

Evaporable luminescent lanthanide complexes based on novel tridentate ligand[†]

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Abstract: A novel tridentate ligand *N*-(6-(diphenylphosphoryl)pyridin-2-yl)-2,2,2-trifluoroacetamide (DPPOPFA) was designed and synthesized. Crystal structure of the ligand revealed the “keto” form of ligand in solid state other than the “enol” one, and it was also found that two kinds of molecules with different conformations were connected by hydrogen bonding between amide N–H and phosphoryl P=O. This ionic ligand was used to coordinate a variety of lanthanide ions, forming neutral 3:1 complexes. Absolute overall quantum yields of these complexes in solid states were 36% for Eu(III), 29% for Tb(III) and 3% for Dy(III) with lifetimes of 1.1, 1.1 and 0.087 ms, respectively. The complexes had excellent thermal stability and did not decompose till 370 °C. And they could sublime in vacuum (1×10^{-4} Pa) at 330 °C due to the weak molecular interaction.

Keywords: luminescent complex; lanthanide; tridentate; evaporable; rare earths

Luminescent lanthanide complexes have been extensively investigated in the use of solid-state lighting and display^[1], bio-imaging and sensing^[2–4], light conversion films and anti-counterfeiting^[5] due to their high efficiency, characteristic narrow emission, long lifetime and large Stokes shift. Especially, the use of lanthanide complexes as luminescent material in organic light emitting diodes (OLEDs) has many advantages involving high color purity and theoretical 100% internal quantum efficiency^[6]. However, the performance of lanthanide complexes based OLEDs is far from perfect with one problem of poor sublimation ability of the lanthanide complexes, which limits the choice of materials for fabricating OLEDs. And possible strategies have been developed such as increasing the decomposition temperature^[7], co-evaporation of neutral ligands^[8] and fluorinating of ligands to decrease molecular interaction^[9]. At the same time, to achieve a high efficiency OLED, the complex should have high photoluminescent quantum yield and proper carrier mobility.

All these requirements need to be taken into consideration when designing a ligand for lanthanide complex. More specifically, the ligand should own: (1) proper triplet energy for efficient energy transfer to the lanthanide ion^[10,11]; (2) less non-radiation pathways such as quenching by LMCT state^[12,13] or high energy oscillator O–H and N–H^[14]; (3) weak intermolecular interaction to im-

prove sublimation ability^[9,15]; (4) electron or hole transporting groups such as phenylphosphine oxide^[16,17] and carbazole^[18,19] for better carrier mobility. A number of ligands have been synthesized to coordinate the lanthanide ion especially the visible emitting Eu(III) and Tb(III) for fabricating OLEDs. Ionic β -diketonate ligand including thenoyltrifluoroacetone (TTA)^[20], 1,3-di-(2-furyl)-1,3-propanedione (DFP)^[21], 1-phenyl-3-methyl-4-isobutyryl-5-pyrazolone (PMIP)^[22] and neutral ligand including phenanthroline derivatives (phen^[21], diphen^[23]) and phenylphosphine oxide derivatives (DPEPO^[7], DPPOC^[15]) are most commonly used ligands for Eu(III), Tb(III) complexes as light emitting materials. Recently, we have developed a novel ligand, namely 6-(diphenylphosphoryl)picolinic acid, which can sensitize Eu(III), Tb(III), Dy(III) ions quite efficiently^[24]. However, the complexes cannot sublime possibly due to the strong intermolecular interaction, and the triplet energy of the ligand is too high to choose a host material for energy transfer when utilized in OLEDs.

In this work, a trifluoroacetamide group was integrated to diphenylphosphoryl pyridine and the tridentate ligand was obtained with expanded π conjugation system and thus lowered triplet energy; and the saturated coordinated lanthanide complexes (ligand:Ln=3:1; Ln=Eu, Gd, Tb, Dy, Tm) show good sublimation ability. Photophysical and thermal properties of the complexes were character-

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ized. The results showed that this kind of complex is a good candidate when it acts as emitting material in OLEDs.

1 Experimental

1.1 General information

^1H , ^{19}F and ^{31}P NMR spectra were recorded on a Bruker 400 MHz NMR spectrometer. Electrospray ionization mass spectra (ESI-MS) were conducted on a Bruker Apex IV Fourier transform ion cyclotron resonance mass spectrometer. Elemental analyses were performed on a VARIO elemental analyzer from Elementar Analysen systeme GmbH. The single crystal data were collected by a RAPID-S image plate diffractometer, determined using SHELXS-97 program package and refined with SHELXL-97 program package. CCDC 1485687 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre. Thermal gravimetric analysis (TGA) was carried out on Q600SDT instruments at an elevation temperature rate of $10\text{ }^\circ\text{C}/\text{min}$ under $100\text{ mL}/\text{min}$ nitrogen flow.

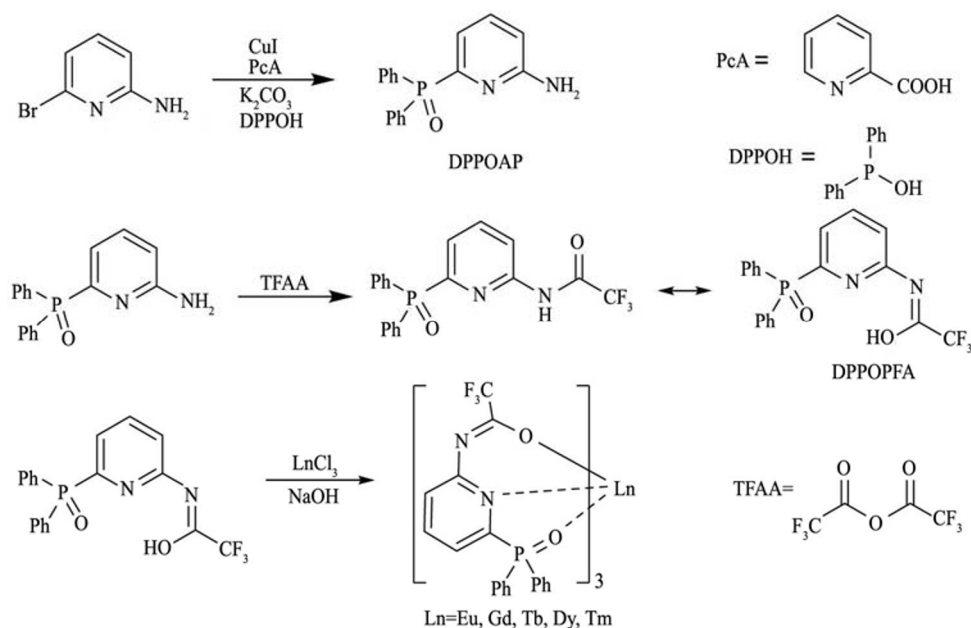
The photophysical properties of the complexes were carried out in dry CH_2Cl_2 solutions or in solid states. For general measurements, the complexes were dissolved in CH_2Cl_2 and methanol solutions with an initial concentration of $1 \times 10^{-3}\text{ mol}/\text{L}$ and diluted to a concentration of $1 \times 10^{-5}\text{ mol}/\text{L}$ by CH_2Cl_2 . All measurements were performed at room temperature except the phosphorescence experiments at 77 K in the solution of ethanol containing 5% methanol and 5% isopropanol. UV-visible absorption spectra were measured by a Perkin-Elmer Lambda 35 spectrometer. Excitation and emission spectra were recorded on an Edinburgh FLS920 fluorescence spectro-

photometer and low temperature phosphorescence spectrum of Gd(III) complex was performed on a Hitachi F7000 fluorescence spectrophotometer in time-resolved mode. Luminescence lifetimes were obtained on a single photon counting spectrometer from Edinburgh FLS920 with micro-second pulse lamp as the excitation source. The data were analyzed by tail fit of the decay profile using a software package provided by Edinburgh Instruments. Absolute overall quantum yields ($\Phi_{\text{L}}^{\text{Eu}}$) were measured on the Edinburgh the FLS920 fluorescence spectrophotometer and the NanoLog infrared fluorescence spectrometer using integral sphere. For solid measurements, Al_2O_3 scatter was used as blank.

1.2 Synthesis of the ligand

The ligand was synthesized by a two-step reaction from starting material of 6-bromopyridin-2-amine (shown in Scheme 1).

(6-aminopyridin-2-yl)diphenylphosphine oxide (DPPOAP): 6-bromopyridin-2-amine (5 g, 289 mmol, 1 eq.), picolinic acid (as ligand, 0.2 eq.), CuI (0.1 eq.) and K_2CO_3 (2 eq.) were placed in a three necked flask with a condenser and a funnel. Air was replaced by N_2 using Schlenk line. Then 100 mL of toluene was added by needle and the solution was stirred for 5 min followed by addition of diphenylphosphine oxide (1.5 eq.). The muddy solution was heated to reflux for 12 h with color change from white to orange. Then 40 mL water was added to the solution to resolve salt and precipitate was filtered under vacuum. The grey solid was dissolved in CH_2Cl_2 and dried by anhydrous Na_2SO_4 and at last purified by column chromatography ($\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}=30/1$). Yield: 73% (6.2 g). ^1H NMR (400 MHz, DMSO): δ 7.91–7.72 (m, 4H), 7.64–7.42 (m, 7H), 7.17 (t, $J=6.8\text{ Hz}$, 1H), 6.58 (dd, $J=8.4, 1.4\text{ Hz}$, 1H), 6.32 (s, 2H). ^{31}P NMR



Scheme 1 Synthetic routes of ligand and complexes

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