (308 nm).

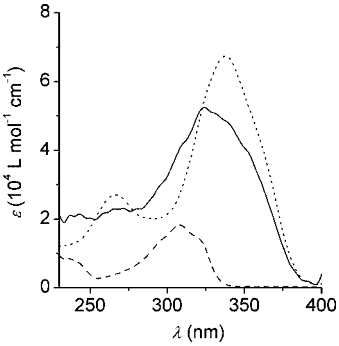

Figure 6. UV absorption spectra of PBI (dashed line), [Eu(TTA)$_3$(H$_2$O)$_2$] (dotted line), and [Eu(TTA)$_3$(PBI)] (solid line) in CH$_3$CN.

### Photo- and Electroluminescent Properties

The excitation spectra for PBO, PBT, and PBI in CH$_3$CN show maximum excitation wavelengths at 300, 305, and 308 nm, respectively; these correspond well to their corresponding maximum UV absorption peaks. However, the excitation spectra for [Eu(TTA)$_3$(PBO)], [Eu(TTA)$_3$(PBT)], and [Eu(TTA)$_3$(PBI)] in CH$_3$CN show maximum excitation wavelengths at 341, 341, and 339 nm, respectively, which correspond well to the maximum UV absorption peak at 338 nm for [Eu(TTA)$_3$(H$_2$O)$_2$], thus indicating that TTA$^-$ rather than neutral 2-(2′-pyridyl)azoles (PBO, PBT and PBI) is mainly involved in intramolecular energy transfer from the excited triplet of TTA$^{-*}$ to the $^5D_0$ state of Eu$^{III}$.[1] The emission spectra of the three complexes show a similar pattern in the Eu$^{III}$ region, with sharp characteristic emission peaks at 595, 613, 654, and 702 nm due to $^5D_0 \rightarrow {}^7F_J$ ($J$ = 1, 2, 3, and 4) transitions, respectively, with the electric dipole transition ($^5D_0 \rightarrow {}^7F_2$) being the strongest. The emission quantum yields of [Eu(TTA)$_3$(PBO)], [Eu(TTA)$_3$(PBT)], and [Eu(TTA)$_3$(PBI)] in CH$_3$CN were determined to be 1.22-, 0.51-, and 0.54-times that of [Eu(TTA)$_3$(H$_2$O)$_2$] in the same solvent, respectively.

By using *N*,*N*′-bis(3-methylphenyl)-*N*,*N*′-diphenyl-1,1′-biphenyl-4,4′-diamine (TPD) as hole-transporting material, 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP) as hole-blocking material, and tris(8-quinolinolato)aluminium (Alq$_3$) as electron-transporting material, we fabricated four-layer electroluminescence (EL) devices with the configuration ITO/TPD (20 nm)/Eu$^{III}$ complex (40 nm)/BCP (10 nm)/Alq$_3$ (40 nm)/Mg$_{0.9}$:Ag$_{0.1}$ (200 nm)/Ag (80 nm). Figure 7 shows the chemical structures of the materials and the configuration of the EL devices. As exemplified in Figure 8 for the electroluminescence spectrum of [Eu(TTA)$_3$(PBO)], the two devices give similar features of an Eu$^{III}$ characteristic emission with good red-emitting purity centered at 613 nm, which corresponds to the $^5D_0 \rightarrow {}^7F_2$ transition. Figures 9 and 10 show current density/luminance/voltage curves for the devices ITO/TPD (20 nm)/[Eu(TTA)$_3$(PBO)] (40 nm)/BCP (10 nm)/Alq$_3$ (40 nm)/Mg$_{0.9}$:Ag$_{0.1}$ (200 nm)/Ag (80 nm) and ITO/TPD (20 nm)/[Eu(TTA)$_3$(PBT)] (40 nm)/BCP (10 nm)/Alq$_3$ (40 nm)/Mg$_{0.9}$:Ag$_{0.1}$ (200 nm)/Ag (80 nm), respectively. The [Eu(TTA)$_3$(PBO)]-based device has a turn-on voltage (the voltage at which the device gives a luminance of 1 cd m$^{-2}$) of about 10 V, which is comparable to the voltage of about 10.5 V for an [Eu(TTA)$_3$(PBT)]-based device. However, the maximum red-emitting brightness of 18 cd m$^{-2}$ achieved at 15 V and 4.3 mA cm$^{-2}$ for the [Eu(TTA)$_3$(PBO)]-based device is much lower than the value of 30 cd m$^{-2}$ observed at 15 V and 165 mA cm$^{-2}$ for an [Eu(TTA)$_3$(PBT)]-based device and much higher than the value of 0.43 cd m$^{-2}$ observed at 26 V and 1.6 mA cm$^{-2}$ for an [Eu(TTA)$_3$(PBI)]-based device;[8i] it is half that (36 cd m$^{-2}$) observed for an [Eu(TTA)$_3$(HEPB)]

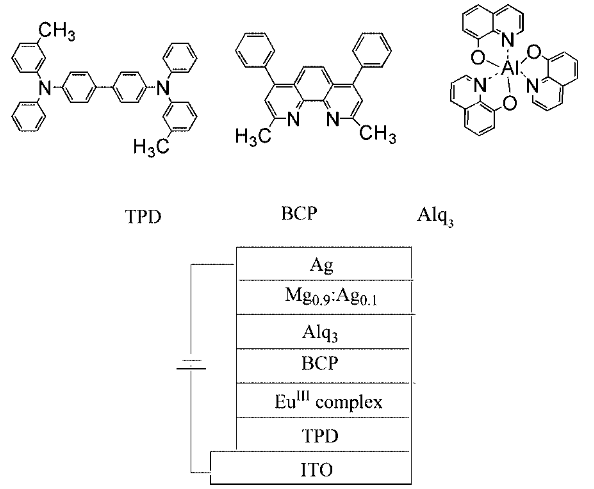

Figure 7. Chemical structures of the materials and the configuration of the EL device.

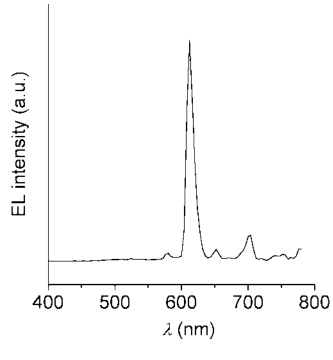

Figure 8. Electroluminescence spectrum of the [Eu(TTA)$_3$(PBO)]-based device ITO/TPD (20 nm)/[Eu(TTA)$_3$(PBO)] (40 nm)/BCP (10 nm)/Alq$_3$ (40 nm)/Mg$_{0.9}$:Ag$_{0.1}$ (200 nm)/Ag (80 nm).

[EPBM = 1-ethyl-2-(2′-pyridyl)benzimidazole] based device.[8c] The poor EL performance observed for the [Eu(TTA)$_3$(PBI)]-based device is mainly attributed to the poor vacuum volatility of [Eu(TTA)$_3$(PBI)] due to the presence of the strongly polar NH group on PBI.

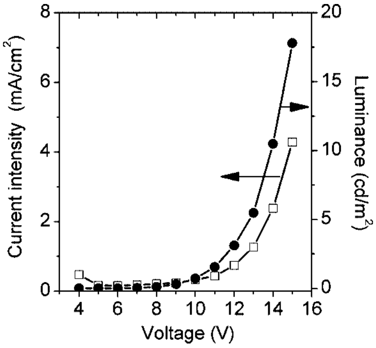

Figure 9. Current/voltage ($I/V$) and luminance/voltage ($L/V$) characteristics for the EL device ITO/TPD (20 nm)/[Eu(TTA)$_3$(PBO)] (40 nm)/BCP (10 nm)/Alq$_3$ (40 nm)/Mg$_{0.9}$:Ag$_{0.1}$ (200 nm)/Ag (80 nm).

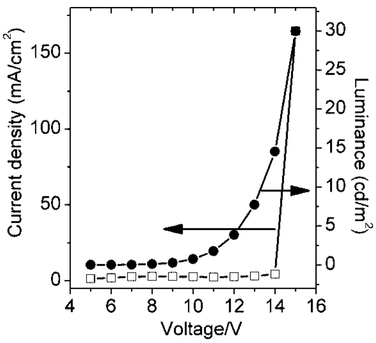

Figure 10. Current/voltage ($I/V$) and luminance/voltage ($L/V$) characteristics for EL device ITO/TPD (20 nm)/[Eu(TTA)$_3$(PBT)] (40 nm)/BCP (10 nm)/Alq$_3$ (40 nm)/Mg$_{0.9}$:Ag$_{0.1}$ (200 nm)/Ag (80 nm).

## Conclusions

We have synthesized two Eu$^{III}$ mixed-ligand complexes with TTA and PBO or PBT. The N,O-bidentate coordination to Eu$^{III}$ by PBO in [Eu(TTA)$_3$(PBO)] has been demonstrated by single-crystal X-ray diffraction. The N,N-Bidentate coordination to Eu$^{III}$ by PBT and PBI in [Eu(TTA)$_3$(PBT)] and [Eu(TTA)$_3$(PBI)] causes more evident changes in the UV spectra than in the N,O-bidentate coordinated [Eu(TTA)$_3$(PBO)]. However, the photoluminescence quantum yield of N,O-coordinated [Eu(TTA)$_3$(PBO)] is the highest and follows the order: [Eu(TTA)$_3$(PBO)] > [Eu(TTA)$_3$(PBI)] ≈ [Eu(TTA)$_3$(PBT)]. The maximum red-emitting EL brightness follows the order [Eu(TTA)$_3$(PBT)] > [Eu(TTA)$_3$(PBO)] >> [Eu(TTA)$_3$(PBI)]. The low brightness of only 0.43 cd m$^{-2}$ observed for the [Eu(TTA)$_3$(PBI)]-based EL device is most probably due to the poor vacuum volatility of [Eu(TTA)$_3$(PBI)], since we noticed serious thermal decomposition during the vacuum deposition of [Eu(TTA)$_3$(PBI)].

## Experimental Section

**Physical Measurements:** C, H, N elemental analyses were performed with a Vario EL elemental analyzer. IR spectra were measured with a Nicolet Avatar 360 FT-IR spectrometer as KBr disks. $^1$H NMR spectra were obtained with a Bruker DRX-500 spectrometer. UV absorption spectra were determined with a GBC Cintra 10e UV/Vis spectrophotometer. Emission spectra were recorded with a Shimadzu RF-5301PC spectrofluorimeter. The PL quantum yields of CH$_3$CN solutions of the complexes were calculated using Equation (1),[29] where $\varphi_s$ and $\varphi_{std}$ are the quantum yields of unknown and standard [Eu(TTA)$_3$(H$_2$O)$_2$], $A_s$ and $A_{std}$ (< 0.1) are the solution absorbance at the excitation wavelength, $I_s$ and $I_{std}$ are the integrated emission intensities, and $n_s$ and $n_{std}$ are the refractive indices of the solvents.

$$\varphi_s = \varphi_{std}(A_{std}/A_s)(I_s/I_{std})(n_s/n_{std})^2 \qquad (1)$$

The EL devices were fabricated by sequentially depositing organic layers in one run under high vacuum (<8 × 10$^4$ Pa) thermal evaporation onto a pre-cleaned indium/tin oxide glass substrate with a sheet resistance of 15 Ω/cm$^2$, which was kindly supplied by China Southern Glass Holding Co., Ltd as a gift. A shadow mask with 5-mm-diameter openings was used to define the cathode of a 200-nm thick Mg$_{0.9}$:Ag$_{0.1}$ alloy layer, with an 80-nm thick Ag cap. The thickness of the deposited layer and the evaporation speed of the individual materials were monitored in vacuo with quartz crystal monitors. The deposition rates were maintained to be 0.1–0.3 nm s$^{-1}$ for organic materials and 1.0–1.3 nm s$^{-1}$ for Mg$_{0.9}$:Ag$_{0.1}$ alloy. All electrical testing and optical measurements were performed under ambient conditions. The EL spectra were measured with a Spectrascan PR650 photometer. The current/voltage ($I/V$) and luminance/voltage ($L/V$) characteristics were measured with a computer-controlled Keithley 2400 Sourcemeter unit with a calibrated silicon diode.

**Materials:** [Eu(TTA)$_3$(H$_2$O)$_2$][30] [TTA = 1,1,1-trifluoro-3-(2-thenoyl)acetonato] was prepared by a literature method. 2-(2′-Pyridyl)benzimidazole (PBI) and [Eu(TTA)$_3$(PBI)] were synthesized as described previously.[8c,8i] The other materials were commercially available and were used without further purification.

**2-(2′-Pyridyl)-1,3-benzoxazole (PBO):** A mixture of powdered 2-picolinic acid (12.3 g, 0.1 mol), 2-aminophenol (10.9 g, 0.1 mol), and syrupy phosphoric acid (50 mL) was stirred at 160 °C for 4 h. The blue slurry was then poured into vigorously stirred cold water (500 mL). Aqueous ammonia was then added up to a pH of about 7. The resulting pink solid product was filtered off and recrystallized from CH$_2$Cl$_2$/hexane. Yield: 8.6 g (43.9 %). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ = 8.86 (d, $J$ = 4.60 Hz, 1 H), 8.40 (d, $J$ = 7.90 Hz, 1 H), 7.94 (m, 1 H), 7.86 (m, 1 H), 7.71 (d, $J$ = 4.60 Hz, 1 H), 7.50 (m, 1 H), 7.44 (m, 2 H) ppm. IR (KBr): $\tilde{\nu}$ = 3058 (w), 1583 (m), 1552 (m), 1454 (vs), 1437 (s), 1347 (m), 1242 (m), 1076 (s), 809 (m), 742 (vs), 704 (m) cm$^{-1}$. C$_{12}$H$_8$N$_2$O (196.21): calcd. C 73.50, H 4.10, N 14.30; found C 73.70, H 4.20, N 14.10.

**2-(2′-Pyridyl)-1,3-benzothiazole (PBT):** This was synthesized as described above for PBO except that 2-aminothiophenol was used instead of 2-aminophenol. Yield: 6.0 g (30.6 %). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ = 8.72 (d, $J$ = 4.70 Hz, 1 H), 8.42 (d, $J$ = 7.91 Hz, 1 H), 8.13 (d, $J$ = 8.13 Hz, 1 H), 8.00 (d, $J$ = 7.94 Hz, 1 H), 7.89 (m, 1 H), 7.54 (m, 1 H), 7.44 (m, 2 H) ppm. IR (KBr): $\tilde{\nu}$

= 3052 (w), 1583 (m), 1562 (m), 1509 (m), 1456 (s), 1432 (vs), 1316 (s), 1292 (m), 1265 (m), 1233 (m), 996 (m), 978 (s), 783 (s), 758 (s), 739 (s), 725 (s), 618 (s) cm$^{-1}$. $C_{12}H_8N_2S$ (212.21): calcd. C 67.90, H 3.80, N 13.20; found C 68.00, H 3.85, N 13.15.

**[Eu(TTA)$_3$(PBO)]:** PBO (0.0785 g, 0.4 mmol) and [Eu(TTA)$_3$(H$_2$O)$_2$] (0.3408 g, 0.4 mmol) were refluxed in ethanol (10 mL) for 1 h. The solid product formed upon cooling was filtered off, washed with hot ethanol, and then vacuum-dried. Yield: 0.29 g (71.6%). UV (CH$_3$CN): $\lambda$ ($\varepsilon$) = 266 (4.03), 302 (5.18), 318 (5.70), 336 ($6.80\times10^4$ M$^{-1}$cm$^{-1}$) nm. IR (KBr): $\tilde{\nu}$ = 1598 (s), 1578 (m), 1541 (m), 1508 (w), 1463 (w), 1413 (m), 1359 (w), 1311 (s), 1250 (w), 1230 (w), 1189 (m), 1136 (s), 1085 (w), 1062 (w), 935 (w), 858 (w), 787 (m), 748 (m), 720 (m), 681 (w), 642 (w), 581 (w), 457 (vw) cm$^{-1}$. $C_{36}H_{20}EuF_9N_2O_7S_3$ (1011.7): calcd. C 42.74, H 1.99, N 2.77; found C 42.66, H 2.06, N 2.96.

**[Eu(TTA)$_3$(PBT)]:** This complex was synthesized as described above for [Eu(TTA)$_3$(PBO)] except that PBT was used instead of PBO. UV (CH$_3$CN): $\lambda$ ($\varepsilon$) = 234 (3.73), 251 (3.77), 330 ($5.69\times10^4$ M$^{-1}$cm$^{-1}$) nm. IR (KBr): $\tilde{\nu}$ = 1625 (m), 1598 (s), 1578 (m), 1540 (m), 1508 (w), 1464 (w), 1413 (m), 1357 (w), 1308 (s), 1248 (w), 1231 (w), 1187 (m), 1142 (s), 1083 (w), 1065 (m), 995 (w), 935 (w), 855 (w), 788 (m), 762 (w), 718 (m), 681 (w), 644 (m), 577 (m), 496 (vw), 461 (vw) cm$^{-1}$. $C_{36}H_{20}EuF_9N_2O_6S_4$ (1027.8): calcd. C 42.07, H 1.96, N 2.73; found C 41.77, H 2.11, N 2.76.

**X-ray Crystallographic Study:** Yellow single crystals with approximate dimensions suitable for X-ray structural analysis were obtained by recrystallization from CH$_2$Cl$_2$/CH$_3$CN. The data were collected at 294(2) K with a CCD area detector Bruker SMART 2000 X-ray diffractometer with graphite-monochromated Mo-$K_\alpha$ radiation ($\lambda$ = 0.71073 Å) in the $\omega$-$2\theta$ scan mode ($2\theta$ range: 5.52–52.48°). The coordinates of all non-hydrogen atoms and anisotropic thermal parameters were refined by full-matrix least squares. The data were processed with a Pentium PC using the Bruker SHELXTL software package.[16] Further details of the data collection and refinement are given in Table 2. CCDC-296449 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 2. Principal crystallographic data and parameters of [Eu(TTA)$_3$(PBO)].

| | |
|---|---|
| Empirical formula | $C_{36}H_{20}EuF_9N_2O_7S_3$ |
| Formula mass | 1011.68 |
| Temp. [K] | 294(2) |
| Wavelength [Å] | 0.71073 |
| Crystal system | monoclinic |
| Space group | *C*/2*c* |
| *a* [Å] | 41.346(4) |
| *b* [Å] | 10.0538(8) |
| *c* [Å] | 20.3793(16) |
| $\beta$ [°] | 110.922(2) |
| *V* [Å$^3$] | 7912.7(11) |
| *Z* | 8 |
| $D_{calcd.}$ [g cm$^{-3}$] | 1.698 |
| Absorption coefficient [mm$^{-1}$] | 1.835 |
| *F*(000) | 3984 |
| Crystal size [mm] | $0.16\times0.14\times0.10$ |
| $\theta$ range [°] | 2.02–25.01 |
| No. of reflections collected | 19608 |
| No. of independent reflections | 6958 |
| No. of observed reflections [$I > 2\sigma(I)$] | 5215 |
| No. of refined parameters | 652 |
| Largest peak/hole [e·Å$^{-3}$] | 0.765/–0.547 |
| Final $R_{int}$ [$I > 2\sigma(I)$] | $R_1$ = 0.0363, $wR_2$ = 0.0911 |
| $R_{int}$ (all data)[a] | $R_1$ = 0.0570, $wR_2$ = 0.1095 |

[a] Structure was refined on $F_o^2$: $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma w(F_o^2)^2\}^{1/2}$, where $w^{-1} = [\Sigma(F_o^2) + (aP)^2 + bP]$ and $P = [\max(F_o^2,0) + 2F_c^2]/3$.

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