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Homometallic Ln(III)-complexes from ILCT ligand vis-NIR with sensitized emission, excitationdependent PL color tuning and white-light emitting

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A facilely available zwitterionic ligand, 1,1'-(1,4-phenylenebis(methylene))dipyridin-4(1H)one (PBPO), has been designed to bear intraligand charge transfer (ILCT) energy states. PBPO was applied to assemble two series of Ln(III) complexes with either 2D (6,3)-hcb network (LIFM-24(Ln), Ln = Pr, Nd, and Sm), or 1D loop-and-chain (LIFM-25(Ln), Ln = Eu, Gd, Tb, Dy, Ho, Er, Tm, and Yb) polymeric structures, which are decided by lanthanide ions radius. Highly efficient photoluminescence (PL) in visible to near-infrared (NIR) regions can be obtained in these Ln-complexes, due to the extended energy transfer from both triplet and ILCT states of the zwitterionic ligand. Among which, LIFM-24(Pr) and LIFM-25(Dy) manifest excitation-dependent color tunable luminescence and white-light emission based on the combination of ligand-centered (LC) and metallic-centered (MC) emission. Uniquely, strict linear relationship is established between the excitation wavelength and emission CIE (Commission Internationale de L'Eclairage) coordinates in a long color range (orange to blue for LIFM-24(Pr), and yellow to blue for LIFM-25(Dy)), which provides prototype models for programmable PL color tuning and white light emitting, which are rarely achievable in homometallic Ln-complexes.

Introduction

Recently, Lanthanide metal-organic complexes have attracted growing attention not only for the novel structural diversity but also for the advanced applications in optics,1,2 adsorption and separation,^{3, 4} proton conductivity,^{5, 6} heterogeneous catalyst,⁷ etc. Especially, Ln-complexes were used to synthesize distinctive luminescent materials for their large Stokes shift, excellent quantum yield, and long lifetime. Among which, Eu³⁺ and Tb³⁺ complexes have been investigated and reported in a plenty of works as multi-functional materials owing to the strong red and green photoluminescence, respectively. While some other lanthanide complexes have been less studied, despite of their uniquely potential applications, such as complexes from Nd³⁺/Yb³⁺ (biological imaging), Er³⁺ (optical fibers), Pr³⁺, Sm³⁺, Dy³⁺, and Tm³⁺ (both vis and NIR emissions), etc.⁸⁻¹⁰ This might be due to the relatively weak emission of these Ln-complexes by inefficient energy transfer from the ligands triplet states.¹¹ To solve this problem, designing reasonable ligands including extended energy levels, which can match the various accepting levels of different lanthanide ions, might enhance energy transfer efficiency to the lanthanide centers, and provide a promising method to achieve highly sensitized emission in both visible and NIR regions.¹²⁻¹⁴ Recently, our group reported a series of Ln-complexes from mono-, bi-, and tri-podal zwitterionic ligands, and it indicated that the ligands could highly sensitize all of the investigated lanthanide ions, which was ascribed to the extended intraligand charge transfer (ILCT) plus triplet energy states in these ligands can better fit the accepting f-levels of different lanthanide ions, and provide more broad energy tansfer and sensitization pathway to the lanthanide centers.15-17

Single component white light emitting (SC-WLE) and photoluminescence color tuning are important in various fields such as displaying, imaging, sensing and anti-counterfeiting, etc.¹⁸⁻

²⁰ To attain this purpose, a common method was to introduce

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different types of lanthanide ions, such as Eu^{3+} and Tb^{3+} , into the same metal-organic framework.²¹⁻²³ Among all of the SC-WLE Ln-complexes, only a few were based on homometallic examples, such as Sm³⁺, Eu³⁺, Dy³⁺, and Pr³⁺-complexes.^{10, 24-27} Therefore, it is still desirable to develop novel homometallic Ln-complexes with SC-WLE and PL color tuning properties, for their advantages of great reproducibility, simple preparation process, and ease of operation.^{19, 28, 29}

Herein, we synthesized a new bipodal zwitterionic ligand, 1,1'-(1,4-phenylenebis(methylene))dipyridin-4(1*H*)-one (PBPO), which possesses the attributes of good solubility, strong coordination ability with lanthanide ions, separated charge distribution and potential ILCT property. Ln-complexes in two series of coordination structures were synthesized and investigated by the visible or/and NIR PL spectra, and it indicated that PBPO ligand could sensitize all of the explored lanthanide ions efficiently. Uniquely, SC-WLE and linearly PL color tuning could be obtained both in Pr- and Dy- homometallic complexes by varying the excitation wavelengths.

Experimental

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Materials and methods

All chemicals were of AR grade attained from commercial sources and used as purchased without further purification. ¹H NMR spectra were recorded on Bruker Avance 400 NMR spectrometer. Thermogravimetric analysis (TGA) curves were conducted on a NETZSCH TG 209 thermal analyzer from room temperature to 800 °C with a heating rate of 10 °C/min. Powder X-ray diffraction (PXRD) data were measured on a Bruker D8 ADVANCE diffractometer (Cu K α , λ = 1.54178 Å) at 40 kV, 30 mA. The UV-Vis absorption spectra were collected on a Shimadzu UV-250PC spectrophotometer with a variable wavelength between 200 and 800 nm. The data of photoluminescence spectra, and decay lifetime were measured on EDINBURGH FLS980 spectrophotometer with the samples inside two clamped quartz pieces.

Crystallography

Both single-crystal diffraction data of LIFM-24(Pr) and LIFM-25(Eu) were collected from an Agilent Gemini S Ultra diffractometer with the Enhance X-ray Source of Cu-K α radiation ($\lambda = 1.54178$ Å) at 293 K or 173 K. Absorption corrections were applied using multiscan technique. Both of the structures were solved by direct method of SHELXS and refined against F^2 using the SHELXL programs. The non-hydrogen atoms were treated with anisotropic parameters, while H atoms were placed in calculated positions and refined using a riding model. Crystallographic data and structural refinement information were listed in Table 1. Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 1819541-1819542.

Syntheses of the ligand

1,1'-(1,4-phenylenebis(methylene))dipyridin-4(1*H***)-one (PBPO**): K₂CO₃ (1.6 g, 12 mmol) and 4-hydroxypyridine (0.627 g, 6.5 mmol) was added into ethanol (30 ml) and refluxed for 4 hours, and then 1,4-bis(bromomethyl)benzene (0.88 g, 3 mmol) was added and another reaction for 24 h was conducted under the same condition. After the reaction, colorless and transparent solution was obtained with solid filtered, ethanol was evaporated until white product was precipitated, into which 100 ml ethyl ether was injected and great amount of white precipitates were acquired after filtering. The product was dried under vacuum for more than 24 h before use (Scheme 1). Yield: 76%. ¹H NMR (400 MHz, D₂O, 25 °C, Fig. S1): δ 7.79-7.64 (m, 4H), 7.12 (s, 4H), 6.50-6.29 (m, 4H), 5.08 (s, 4H).



Scheme 1 Synthetic route for PBPO ligand.

Syntheses of the Ln-Complexes

LIFM-24(Ln), $[Ln_2(PBPO)_4(NO_3)_6]$ (Ln = Pr, Nd, and Sm): A mixture of PBPO (0.03 mmol) ligand in water (1 ml) was added to a solution of $Ln(NO_3)_3 \cdot xH_2O$ (0.02 mmol, x = 3-6) in acetone (3 ml). The solution was stirred for 30 min. Slow diffusion of acetone into the filtrate over 10 days afforded block crystals suitable for single crystal X-ray diffraction. Yield: 67-70%.

LIFM-25(Ln), $[Ln(PBPO)_2(NO_3)_2] \cdot 0.5PBPO \cdot (NO_3) \cdot solvents$ (Ln = Eu, Gd, Tb, Dy, Ho, Er, Tm, and Yb): These complexes were obtained by a similar method mentioned above but using the corresponding lanthanide salts for instead. Yield: 63-69%.

Results and discussion

Crystal Structures

The series of LIFM-24(Ln) isomorphous complexes were obtained by slow diffusion of acetone into the mixture of PBPO and $Ln(NO_3)_3$ (Ln = Pr, Nd, and Sm). LIFM-24 (Pr) was taken as a representative and the single-crystal X-ray diffraction data was collected. It indicated that LIFM-24 (Pr) crystallized in the triclinic space group P-1 (Table 1). And the asymmetric unit included one Pr^{3+} ion, two PBPO ligands, and three coordinated NO₃⁻ (Fig. 1a). The Pr^{3+} center was 10-coordinated by three chelated NO₃ anions and four oxygen atoms from the PBPO ligands, which resulted in a 2D flat structure with (6,3) hcb-network (Fig. 1b and c). Accordingly, this (6,3) hcb-networks were packed into an ABAB fashion in the crystal lattice (Fig. 1d). Similarly, the Nd- and Smcomplexes could be synthesized in this strategy, and all of them showed almost the same result in PXRD patterns, which suggested the isomorphous structure of LIFM-24(Ln) (Fig. S2). The LIFM-25(Ln) series of isomorphous complexes (Ln = Eu, Gd, Tb, Dy, Ho, Er, Tm, and Yb) were prepared in a similar method but resulted in different crystal structures. Taking LIFM-25(Eu) as an example, it crystallized into orthorhombic space group Pbca. And the asymmetric unit included one Eu³⁺ ions, two PBPO ligands, two coordinated NO3⁻ ions, one uncoordinated NO3⁻ ion and three coordinated water molecules (Fig. 1e). The Eu³⁺ ion was 8Published on 02 March 2018. Downloaded by Fudan University on 03/03/2018 00:46:51

coordinated by four oxygen atoms from the PBPO ligands and two chelated NO₃- anions, linking into 1D coordinated chain (Fig. 1f and g). According to the PXRD patterns of **LIFM-25** series of complexes, they all indicated the isomorphous structures (Fig. S3).

 Table 1 Crystallographic data for complexes LIFM-24(Pr) and LIFM-25(Eu).

	LIFM-24(Pr)	LIFM-25(Eu)
Formula	C72H64N14O26Pr2	C45H40N8O17Eu
F.w.	1823.20	1116.82
$T(\mathbf{K})$	293	173
Crystal system	triclinic	orthorhombic
Space group	P-1	Pbca
a (Å)	10.0807(3)	22.1509(4)
b (Å)	11.0770(5)	16.0378(7)
<i>c</i> (Å)	32.5012(13)	27.6728(12)
α	91.153(4)	90
β	94.746(3)	90
γ	91.904(3)	90
$V(\text{\AA}^3)$	3613.7(2)	9830.81(8)
Z	2	8
$D_{\rm c} ({\rm g cm^{-3}})$	1.676	1.509
μ (mm ⁻¹)	11.027	9.816
<i>F</i> (000)	1840	4520
R_1 (>2 σ)	0.0604	0.0530
wR_2 (all data)	0.1970	0.1545
GOF	1.076	1.144



Fig. 1 Crystal structures of LIFM-24(Pr): asymmetric unit (a), 2D (6,3)-hcb network (b), simplified topology (c), ABAB packing

From the above analysis, we can see that the coordination environment of Ln^{3+} center and obtained networks were decided by the ionic radii of lanthanide ions. To the large ions of Pr^{3+} , Nd^{3+} , and Sm^{3+} , the coordinated number of lanthanide center was 10 and it resulted in a (6,3)-**hcb** network. To the small ions of Eu^{3+} , Gd^{3+} , Tb^{3+} , Dy^{3+} , Ho^{3+} , Er^{3+} , Tm^{3+} , and Yb^{3+} , the lanthanide center adopt 8-coordinated geometry and linking four PBPO ligands into a 1D loop-and-chain. Furthermore, all of the lanthanide ions were coordinated by ligands and NO_3^{-1} ions but without water molecules, which might help to enhance the sensitization efficiency of lanthanide ions.³⁰

Thermal stability of Ln-Complexes

The thermogravimetric analyses (TGA) of **LIFM-24**(Pr) and **LIFM-25**(Ho) were carried out and the results were shown in Fig. S4. To **LIFM-24**(Pr), no obvious weight loss until the decomposition of the framework appeared at about 330 °C, indicating of good thermal stability (Fig. S4a). To **LIFM-25** (Ho), there was a 10.2% weight loss occurred when heated from room temperature to 325 °C, which indicated the loss of one acetone and three water molecules (cacl. 10.7%). Another weight loss of 19.8% appeared from 325 to 366 °C, suggesting the decomposition of three NO₃⁻ ions (cacl. 19.7%). Then the obvious weight loss from 400 °C should be ascribed to the collapse of metal-ligand framework.

Visible and NIR emissions

Luminescence property of PBPO ligand was investigated and the excitation and emission spectra were shown in Fig. S5. PBPO showed a broad excitation from 300 to 400 nm, ascribing to the $S_0 \rightarrow {}^1S_1^*$ and $S_0 \rightarrow ILCT$ excited state.^{15, 16} When excited at 355 nm, the emission peak of PBPO was at about 420 nm showing blue light emitting, which should be ascribed to the ligand-based ${}^{1}S_{1}^{*}$ state emission. As obtained from the phosphorescence spectrum of LIFM-25(Gd) at 77 K (Ex=305 nm), the emission broad peak was from 425 to 650 nm (Fig. S6), and the decay lifetime was tested to be 2.7 ms (503 nm), showing phosphorescence nature compared with the lifetime of 1.1 ms detected at RT. As a result, the combined ILCT plus triplet energy levels of PBPO was determined to be between 15385 and 23809 cm^{-1} (420 to 650 nm). This value was suitable to most of the lanthanide excited states, including Pr³⁺ $({}^{3}P_{0}, 21000 \text{ cm}^{-1}), \text{ Nd}^{3+} ({}^{4}F_{3/2}, 11666 \text{ cm}^{-1}), \text{ Eu}^{3+} ({}^{5}D_{0}, 17500 \text{ cm}^{-1}),$ Tb^{3+} (⁵D₄, 20400 cm⁻¹), Dy^{3+} (⁴F_{9/2}, 22200 cm⁻¹), Sm^{3+} (⁴G_{5/2}, 17730 cm⁻¹), and Yb³⁺ (${}^{4}F_{5/2}$, 10250 cm⁻¹), and might result in highly sensitized visible to NIR emission by efficient energy transfer from ligand to lanthanide,¹⁷ as shown below.

The luminescence of Ln-complexes achieved from lanthanide ions and PBPO ligand were therefore investigated (Fig. S7). It indicated that the PBPO ligand could sensitize all of the explored lanthanide ions to emit the characteristic $f \rightarrow f$ transitions in visible or NIR regions. Meanwhile, the decay lifetimes of Ln-complexes were measured and shown in Table 2 for comparison. In visible Published on 02 March 2018. Downloaded by Fudan University on 03/03/2018 00:46:51

region, the emission peaks of LIFM-24(Pr) should be assigned to the Pr³⁺ transitions of ${}^{3}P_{0} \rightarrow {}^{3}H_{4}$ (486 nm), ${}^{3}P_{0} \rightarrow {}^{3}H_{5}$ (543 nm), ${}^{1}D_{2}$ \rightarrow ³H₄ (596 nm), ³P₀ \rightarrow ³H₆ (612 nm), ³P₀ \rightarrow ⁶F₂ (641 nm), and ³P₀ \rightarrow ⁶F₃ (698 nm), respectively. And the luminescence lifetime was determined to be 61 µs at the most efficiently sensitized 641 nm. To LIFM-24(Sm), the sharp peaks at 562, 596, 643 and 703 should be ascribed to the Sm³⁺ transitions of ${}^{4}G_{2/5} \rightarrow {}^{6}H_{I}$ (J = 5/2, 7/2, 9/2 and 11/2, respectively. And the luminescence lifetime detected at 643 nm was found to be 65 µs, which was a rather better value with comparison to some previous Ln-complexes.^{31,32} To LIFM-25(Eu), the red luminescence consisted of peaks at 586, 594, 616, 655, and 698 nm corresponds to the Eu³⁺ transitions of ${}^{5}D_{0} \rightarrow {}^{7}F_{I}$ (J = 0, 1, 2, 3 and 4, respectively). The highest peak 616 nm was detected to obtain the decay lifetime of 1056 µs. Similarly, to LIFM-25(Tb), the green luminescence was combined by the peaks at 487, 545, 588 and 625 nm which were assigned to the transitions of $\text{Tb}^{3+5}\text{D}_4$ \rightarrow ⁷F₁ (J = 0, 1, 2 and 3, respectively). The rather long lifetimes of LIFM-25(Eu, 1056 µs) and LIFM-25(Tb, 1092 µs) could be compared to many other reported Ln-complexes.33-35 To LIFM-**25**(Dy), corresponding to the Dy³⁺ transitions of ${}^{4}F_{9/2} \rightarrow {}^{6}H_{15/2}$, ${}^{4}F_{9/2} \rightarrow {}^{6}H_{13/2}, {}^{4}F_{9/2} \rightarrow {}^{6}H_{11/2}$ and ${}^{4}F_{9/2} \rightarrow {}^{6}H_{9/2}$, the emission peaks were found at 480, 575, 660 and 750 nm, respectively. The lifetime was measured and determined to be 43 µs by detecting at 575 nm, which is among the best for the rarely reported Dy-complexes compared with earlier literatures.^{17, 26} The luminescence spectrum of LIFM-25(Tm) was also investigated, when excited at 330 nm, the emission peaks at 796 nm in visible region was found, which should be ascribed to the Tm³⁺ transition of ${}^{3}H_{4} \rightarrow {}^{3}H_{6}$.

 Table 2 Photophysical properties of Ln-complexes from PBPO ligand (solid state, 298 K).

Complex	$\lambda_{max}\left(nm\right)$ and assignment	$\tau_{obs}\left(\mu s\right)^{a}$
LIFM-24(Pr)	$641 (^{3}P_{0} \rightarrow ^{3}F_{3})$	61
	$1010 ({}^{1}D_{2} \rightarrow {}^{3}F_{4})$	4.9
LIFM-24(Nd)	$1055 ({}^{4}F_{3/2} \rightarrow {}^{4}I_{11/2})$	2.8
LIFM-24(Sm)	$643 \ ({}^{4}\text{G}_{5/2} \rightarrow {}^{6}\text{H}_{9/2})$	65
	$940 ({}^{4}G_{5/2} \rightarrow {}^{6}F_{5/2})$	66
LIFM-25(Eu)	$616 ({}^{5}D_{0} \rightarrow {}^{7}F_{2})$	1056
LIFM-25(Tb)	$545~(^{5}\mathrm{D}_{4} \rightarrow ^{7}\mathrm{F}_{5})$	1092
LIFM-25(Dy)	575 (${}^{4}F_{9/2} \rightarrow {}^{6}H_{13/2}$)	43
	$839 ({}^{4}F_{9/2} \rightarrow {}^{6}H_{7/2} + {}^{6}F_{9/2})$	38
LIFM-25(Ho)	$980 \ ({}^{5}F_{5} \rightarrow {}^{5}I_{6})$	1.9
LIFM-25(Er)	$1533 \ ({}^{4}I_{13/2} \rightarrow {}^{4}I_{15/2})$	1.2
LIFM-25(Tm)	796 (${}^{3}\text{H}_{4} \rightarrow {}^{3}\text{H}_{6}$)	n.d.*
	$1226 (^{3}H_{5} \rightarrow ^{3}H_{6})$	2.8
LIFM-25(Yb)	$982 \ ({}^{2}F_{5/2} \rightarrow {}^{2}F_{7/2})$	17

^a The data of photophysical properties written in non-italicized text represent visible-light emission, while those in italicized text represent NIR emission.

PBPO ligand can sensitize the lanthanide ions emission not only in visible region but also NIR region, as shown in Fig. S7 and the photophysical data were summarized in Table 2. In detail, the emission bands of LIFM-24(Pr) centered at 855, 1010 and 1420 nm were assigned to the ${}^{1}D_{2} \rightarrow {}^{3}F_{2}, {}^{1}D_{2} \rightarrow {}^{3}F_{2}$ and ${}^{1}D_{2} \rightarrow {}^{1}G_{4}$, respectively.³⁶ And the decay lifetime detected at 1010 nm was determined to be 4.9 µs, which was quite shorted than that in visible region. LIFM-24(Nd) has the NIR emission peaks at 896, 1055 and 1326 nm, which correspond to the Nd³⁺ transitions of ${}^{4}F_{3/2} \rightarrow {}^{4}I_{I}$ (J = 9/2, 11/2, and 13/2, respectively). LIFM-24(Sm) showed the peaks at 788, 875, 895, 940, 1020, and 1166 nm corresponding to the Sm³⁺ transitions of ${}^{4}G_{2/5} \rightarrow {}^{6}H_{13/2}$, and ${}^{4}G_{2/5} \rightarrow {}^{6}F_{J}$ (J = 1/2, 3/2, 5/2, 7/2, and 9/2). Its value of decay lifetime at 940 nm was high to 66 µs which was almost identical to that in visible region (65 μ s), suggesting the good sensitization to Sm³⁺ by PBPO ligand in NIR region. LIFM-25(Dy) showed major peaks at 836, 928, 995 and 1163 nm which should be ascribed to the Dy³⁺ transitions of ${}^{4}F_{9/2} \rightarrow {}^{6}H_{7/2} + {}^{6}F_{9/2}$, ${}^{4}F_{9/2} \rightarrow {}^{6}H_{5/2}$, ${}^{4}F_{9/2} \rightarrow$ ${}^{6}F_{7/2}$ and ${}^{4}F_{9/2} \rightarrow {}^{6}F_{5/2}$, respectively. The lifetime determined to be 38 µs, a little bit shorter comparing with that in visible region (43 us). Four major emission peaks of LIFM-25(Ho) was found at 810, 975, 1183 and 1480 nm. And these peaks were corresponding to ${}^{5}F_{4} \rightarrow {}^{5}I_{7}, {}^{5}F_{5} \rightarrow {}^{5}I_{7}, {}^{5}I_{6} \rightarrow {}^{5}I_{8} \text{ and } {}^{5}F_{5} \rightarrow {}^{5}I_{6}, \text{ respectively. LIFM-}$ 25(Er) displayed two emission peaks at 816 and 1533 nm which can be attributed to Er^{3+} transitions of ${}^{4}\text{I}_{9/2} \rightarrow {}^{4}\text{I}_{15/2}$ and ${}^{4}\text{I}_{13/2} \rightarrow {}^{4}\text{I}_{15/2}$. respectively. To LIFM-25(Tm) complex, the Tm³⁺ transitions of ${}^{3}\text{H}_{4} \rightarrow {}^{3}\text{H}_{6}, {}^{3}\text{H}_{5} \rightarrow {}^{3}\text{H}_{6} \text{ and } {}^{3}\text{F}_{4} \rightarrow {}^{3}\text{H}_{4} \text{ charactered at 796, 1226 and}$ 1550 nm, respectively. The lifetimes of LIFM-25(Ho), LIFM-25(Er), LIFM-25(Tm) were determined to be 1.9, 1.2 and 2.8 µs, respectively. The NIR peaks detected at 982 and 1030 nm for **LIFM-25**(Yb) should be assigned to the transition of ${}^{2}F_{5/2} \rightarrow {}^{2}F_{7/2}$. Its lifetime (determined to be 17 µs) was quite high comparing to some other reported cases.³⁷

Color tuning and white-light emitting

Among the above investigated Ln-complexes, LIFM-24(Pr) and LIFM-25(Dy) were found to be able to produce direct tunable and white light emission by varying the excitation wavelength. For LIFM-24(Pr), the emission spectra were explored by excitation varying from 300 to 360 nm, showing different emitting colors and intensity. When excited at high energy wavelength, for example 290 nm, almost only emission of Pr³⁺ f-f transition was found, resulting in orange color light (Fig. 2). It suggested that all of the absorbed energy at this wavelength was transferred from PBPO ligand to lanthanide center efficiently. This can be further proven by the excitation spectra of LIFM-24(Pr) monitored by 430 nm (based on ligand emission) and 641 nm (based on Pr^{3+} emission) in Fig. S8. When excited at 290-300 nm, the ligand emission was negligible, but Pr³⁺ emission could happen efficiently. However, when excited at lower energy wavelength between 300 and 350 nm, two new broad emission peaks were detected covering from 400 to 600 nm. These two peaks should be ascribed to ILCT and Pr³⁺affected ligand emissions. It indicated that the energy transfer from ligand to Pr³⁺ was incomplete, resulting in a combined spectra of

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 Pr^{3+} -based f-f and ligand-based ILCT emission. Especially, when excited at 330 and 345 nm, pink and white light emission could be obtained. CIE coordinates of this white light emission was (0.34, 0.30), with correlated color temperature (CCT) and color rendering index (CRI) of 5468 K and 98, respectively. It emphasized **LIFM-24**(Pr) a potential white-light material and could be applied in some applications, for example barcode module.¹⁰ Further, when excited at even lower energy wavelength, no efficient energy transfer appeared from ligand to Pr^{3+} , thus the ILCT emission of ligand was dominant, leading to blue light emission. On this basis, a series of CIE coordinates were obtained from emission spectra excited at various wavelengths from 300 to 360 nm, which showed a linear relationship.



Fig. 2 Tunable and white light emission of **LIFM-24**(Pr) at room temperature. Photo-excited images (a) and emission spectra (c) excited at 290 (orange), 330 (pink), 345 (white), and 355 (blue) nm, respectively. (b) CIE coordinates of the emission spectra at the excitation wavelength from 300 to 360 nm (the excitation wavelength interval was 3 nm).

The emission spectra of **LIFM-25**(Dy) were also measured at different excitation wavelengths (Fig. 3). When excited at high energy wavelength below 310 nm, only Dy^{3+} -based emission was found, leading to a yellow color light. This resulted from the efficient energy transfer from PBPO ligand to Dy^{3+} center similar to the case of **LIFM-25**(Pr), which was proved by the excitation spectrum (Fig. S9). And when the wavelength increased from 320 to 360 nm, white light could be obtained from the combination of ligand-based and Dy^{3+} -based emissions. Especially, when the excitation wavelength was 339 nm, the white light with CIE coordinates of (0.32, 0.33) was quite near to that of standard white

light (0.33, 0.33). Its CCT and CRI were 5461 K and 97, respectively. Accordingly, a series of CIE coordinates were obtained from emission spectra excited at various wavelengths from 290 to 360 nm, which also showed a good linear relationship (Fig. 3b). Based on this, materials and devices with programmable PL color tuning strategies can be established. For example, in a typical fluorescent plate model designed from LIFM-24(Pr) and LIFM-25(Dy) as shown in Fig. 3c, by swapping the excitation wavelengths controllable by a computer program, continuously varied displaying color can be achieved. Compared with other models, the PL color tuning herein is dependent on programmable switch of different exciting wavelengths applied on a homometallic Ln-complex material, which is more reliable, practicable and reproducible.



Fig. 3 Tunable and white light emission of **LIFM-25**(Dy) at room temperature. Emission spectra (a) excited at 290, 320, 339, and 360 nm, respectively. (b) CIE coordinates of the emission spectra at the excitation wavelength from 300 to 360 nm (the excitation wavelength interval was 3 nm). (c) Schemiatic model for excitation-dependent fluorescent plate made from **LIFM-24**(Pr) and **LIFM-25**(Dy).

Conclusions

In summary, a zwitterionic ligand PBPO with ILCT property was used to assemble eleven Ln-complexes which crystallized in two series of coordination structures. The ligand can sensitize both visible and NIR emissions in these Ln-complexes efficiently. Especially, two singe-component homometallic Ln-complexes, LIFM-24(Pr) and LIFM-25(Dy) show color tunable and whitelight emission from the combination of ligand-based and lanthanide-based emissions when excited at appropriate wavelength. A good linear relationship is established between the excitation wavelength and CIE coordinate, which has not been reported for homometallic Ln-complexes before. This provides new opportunities for designing photoluminescent materials and devices with programmable PL color tuning strategies, which can be potential for further applications in displaying, sensing, and anticounterfeiting.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

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Homometallic Ln(III)-complexes with sensitized vis-NIR emission, excitation-dependent PL color tuning and white-light emitting from an ILCT ligand.