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Introduction

White-light-emitting materials have attracted much attention because of their broad applications in lighting, backlights, and full-colour displays.¹ Generally, the realization of white light emission requires the generation and intensity control of the three fundamental red, green and blue (RGB) light emissions in bulk materials. The trichromatic approach is mostly employed for producing white-light materials.² In addition, monochromatic, dichromatic and tetrachromatic approaches are often used for achieving this goal.³ So far, reported whitelight-emitting materials contain small organic molecules,⁴ polymers,⁵ metal complexes,⁶ lanthanide-doped inorganic nanocrystals,⁸ quantum dots,⁹ and hybrid materials,7 materials based on rare earth complexes.¹⁰ Benefitting from unique optical properties of lanthanide ions, the luminescence from Ln(III) ions is featured by high colour purity and longlived excited lifetimes and the emission covers the whole visible range from 400 to 700 nm. Specifically, Eu(III) and

Aggregation-induced white-light emission from the triple-stranded dinuclear Sm(III) complex†

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A novel bis- β -diketone ligand, 4,4'-bis(4,4,4-trifluoro-1,3-dioxobutyl)(phenoxy)-1,1'-binaphthalene (BTPB), is designed for synthesis of a white light emissive lanthanide complex. The ligand bears two benzoyl β -diketonate sites linked by a 1,1'-binaphthoxy spacer. Reaction of the doubly negatively charged bis-bidentate ligand with lanthanide ions forms triple-stranded dinuclear complexes Sm₂(BTPB)₃(H₂O)₄ (1) and Gd₂(BTPB)₃(H₂O)₄ (2), which have been fully characterized by various spectroscopic techniques. UV-Vis absorption and emission spectroscopic techniques are used to investigate photophysical properties of the ligand and its complexes in THF and CHCl₃. In some cases aggregation of the ligand results in the appearance of a new luminescence band at about 510 nm in addition to the monomer fluorescence. In complex 1, partial energy transfer from BTPB results in Sm(m)-based red light emission in addition to the BTPB-based blue/green emission. With the variation of the excited wavelength and concentration of the solution, complex 1 shows a tunable white light emission from a single molecule Sm(m) complex.

Tb(III) ions can emit intense red and green light, respectively. Thus, the lanthanide complexes, which combine red- (Eu^{III}, Sm^{III}) and green-emissive (Tb^{III}) ions and blue/green emitting organic chromophores, should be perfect candidates for designing the white-light-emitting materials.

Presently, there mainly exist two types of lanthanide complexes for constructing the white-light emitters. One is the lanthanide metal-organic frameworks $(LnMOFs)^{11}$ and the other is single molecule Eu(m) complexes.¹² In LnMOFs, white light emission is generally achieved by co-doping Eu(m) and/or Tb(m) ions into the corresponding isostructural LnMOFs (Ln = La and Gd) through adjusting the ratio of the lanthanide ions. For example, Zang *et al.* used a combination of blue-emitting ligand/La(m), green-emitting Tb(m) and red-emitting Eu(m) units to generate white light from La(m)/Tb(m)/Eu(m)-MOFs.¹³ This is known as a three-component approach. Another strategy for generating white light emission is to dope Eu(m) ions into Gd(m) frameworks. It is named the two-component approach.¹⁴

In single molecule Eu(m) complexes, the white light emission is achieved by incorporating the Eu(m) ion red light emission and ligand-based blue/green light emission. In comparison with the LnMOFs, the single molecules have advantages such as facile preparation, high emission quantum yields and simpler device fabrication.¹⁵ To obtain effective white light emission, the complexes are generally composed of two different kinds of ligands simultaneously, one as a sensitizer of the Eu(m) ion luminescence and the other as blue/



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[†]Electronic supplementary information (ESI) available: The ¹H NMR spectrum of 4,4'-bis-(acetyl)phenoxy-1,1'-binaphthalene (BAPB), ESI-MS for the ligand, the phosphorescence spectrum of complex 2 at 77 K and the CIE coordinates of 1 at excitation wavelengths 350–390 nm. See DOI: 10.1039/c4dt00820k

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green light emissive chromophores to balance the red-emission bands. For example, Duan reported a single molecule Eu(m) complex, in which the Eu(m) moiety acted as the source of red light, while a covalently linked coumarin–rhodamine ligand acted as the blue- and green-emitting source.¹⁶ De Cola *et al.* reported an Ir(m)/Eu(m) trinuclear complex that exhibited white light emission by combining a blue-emitting Ir(m) and a red-emitting Eu(m) moiety.¹⁷

Recently, a new approach to obtain white light emission from the single molecule Eu(m) complex was reported in which only one kind of ligand is used to tune the luminescent colors.¹⁸ We name it the one-ligand approach. In the complex, partial energy transfer from the ligand results in sensitized Eu(m)-based emission in addition to the ligand-based blue or blue/green luminescence. The one-ligand approach will considerably simplify the preparation of the white-light-emitting complexes. To the best of our knowledge, this is the only example to achieve white light emission from a single molecule lanthanide complex where only one type of ligand is present.

We are interested in exploring new white-light-emitting materials of the single molecule lanthanide complex. Herein, a novel bis-β-diketone, 4,4'-bis(4,4,4-trifluoro-1,3-dioxobutyl)-(phenoxy)-1,1'-binaphthalene (BTPB) (see Scheme 1), is designed for syntheses of white-light-emitting lanthanide complexes. It is known that the β -diketones are perfect sensitizers for Ln(III) ion luminescence due to their effective sensitization ability to the metal.¹⁹ Recently, we and others developed several bis-β-diketone ligands, which coordinate to lanthanide ions to form triple-stranded helicates and effectively sensitize lanthanide ion visible or NIR luminescence.²⁰ In this ligand, binaphthol is used as a spacer to link the two β -diketone units. Binaphthol has a free rotation C2 axis, so the ligand is prone to twist and wrap about the metal ions to form the triplestranded dinuclear structure. Meanwhile, the large amounts of aromatic ring structures make the ligand to be more prone to accumulate and form aggregates. Compared to the monomer, the aggregate often provides a red-shifted and enhanced emis-

 $H_{O} \xrightarrow{O}_{HO} \xrightarrow{H_{O}}_{K_{2}CO_{3}/DMF} \xrightarrow{O}_{HO} \xrightarrow$

Scheme 1 Syntheses of the BTPB and complexes $Ln_2(BTPB)_3(H_2O)_4$ (Ln = Eu, Gd).

BTPB



Results and discussion

Characterization of the ligand and complexes

The ¹H NMR spectrum of BTPB obtained at 400 MHz in CDCl₃ is shown in Fig. 1. The β -diketones generally exhibit keto-enol tautomerism. The amounts of keto and enol forms can be determined by integration of the keto and the enol resonance peaks in the ¹H NMR spectrum. The observed broad single peak, 2H at δ 15.20, shows the characteristic H^{enol} protons (Hj), and the singlet, 2H at δ 6.35, is assigned to methine H^{keto} protons (Hi). By integrating the areas corresponding to both species, it is found that the ligand exists completely in the enolic form in CDCl3. The observed two double peaks at δ 6.74–6.76 and δ 7.61–7.63 are attributed to the Hg, Hh in phenylene, with the areas that integrate to a relative value of 4H atoms, respectively. The double peaks are the results of the spin-spin coupling of the adjacent protons, and being close to the withdrawing carboxyl group makes the Hh present at downfield. A doublet peak, 2H observed at δ 7.96–7.98, is assigned to the protons Hd due to coupling of Hc protons.



Fig. 1 400 MHz ¹H NMR spectrum of BTPB in CDCl₃.



Fig. 2 Expanded regions of the ESI-TOF-MS of Sm₂(BTPB)₃ in acetone.

A doublet, 2H, Ha is observed at δ 7.92–7.94 due to the coupling of Hb protons. Protons Hb, Hc appear as two triplet peaks at δ 7.31–7.49 and correctly integrate for four protons. Multiple signals in the range of δ 7.24–7.28 are attributed to the methine protons Hf, He, integrating for four protons.

In view of the soft ionization of the sample provided by ESI-TOF mass spectrometry, which avoids destructive fragmentation of the complexes, we have resorted to this technique to ascertain the formation of the dinuclear complexes. The mass spectrum of complex 1 is shown in Fig. 2. The patterns of mass spectra show characteristic mass distribution of the complexes $Sm_2(BTPB)_3$. The peak centred at m/z 2461 is attributed to $[Sm_2(BTPB)_3 + Na]^+$ for the dinuclear complex.

The FT-IR spectra of the complexes (1 and 2) show a broad absorption in the 3657–3220 cm⁻¹ region, thereby indicating the presence of solvent molecules in the coordination sphere of the Ln(m) ions. The carbonyl stretching frequency of BTPB (1625 cm⁻¹) has been shifted to lower wavenumbers in the complexes (1, 1615 cm⁻¹; 2, 1617 cm⁻¹), indicating the coordination of the oxygen atoms to the lanthanide ions. This coordination is further supported by the appearance of bands in the range of 461–488 cm⁻¹ due to Ln–O stretching vibrations. The ligand is indicated to be in the enolic form by the presence of a band at 1430 cm⁻¹ of a C=C–O stretching vibration, which is shifted to 1361–1398 cm⁻¹ in complexes **1** and **2**. In addition, the absorbance frequency due to C=C of benzene rings at 1502 and 1470 cm⁻¹ of the ligands is split into two peaks at 1529–1595 cm⁻¹ and 1463–1497 cm⁻¹, respectively, in the complexes. To examine the thermal stability and water content of the complexes, thermogravimetric analysis is carried out for **1** (Fig. S3†). It is clear from the TG curve that complex **1** undergoes a mass loss of about 2.9% (calcd 3.0%) in the first step, which corresponds to the loss of four coordinated water molecules. Then, a long plateau is observed until a full decomposition at *ca.* 310 °C.

UV-Vis absorption spectra

The UV-Vis absorption spectra of the ligand BTPB in THF at 10^{-6} - 10^{-4} M are shown in Fig. 3 (a, top). Clearly, the absorption of a ligand in solution is dependent on its concentration. They all show a typical binaphthol absorption band at 279 nm, and an absorption maxima at about 329 nm corresponding to the singlet–singlet π – π * electronic transition of the ligand. At a concentration above 10⁻⁶ M, the absorption maximum redshift from 329 to 341 nm and the intensity of the shoulder at 369 nm increase significantly. These changes can be explained by the aggregation behaviors of the aromatic units. Binaphthol possesses a C2-axis of free rotation and a large conjugate plane, which make it prone to form aggregates. In addition, the clear red shift of the absorption bands suggests that the molecules self-assembled into J-aggregates in solution at higher concentrations.²² In CHCl₃, the absorption spectra of the ligand are about the same over the 10^{-6} – 10^{-4} M concentration range, and are very similar to that observed in THF at high concentrations. It means that the aggregate of the ligand is more easily formed in CHCl₃ than in THF, even in highly dilute solution (10^{-6} M) .



Fig. 3 Normalized UV-Visible absorption spectra of BTPB (a) and 1 (b) in CHCl₃ and THF at different concentrations.

The absorption spectra of complex **1** at 10^{-6} – 10^{-4} M are shown in Fig. 3(b), which is very similar to that observed in the free ligand BTPB at 10^{-6} M in THF. It is noted that the relative intensity of the low-energy bands at 369 nm decreases significantly in complexes compared to that observed in ligands. It means that the intermolecular aggregation begins to reduce or disappear in complexes. In addition, the absorption maxima of complexes are blue-shifted by about 8 nm compared to the ligand. To investigate the aggregation behaviors of the complex in both solvents, the absorption spectra of **1** at 10^{-5} M are compared in Fig. 3 (b, middle). In CHCl₃, the low-energy tail redshifts by 10 nm in comparison with that observed in THF, and extends to 395 nm. This result means that the complexes still exhibit aggregation behaviors in CHCl₃.

Luminescence properties

The emission spectra of BTPB in THF at various concentrations are shown in Fig. 4(a). At low concentrations ($\approx 10^{-6}$ M), the ligand shows characteristic emission of the β -diketonate monomer (BTPB) with the emission maximum at 430 nm [see Fig. 4(a) (inset)]. An increase in the concentrations leads to a relative decrease in the intensity of this emission band and the appearance of a new luminescence band at 510 nm. According to the results observed in UV-Vis absorption spectra, we can confirm that the new bands should originate from the emission of a preformed aggregate. The emission spectra of BTPB in $CHCl_3$ also show aggregates' emission, which is similar to that observed in THF solution (Fig. 4(b)). Notably, we simultaneously observed the emission of the monomers and aggregates, even at 10^{-6} M concentration. With the increase of the concentration, the ligand shows similar behaviors to that in THF.

The emission spectra of complex 1 in THF at different concentrations are shown in Fig. 4(c). Upon excitation at 360 nm, 1 displays a series of characteristic narrow band emissions of Sm(m) ions at 565 nm, 602 nm, and 645 nm, corresponding to the ${}^{4}G_{5/2} \rightarrow {}^{6}H_{J}$ (J = 5/2, 7/2, 9/2) transitions. Among them, the most intense emission peak at 645 nm belongs to the hypersensitive ${}^{4}G_{5/2} \rightarrow {}^{6}H_{9/2}$ transition. It is worth noting that the emission of the ligand is hardly observed, indicating efficient energy transfer from the ligand to Sm(m) ions. In CHCl₃, the emission spectra of 1 (Fig. 4(d)) likewise are dominated by the characteristic emission bands of Sm(m) ions. In addition, we also observed the emission bands of the ligand again, which



Fig. 4 Emission spectra of (a) BTPB in THF (inset: enlarged figure of the green line); (b) BTPB in CHCl₃; (c) complex 1 in THF; (d) complex 1 in CHCl₃ [the inset shows how the CIE coordinates vary: a, 1.0×10^{-4} M (0.498, 0.373); b, 1.0×10^{-5} M (0.447, 0.356); c, 5.0×10^{-6} M (0.381, 0.321); d, 1.0×10^{-6} M (0.293, 0.269)] (λ_{Ex} = 360 nm).

Paper

indicates that the energy transfer from the ligand to the metal center is not complete. Upon excitation at 360 nm, the relative intensity of the Sm(III) ion emission increases and that of the ligand emission decreases as the 1 concentration increases. The decrease in the relative intensity of ligand emission is mainly due to the red-shift of the excitation bands with the concentration increase, which result in the ligand having a lower molar extinction coefficient at 360 nm. As shown in Fig. S4,[†] the high energy band of the excitation spectra for complex 1 shows obvious red-shift following the increase of solution concentration. It indicates that the complex will display relatively lower emissive intensity in the region of 400-550 nm with the increase of solution concentration, as the excitation wavelength is located at high energy bands (360 nm). Notably, the emission spectra cover the whole visible range from 390 to 680 nm. Therefore, through changing the concentration of 1 in CHCl₃ achievement of white light emission is possible. As expected, the CIE chromaticity diagram with the change of concentration exhibited a color shift from yellow to white with the excitation at 360 nm. As shown in Fig. 4(d) (inset), the c point $(5 \times 10^{-6} \text{ M})$ is the closest to the white light emission to the eye with CIE coordinates of (0.381, 0.320), which fall well within the white region of the 1931 CIE diagram (for pure white x = 0.33, y = 0.33).

Furthermore, we also investigated the variation trends of the emission spectra for 1 with the change of excitation wavelengths. Fig. 5 shows the emission spectra of 1 in CHCl₃ $(1.0 \times$ 10^{-5} M) with the excitation wavelength varying from 355 to 390 nm. For comparison of the relative intensity of the ligand and Sm(III) ion emission, the ${}^{4}G_{5/2} \rightarrow {}^{6}H_{9/2}$ transition is normalized. It is found that the relative emission intensity of the ligand increases gradually as excitation wavelengths vary from 355 nm, every 5 nm, to 390 nm. The corresponding emission colors are illustrated in the CIE chromaticity diagram, while the corresponding CIE color coordinates are listed in Table S1.† It can be seen that most of the colours of emissions fall within the white region of the 1931 CIE chromaticity diagram. At excitation at 385 nm, 1 exhibited a nearly white light emission with CIE coordinates of (0.335, 0.318), which are very close to that for pure white light (x = 0.33, y = 0.33) according to the 1931 CIE diagram.

In addition to the steady-state emission, we also carried out the luminescence quantum yields and the time-resolved PL decay dynamics study. The calculation results are listed in Table 1. The luminescence quantum yields of the BTPB in THF and CHCl₃ are measured to be in the range of 0.08-0.74%and 0.53-0.90%, respectively. An increase in the concentration leads to the decrease of the luminescence quantum yields, indicating the presence of the concentration quenching effect in solution. The luminescence quantum yields of 1 in THF are measured to be 0.19-0.27%, in which only the Sm(III) ion luminescence is observed. The luminescence quantum yields of 1 are measured to be 0.48-1.43% in CHCl₃. However, the values are comprised of two part emissions of the ligand and Sm³⁺ ions. At a concentration of 1.0×10^{-5} M, complex 1 shows the maximum luminescence quantum yield of 1.43%.



Fig. 5 Emission spectra (top) and CIE chromaticity diagram (bottom) of 1 at different excitation wavelengths in $CHCl_3$ (1.0 × 10⁻⁵ M).

The luminescence lifetimes of the BTPB are determined by monitoring the emission decay curves of the ligand at 510 nm (at 430 nm, 1.0×10^{-6} M, THF). In THF, the decay curves can be fitted by single-exponential functions at 1.0×10^{-6} M, whereas the kinetic behavior at higher concentrations $(10^{-5} 10^{-4}$ M) requires two exponential decay parameters to fit the data. Similar kinetic behaviors for ligand emission bands are also observed in 1, and the lifetimes used for the two-component decay model for these are included in Table 1. The lifetime of 1.49 ns for the free ligand calculated according to the single-exponential function can be attributed to the monomer luminescence. The aggregate luminescence decay measured at a higher concentration has two components, one at 1.10-1.59 ns and a longer-lived one at 2.9-3.96 ns. The lifetimes of the shorter lived components are very close to that observed in monomers (1.49 ns), so it is likely to arise from the contribution of monomers. The luminescence lifetimes of the Sm(III) ions are determined by monitoring the emission decay curves within the ${}^{4}G_{5/2} \rightarrow {}^{6}H_{9/2}$ transition at 645 nm. All the decay curves give satisfactory fits to the double-exponential lifetimes, which suggests that there exist two species in the excited state for 1 in both solvents. It is noted that the lifetimes of Sm(m) ions in CHCl₃ are obviously longer than that observed in THF. The relatively shorter lifetimes observed for Sm(m) ions in THF may be caused by the vibronic coupling of

Table 1 Summary of fluorescence decay kinetics and quantum yields of BTPB and 1 at different concentrations in THF and CHCl₃ with 360 nm excitation

Conc. (mol L^{-1})	BTPB (THF)		BTPB (CHCl ₃)		1 (THF)		1 (CHCl ₃)		
	$\tau_{\rm obs} ({\rm ns})$	QY (%)	$\tau_{\rm obs} ({\rm ns})$	QY (%)	$\mathrm{Sm}^{3+} au_{\mathrm{obs}} (\mu \mathrm{s})$	QY (%)	BTPB $\tau_{\rm obs}$ (ns)	$\mathrm{Sm}^{^{3+}} au_\mathrm{obs}$ (µs)	QY (%)
1.0×10^{-6}	1.49	0.74	1.59	0.90	7.43	0.25	1.06	13.93	0.48
			2.98		26.22		3.67	46.26	
1.0×10^{-5}	1.52	0.56	1.47	0.86	5.90	0.24	1.07	12.24	1.43
	3.11		3.22		27.92		3.59	45.75	
$5.0 imes 10^{-5}$	1.52	0.40	1.19	0.63	8.39	0.27	1.28	14.57	0.71
	3.45		2.90		28.88		3.32	46.25	
$1.0 imes 10^{-4}$	0.92	0.08	1.10	0.53	6.15	0.19	1.49	15.07	0.60
	3.96		3.64		29.00		3.12	47.79	

the C–H oscillators in THF with the metal centers, which increases the nonradiative decay rates.

Energy transfer between the ligand and Sm(III) ions

In general, the widely accepted energy transfer mechanism for the sensitization of Ln(m) ion luminescence with a ligand is proposed by Crosby.²³ In order to make energy transfer effective, the energy-level match between the triple states of the ligand and the Ln(m) ion becomes one of the most important factors dominating the luminescence properties of the complexes. To elucidate the energy transfer process of the samarium complexes, the energy levels of the relevant electronic states should be estimated. The singlet and triplet energy levels of BTPB were estimated by referring to wavelengths of UV-Vis absorbance edges and the lower wavelength emission peaks of the corresponding phosphorescence spectra.

On account of the difficulty in observing the phosphorescence spectra of the ligand, the emission spectrum of complex 2 at 77 K can be used to estimate the triplet state energy level. Because the lowest excited energy level of the Gd^{3+} ion $({}^{6}P_{7/2})$ is too high to accept energy from the ligand, the triplet state energy level of the ligand is not significantly affected. As shown in Fig. S5,† the triplet energy level of 2 is 20 243 cm⁻¹, which corresponds to their lower emission peak wavelength at 494 nm. Obviously, the triplet levels of the BTPB is higher than the ${}^{4}G_{5/2}$ level (17 900 cm⁻¹) of Sm³⁺ ions, and their energy gap is 2343 cm⁻¹, which is large enough to allow back energy transfer. Therefore, the ligand can transfer energy effectively to the emitting states of the Sm(III) ion. The single state energy $({}^{1}\pi\pi^{*})$ level of the ligand is estimated by referring to its absorbance edge, which is 25 641 \mbox{cm}^{-1} (390 nm). It is noted that the energy gap between the ${}^{3}\pi\pi^{*}$ and ${}^{1}\pi\pi^{*}$ levels is 5398 cm⁻¹ for the ligand BTPB. According to Reinhoudt's empirical rule,²⁴ the intersystem crossing process becomes effective when $\Delta E ({}^{1}\pi\pi^{*} - {}^{3}\pi\pi^{*})$ is at least 5000 cm⁻¹, and hence the intersystem crossing process is effective for this ligand. According to the above experimental results, the schematic energy level diagram and the energy transfer process of 1 are shown in Fig. 6. In conclusion, the effective intersystem crossing and ligand-to-metal energy transfer make the ligand suitable for sensitizing the Sm(III) luminescence.



Fig. 6 Schematic energy level diagram and energy transfer process for complex 1. (S1_{BTPB}: first excited singlet; T1_{BTPB}: first excited triplet state).

Conclusions

In summary, we have successfully designed and synthesized a new single molecule Sm(m) complex $Sm_2(BTPB)_3(H_2O)_4$ to achieve white light emission. The complex displays different luminescence behaviors in THF and CHCl₃. In CHCl₃, a tunable blue/green emission from the ligand according to its degree of aggregation, and a sensitized red emission from the Sm(m) center produce a concentration and excitation wavelength dependent white light emission from complex **1**. This work realized the idea of only one type of ligand participation in the construction of single molecule white-light-emitting materials. Our future research will focus on exploiting Eu(m)based white light systems with high quantum yield based on similar components.

Experimental

Materials and instruments

The commercially available chemicals were of analytical reagent grade and used without further purification. 1,1-Bi-2-naphthol (BINOL) (99%, A. R.) was purchased from Shanghai Darui Finechemical Co. (Shanghai, China); LnCl₃·6H₂O was prepared according to the literature by dissolving 99.99%

FT-IR spectra were obtained on a Perkin-Elmer Spectrum One spectrophotometer using KBr disks in the range of 4000-370 cm⁻¹. UV spectra were recorded on a Perkin-Elmer Lambda 25 spectrometer. The absorbance was recorded using quartz cells with an optical path length of 1.0 mm for 1.0 \times 10⁻⁴ M, and 10 mm for the rest of solutions. The ¹H NMR spectra were recorded on a Bruker Avance III 400 MHz spectrometer in CDCl₃ solution. Electron ionization (EI) and Electrospray TOF (ESI-TOF) mass spectra were recorded on Agilent 5973 N and Bruker maXis mass spectrometers, respectively. Excitation and emission spectra were measured with an Edinburgh FLS 920 fluorescence spectrophotometer. Luminescence lifetimes were recorded on a single photon counting spectrometer with an Edinburgh FLS 920 fluorescence spectrophotometer with a microsecond pulse lamp and a picosecond laser as the excitation sources. The data were analyzed using the software supplied by Edinburgh Instruments. Luminescence quantum yields for the ligand and Sm(III) complex were measured by an optically dilute relative method²⁵ using $Ru(bpy)_{3}Cl_{2}\cdot 6H_{2}O(0.028 \text{ in aerated } H_{2}O)^{26}$ as a standard. The calculated process is given by the well-known equation:

$$\varphi_{\text{overall}} = \frac{A_{\text{ref}} n^2 I}{A n_{\text{ref}}^2 I_{\text{ref}}} \varphi_{\text{ref}}$$

where *n*, *I*, and *A* denote the refractive index of the solvent, the area of the emission spectrum, and the absorbance at the excitation wavelength, respectively, and φ_{ref} represents the quantum yield of the standard. The subscript ref denotes the reference, and the absence of a subscript implies an unknown sample.

of 4,4'-bis-(acetyl)phenoxy-1,1'-binaphthalene Syntheses (BAPB). The reaction (Scheme 1) was conducted in a 1000 mL three-necked round-bottom flask that was equipped with a mechanical stirrer, a nitrogen inlet and a condenser. A mixture of DMF (400 mL), potassium carbonate anhydrous (13.86 g, 0.10 mol), and 4'-fluoroacetophenone (104.60 mL, 1.0 mol) was added into the reaction vessel and heated to reflux under pure nitrogen with stirring. Then a DMF solution (100 mL) of 1,1-bi-2-naphthol (28.63 g, 0.10 mol) was added over a period of 1 h. The solution was kept under reflux for another 12 h to ensure the completion of the reaction, and then it was cooled and filtered to remove the salt. The solution was poured to 1000 mL distilled water to precipitate the product. The precipitate was collected by filtration and washed with water three times, and then it was washed with ethanol three times. The solid was dried by drawing air through the filter cake for 1 h. The crude product was purified by crystallization from acetone to give white crystals (37.53 g, 72%). Anal. Calc. for C₃₆H₂₆O₄: C, 82.74; H, 5.01; O, 12.25. Found: C, 82.79; H, 4.98; O, 12.30. IR (KBr, cm⁻¹): 3053, 1675, 1583, 1501, 1245, 810. ¹H NMR (DMSO, 400 MHz): 8.13-8.11 (d, 2H, Hd), 8.05-8.03 (d, 2H, He), 7.75-7.73 (d, 4H, Hh), 7.51-7.47 (d, 2H, Hb), 7.39-7.34 (m, 4H, Hc, Ha), 7.17-7.15 (d, 2H, Hf), 6.83-6.81 (d, 2H, Hg), 2.44 (s, 6H, Hi). ESI-MS m/z 545 [M + Na]⁺.

Syntheses of 4,4'-bis(4,4,4-trifluoro-1,3-dioxobutyl)-(phenoxy)-1,1'-binaphthalene (BTPB). A mixture of sodium methoxide (2.16 g, 0.04 mol) and ethyl trifluoroacetate (7.14 mL, 0.06 mol) in 120 mL dry DME (DME = dimethoxyethane) was stirred for 10 min, followed by the addition of BAPB (10.45 g, 0.02 mol) in portions, which was further stirred at room temperature for 24 h (Scheme 1). The resulting solution was quenched with water and was acidified to pH 2-3 using hydrochloric acid (2 M solution). The resulting yellow precipitate was filtered and dried at 40 °C under reduced pressure. Recrystallization from acetone gave yellow flake crystals (13.20 g, 92%). Anal. Calc. for C₄₀H₂₄F₆O₆: C, 67.23; H, 3.39; O, 13.43. Found: C, 67.29; H, 3.48; O, 13.47. IR (KBr, cm⁻¹): 3060, 1594, 1504, 1243, 1167, 1108, 797. ¹H NMR (CDCl₃, 400 MHz): 15.20 (s, 2H, Hj), 7.96-7.98 (d, 2H, Hd), 7.92-7.94 (d, 2H, He), 7.61-7.63 (d, 4H, Hh), 7.31-7.49 (m, 4H, Hb, Ha), 7.24-7.28 (m, 4H, Hc, Hf), 6.74-6.76 (d, 4H, Hg), 6.35 (s, 2H, Hi). ESI-MS m/z 737 [M + Na]⁺.

Syntheses of the complexes $Ln_2(BTPB)_3(H_2O)_4$ [Ln = Sm (1), Gd (2)]. To a 100 mL methanol solution of BTPB (1.0 g, 1.40 mmol), NEt₃ (0.40 mL, 2.80 mmol) was added, and the mixture was allowed to stir for 5 min. To this solution, LnCl₃·6H₂O (0.34 g, 0.93 mmol) in methanol (50 mL) was added dropwise and stirred overnight at room temperature. The product was filtered and washed with H₂O (2 × 10 mL) and CH₃OH (2 × 10 mL) and dried under vacuum to give the desired product Ln₂(BTPB)₃(H₂O)₄ (Ln = Sm, Gd).

 $Sm_2(BTPB)_3(H_2O)_4$ (1). Yield: 84%. Anal. Calc. for $C_{120}H_{74}F_{18}O_{22}Sm_2$: C, 57.41; H, 2.97; O, 14.02. Found: C, 57.29; H, 2.88; O, 13.97. IR (KBr, cm⁻¹): 3060, 1594, 1504, 1243, 1167, 1108, 797. ESI-MS m/z 2461 [Sm₂(BTPB)₃ + Na]⁺.

 $Gd_2(BTPB)_3(H_2O)_4$ (2). Yield: 80%. Anal. Calc. for $C_{120}H_{74}F_{18}O_{22}Gd_2$: C, 57.10; H, 2.95; O, 13.94. Found: C, 57.27; H, 2.90; O, 13.87. IR (KBr, cm⁻¹): 3060, 1598, 1501, 1235, 1170, 1109, 795. ESI-MS m/z 2475 [Gd₂(BTPB)₃ + Na]⁺.

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