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Accurate tuning of rare earth metal—organic frameworks with unprecedented topology for white-light emission[†]

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A series of isostructural rare-earth metal-organic frameworks (RE-MOFs), namely {[RE(L-X)(H₂O)]·2DMF)_n (UPC-38, RE = Eu, Tb, X = H, F, Cl, NH₂, CH₃, OCH₃; L = [1,1':3',1"-terphenyl]-4,4",5'-tricarboxylic acid) have been successfully synthesized under solvothermal conditions. Single-crystal X-ray diffraction analysis shows that UPC-38 is an unprecedented three-dimensional (3D) (3,4,5)-c zkf topological framework with one-dimensional (1D) chain secondary building units. Different functional groups can be attached to the ligand (L), and the effects of the different functional groups on the fluorescence intensity, emission wavelength and guantum yield of UPC-38 were systematically studied. It was found that the introduction of an amino group causes the emission wavelength to red shift significantly, while that of other groups causes slight effects on the emission wavelengths. UPC-38(Eu)-H and UPC-38(Tb)-H without modified functional groups in these twelve crystals exhibit the highest quantum yield ratios of 16.64% and 28.06%, respectively. Remarkably, by adjusting the ratio of Eu^{3+} to Tb^{3+} and the $L-OCH_3^{3+}$ ligand with the strongest blue emission, a series of double-doped rare-earth metal-organic frameworks, UPC-38(Eu_xTb_{1-x})-OCH₃ $(0 \le x \le 1)$, are successfully acquired. The calculated CIE coordinates of **UPC-38(Eu)-OCH₃** and UPC-38(Tb)-OCH₃ are (0.50, 0.28) and (0.23, 0.45), respectively. It is exciting that a white light emitting material, UPC-38(Eu_{0.34}Tb_{0.66})-OCH₃, can be successfully obtained through careful tuning of the Eu³⁺/Tb³⁺ ratio in the framework. The CIE coordinate is (0.335, 0.325), which is very close to the standardized value of (0.333, 0.333).

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Introduction

In the past decade, white light emitting materials have been extensively investigated and widely applied in illumination, lasers, and displays.¹ Especially in the field of illumination, incandescent lamps have been gradually replaced by fluorescent lamps and white light-emitting diodes (WLEDs) because they are more environmentally friendly, safe, efficient and energy-saving.² Currently, almost all commercial phosphors are

rare-earth (RE)-doped materials, because of the special luminescence properties.³ However, according to the Laporte rule and screening effect, rare-earth ions have very weak emissions when they are directly excited.⁴ The "antenna effect" produced by introducing organic chromophores is an effective way to increase the light absorption and enhance the luminescence ability of rare earth ions.⁵

More than half of rare earth elements with 4f electrons can be stimulated and emit visible or near infrared light, for example Nd³⁺, Sm³⁺, Eu³⁺, Tb³⁺, Dy³⁺, Er³⁺, Tm³⁺, Yb³⁺ and so on, and the light covers the whole visible region.⁶ Moreover, they emit three primary colors in nature: red, green and blue, which enables them to theoretically regulate the luminescence of rare earth complexes. According to RGB (Red, Green and Blue) models, various colors of light in nature can be obtained by adjusting red, green and blue light.^{7–10} However, controllable doping of different rare earth ions to increase the antenna effect remains a huge challenge.

Metal–Organic frameworks (MOFs) have been extensively applied in recent years, such as gas storage/separation, heterogeneous catalysis, molecular magnetism, photoluminescence

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and fluorescent probes.^{11–15} Particularly, rare-earth metal-organic frameworks (RE-MOFs) show great application prospects in photoluminescence and fluorescent probes. Recently, some RE-MOF materials with white light emitting properties have been obtained through reasonable design.¹⁶ By carefully adjusting the proportion of Eu³⁺, Tb³⁺, and Dy³⁺ ions, Yin et al. obtained a ternary doped white light emitting RE-MOF.¹⁷ Wu et al. realized a highly efficient white light emitting MOF through packaging of Red-Green-Blue fluorescent dyes, and high color-rendering index values up to 92% and quantum yields up to 26% were reported.18 A multicomponent MOF with white light emission has been reported by Telfer et al., which contains three controllable photoactive ligands.¹⁹ However, few studies focusing on the generation of white-light emission through combining the photo physical characteristics of the organic ligand and metal ions have been reported, although MOFs have the advantage of being an adjustable luminescent material.

It is well known that ligands with a rigid structure and π -electron conjugation system have strong fluorescence emission properties.²⁰ Moreover, the introduction of functional groups to aromatic hydrocarbons will affect the fluorescence intensity and wavelength. Thus, careful tuning of the organic ligand and doping of RE ions in RE-MOFs are reasonable to achieve white-light emission. Herein, we report the design and synthesis of a series of three-dimensional RE-MOFs {[RE(L-X)(H₂O)]·2DMF}_n (UPC-38, RE = Eu, Tb, X = H, F, Cl, NH₂, CH₃, OCH₃; L = [1,1':3',1"-terphenyl]-4,4",5'-tricarboxylic acid) with the unprecedented **zkf** topology based on tricarboxylic acid ligands with different functional groups (-H, -F, -Cl, $-NH_2$, $-CH_3$ and $-OCH_3$). Through careful selection of the organic ligand and doping of different ratios of Eu³⁺

and Tb³⁺, the luminescence characteristics of the RE-MOFs can be fine-tuned to achieve white-light emission.

Results and discussion

Crystal structure

Single-crystal X-ray diffraction analysis shows that UPC-38-H. UPC-38-F, UPC-38-Cl, UPC-38-NH₂, UPC-38-CH₃, and UPC-38-OCH₃ are isostructural with the monoclinic space group I_2/c . The crystal structure of UPC-38-F (Eu) is described representatively. The asymmetrical unit contains half deprotonated $L-F^{3-}$ ligand, half Eu³⁺ ion, and two coordinated water molecules. Each Eu³⁺ ion adopts eight-coordination mode, which is coordinated by six carboxylate oxygen atoms from five different ligands and two water molecules (Fig. 1a). The spatial geometry of each Eu^{3+} ion is distorted by the plane rotation of oxygen atoms (Fig. 1a). As shown in Fig. 1b, the carboxylate groups of the L- \mathbf{F}^{3-} ligand adopt two coordination modes: chelating bidentate mode for the group on the central benzene ring, and *cis-cis* bridging bidentate mode for the groups on the side benzene ring. Thus, each eightcoordinated Eu³⁺ ion is bridged by μ_2 - η^1 : η^1 *p*-benzoate carboxylate groups from L-F³⁻ ligands to form a one-dimensional (1D) rod-shaped secondary building unit (SBU) with a Eu-Eu distance of 4.927 Å (Fig. 1d). The 1D chain SBUs are further linked by the backbone of the L-F³⁻ ligands to form a 3D framework structure (Fig. 1g). With the introduction of different functional groups, the twist angle between the central benzene ring and the side benzene ring is changed (Fig. S1, ESI⁺). We systematically studied the effect of steric hindrance on the structure control of multinuclear RE-MOFs in our previous work.²¹ In contrast, here they tend to form non-multinuclear



Fig. 1 (a) The coordination environments of Eu^{3+} ions and the distortion of the cubic geometry through a rotation of the plane formed by oxygen atoms O1', O2', O3' and O4'; (b) the coordination environments of **L-F**; (c) the simplified diagram of ligands; (d and e) 1D chain secondary building units; (f) the simplified diagram of SBUs; (g and h) view of the 3D open framework along the *c*-axis; (i) (3,4,5)-*c* **zkf** topological frameworks.

clusters when there are no templates in the reaction system. The rod-shaped SBUs have better compatibility, which can well tolerate the twist of the ligands. **UPC-38** has an unprecedented topology with a 3, 4, 5-connected net, in which carboxylate C atoms on the rod define diamond ladders (Fig. 1f), and the ligands are simplified to a three-link point (Fig. 1c). The net in this case has the Reticular Chemistry Structure Resource (RCSR) symbol **zkf** and is shown in Fig. 1i.

Solid-state luminescence properties

H₃L-H, H₃L-F, H₃L-Cl, H₃L-NH₂, H₃L-CH₃ and H₃L-OCH₃ at room temperature exhibit an emission peak at 429, 427, 425, 473, 426 and 425 nm (λ_{ex} = 330 nm), respectively (Fig. 3a). These blue emissions could be ascribed to the intra ligand n–π or π–π* electron transition. Compared with that of H₃L-H, the emission peak of H₃L-NH₂ with an inserted amino group was red-shifted. For UPC-38(Eu)-X and UPC-38(Tb)-X (X = H, F, Cl, NH₂, CH₃, OCH₃), the characteristic bands of Eu³⁺ and Tb³⁺ ions appeared. As shown in Fig. 2b, UPC-38(Eu)-X shows four emission bands at 592, 615, 652, and 698 nm, which are attributed to the characteristic ⁵D₀ → ⁷F_J (J = 1–4) transitions of Eu³⁺ ions. The isolated coordination geometry of Eu³⁺ metal ions leads to a strong ⁵D₀ → ⁷F₄ peak due to the distorted noncubic configuration,²² but ⁵D₀ → ⁷F₂ emission dominates in these chain SBUs (Fig. 1a).

As shown in Fig. 2c, UPC-38(Tb)-X shows four emission bands at 490, 545, 586, and 622 nm, which are attributed to the characteristic ${}^{5}D_{4} \rightarrow {}^{7}F_{J}$ (J = 3-6) transitions of the Tb³⁺ ion. With the introduction of functional groups, the quantum yield drastically changed. Compared with that of UPC-38(Eu/Tb)-X (X = F, Cl, NH₂, CH₃, OCH₃), the highest quantum yields of UPC-38(Eu)-H and UPC-38(Tb)-H are 16.64% and 28.06%, respectively. The lowest quantum yields of UPC-38(Eu)-Cl and UPC-38(Tb)-Cl are 2.98% and 4.89%, respectively (Table S2, ESI†).

Considering comprehensively, we choose UPC-38-OCH₃ as the representative research object. As shown in Fig. 3a, under a 365 nm UV lamp, UPC-38(Tb)-OCH₃ shows green light. The CIE coordinate is calculated to be (0.226, 0.448), corresponding to green emission (λ_{ex} = 330 nm). UPC-38(Eu)-OCH₃ shows red light under a 365 nm UV lamp, with the CIE coordinate of



Fig. 3 (a) Solid-state emission spectra of UPC-38(Tb)-OCH₃; (b) solidstate emission spectra of UPC-38(Eu)-OCH₃; (c) solid-state emission spectra of HL-OCH₃; (d) solid-state emission spectra of UPC-38(Eu_{0.34}Tb_{0.66})-OCH₃ (the insets show the corresponding luminescent materials under UV-light irradiation at 365 nm and the CIE coordinates at 330 nm).

(0.503, 0.278) and red emission ($\lambda_{ex} = 330 \text{ nm}$) (Fig. 3b). The emission wavelength of H_3 L-OCH₃ locates just in the blue region. The CIE coordinate is calculated to be (0.158, 0.032), corresponding to blue emission ($\lambda_{ex} = 330 \text{ nm}$) (Fig. 3c). This makes it possible to provide white-light emission through careful tuning of the ratios of Eu³⁺ and Tb³⁺ ions in the framework.

Tunable emission of bimetallic doped Eu_xTb_{1-x} MOFs

All GRB colors can be obtained based on red, green and blue. The aforementioned results clearly demonstrate that isomorphic **UPC-38** can produce all the three primary colors. Thus, in theory, color adjustment can be achieved by adjusting the ratio of Eu^{3+}/Tb^{3+} . Therefore, bimetallic doped **UPC-38(Eu_xTb_{1-x})-OCH_3** ($0 \le x \le 1$) was obtained by doping Eu^{3+}/Tb^{3+} in different proportions. As shown in the PXRD patterns (Fig. S9, ESI†), bimetallic doped **UPC-38(Eu_xTb_{1-x})-OCH_3** are isostructural to the corresponding **UPC-38.** The relative molar ratios of Eu^{3+}/Tb^{3+} calculated through the ICP measurements are listed in Table S9 (ESI†). As shown in Fig. 4b, these bimetallic complexes demonstrate the characteristic emissions of both Eu^{3+} and Tb^{3+}



Fig. 2 (a) The solid-state fluorescence of L-X; (b) the solid-state fluorescence of UPC-38(Eu)-X; (c) the solid-state fluorescence of UPC-38(Tb)-X (X = H, F, Cl, NH₂, CH₃, OCH₃; λ_{ex} = 330 nm, at room temperature).



Fig. 4 (a) The UPC-38(EuxTb₁_x)-OCH₃ luminescent materials under UV-light irradiation at 365 nm (1–11); (b) solid-state emission spectra of UPC-38(EuxTb₁_x)-OCH₃ (λ_{ex} = 330 nm); (c) the CIE coordinates of UPC-38(EuxTb₁_x)-OCH₃ (λ_{ex} = 330 nm); (d) solid-state emission spectra of UPC-38(Eu_{0.34}Tb_{0.66})-OCH₃ at different excitation wavelengths; (e) the CIE coordinates of UPC-38(Eu_{0.34}Tb_{0.66})-OCH₃ at different excitation wavelengths.

ions. With the increase of Eu³⁺, the emission intensity of Eu³⁺ ions from $^5D_0 \rightarrow \ ^7F_2$ increases and that of Tb^{3+} ions from $^5D_4 \rightarrow \ ^7F_5$ decreases. The color of UPC-38(Eu_xTb_{1-x})-OCH₃ is from green to yellow, white, pink and finally to red under a 365 nm UV lamp (Fig. 4a). The CIE coordinates cross the green-red region (Fig. 4c). As shown in Fig. 4c, the CIE coordinates of these doped MOFs are closest to the white light region when the proportions of Eu³⁺ are 20%, 30% and 40%. Hence, the emission wavelengths of these doped MOFs were measured at different excitation wavelengths. The results show that the sample with 30% doping of Eu³⁺ has the ability to emit white light, and its emission intensity decreases with the increase of the excitation wavelength (Fig. 4d). When the excitation wavelength is 335 nm, UPC-38(Eu_{0.34}Tb_{0.66})-OCH₃ exhibits white light emission, and its CIE coordinates are (0.335, 0.325), closest to the standard values (0.333, 0.333) (Tables S3-S8, ESI⁺). Therefore, by the precise adjustment of the Eu³⁺/Tb³⁺ ratios, the emission colors of this series of doped complexes can be systematically tuned (Fig. S14-S19, ESI⁺). The quantum yield of UPC-38(Eu_{0.34}Tb_{0.66})-OCH₃ is 13.96%, which is between UPC-38(Eu)-OCH₃ (9.24%) and UPC-38(Tb)-OCH₃ (24.37%).

Energy-transfer process

Photoluminescence is caused by electron transitions and energy transfer. In order to study the process of energy transfer in **UPC-38**, the singlet (S₁) state of the ligand is estimated to be 30769 cm^{-1} by UV-vis absorbance (Fig. S30, ESI†), and the triplet (T₁) state of **UPC-38-Gd** is calculated to be 19 455 cm⁻¹



from the low temperature phosphorescence spectrum (Fig. S31, ESI†). On the basis of Reinhoudt's empirical rule, when the energy gap ΔE (S₁ – T₁) surpasses the limit value of 5000 cm⁻¹, the intersystem crossing (ISC) process will be effective.²³ Therefore, the characteristic luminescence emissions of **UPC-38(Eu_{0.34}Tb_{0.66})-OCH₃** indicated the occurrence of the antenna effect. That is, the light was first absorbed by the ligands, followed by ISC, and then antenna transfer from T₁ to f levels of RE³⁺, leading to f–f emissions (Scheme 1).

In order to test its white light emission performance, as phosphor, UPC-38($Eu_{0.34}Tb_{0.66}$)-OCH₃ is coated on the surface of a commercially available ultraviolet LED, to make a WLED. The resultant WLED exhibits bright white light at an applied voltage of 3.0 V (Fig. 5). On the basis of these results, it is clear that UPC-38($Eu_{0.34}Tb_{0.66}$)-OCH₃ has potential for practical lighting applications.

PXRD, IR, PL and thermogravimetric analysis of UPC-38-(H, F, Cl, NH₂, CH₃, OCH₃)

The phase purity of different Eu^{3+}/Tb^{3+} concentration doped UPC-38(Eu_xTb_{1-x})-OCH₃ powders and different ligands UPC-38(Eu/Tb)-X (X = H, F, Cl, NH₂, CH₃, OCH₃) was identified by the X-ray powder diffraction patterns shown in Fig. S3–S10 (ESI⁺). Photoluminescence tests of different solvents are shown in Fig. S12 and S13 (ESI⁺). We found that only nitrobenzene has



Fig. 5 (a) An illuminating 5 mm ultraviolet LED (not turned on); (b) the same LED turned on; (c) the same LED coated with a thin layer of the sample of $UPC-38(Eu_0.34Tb_0.66)-OCH_3$ (not turned on); (d) the coated LED was turned on and illuminates bright white light.

a strong quenching effect on **UPC-38**. The infrared spectra are tested and show a specific functional group absorption vibration peak (IR, Fig. S20–S25, ESI†). The thermal stability of **UPC-38** was determined by thermogravimetric analysis (TGA, Fig. S26–S29, ESI†) and X-ray powder diffraction patterns (Fig. S11, ESI†). The initial weight loss before 120 °C is attributed to the removal of the solvent molecules, whereas the weight loss from 150 to 200 °C can be attributed to the removal of strongly coordinated DMF cations trapped inside the pores. The crystal structure can be maintained at 200 °C. The decomposition of **UPC-38** starts at 550 °C, leading to the removal of organic linkers and structural collapse.

Conclusions

In conclusion, a series of isomorphic three-dimensional rare earth metal–organic frameworks were synthesized and their photoluminescence properties were systematically studied. Singlecrystal X-ray diffraction analysis shows that UPC-38 is an unprecedented 3D (3,4,5)-*c* **zkf** topological framework with 1D rodshaped SBUs. Through precise tuning of the ratio of Eu^{3+}/Tb^{3+} ions in the framework, a white light emitting material UPC-38($Eu_{0.34}Tb_{0.66}$)-OCH₃ was successfully obtained. The WLED covered with the UPC-38($Eu_{0.34}Tb_{0.66}$)-OCH₃ material emits bright white light. It is clear that UPC-38($Eu_{0.34}Tb_{0.66}$)-OCH₃ has potential for practical lighting applications. The present work provides a promising tri-component approach to the design of tunable color and solid state white-light emitting MOF materials, which could find applications in displays and lighting in the future.

Experimental

Materials and measurements

All chemical reagents were obtained from commercial sources and can be used without further purification. H₃L-X (X = H, F, Cl, NH₂, CH₃, OCH₃) were synthesized through the procedures in ESI† Section 1. ¹H NMR spectra were obtained using an Inova 500 MHz spectrometer. Single crystal X-ray diffraction experiments were carried out using a SuperNova diffractometer equipped with mirror Cu-K α radiation (λ = 1.54184 Å) and an Eos CCD detector under 150 K. Powder X-ray diffraction (PXRD) was carried out using a Bruker D8-Focus Bragg–Brentano X-ray Powder Diffractometer equipped with a Cu sealed tube (λ = 1.54178 Å) at 40 kV and 40 mA. The photoluminescence spectra were measured using a Hitachi F7000 fluorescence spectrometer. The absolute fluorescence quantum yields were measured using an integrating sphere.

Synthesis of UPC-38

Synthesis of UPC-38(Eu)-H. A mixture of H_3L -H (10.0 mg, 0.02 mmol) and $Eu(NO_3)_3 \cdot 6H_2O$ (20.0 mg, 0.04 mmol) was dissolved in a mixed solvent of DMF (1 mL) and H_2O (1 mL) in a 10 mL vial and heated at 100 °C for 24 h. Then, the mixture was slowly cooled to room temperature over 3 h. The crystals were collected with 79.8% yield based on the H_3L -H. IR data

(KBr, cm⁻¹): 3406(m), 2925(w), 1659(s), 1585(s), 1540(s), 1412(s), 1183(w), 1095(m), 1011(w), 857(m), 782(s), 711(w), 658(w).

Synthesis of UPC-38(Eu)-F. The procedure was the same as that for **UPC-38(Eu)-H**, except for H_3L -H instead of H_3L -F. **UPC-38(Eu)-F** was obtained in 67.5% yield. Anal. calcd for $C_{13.5}H_{14}Eu_{0.5}F_{0.5}NO_5$: C, 45.57; H, 3.96; N, 3.93. Found: C, 45.46; H, 3.68; N, 4.06. IR data (KBr, cm⁻¹): 3382(s), 2934(w), 2866(w), 1660(s), 1585(s), 1412(s), 1096(m), 917(m), 868(m), 786(s), 724(s), 662(m), 552(m).

Synthesis of UPC-38(Eu)-Cl. The procedure was the same as that for **UPC-38(Eu)-H**, except for H₃**L-H** instead of H₃**L-Cl. UPC-38(Eu)-Cl** was obtained in 70.8% yield. Anal. calcd for $C_{21}H_{14}ClEuO_8$: C, 43.35; H, 2.42. Found: C, 44.06; H, 2.28. IR data (KBr, cm⁻¹): 3245(s), 2928(w), 2872(w), 1950(w), 1660(s), 1543(m), 1406(s), 1255(w), 1096(m), 1034(m), 910(m), 779(s), 662(m), 593(m), 538(w).

Synthesis of UPC-38(Eu)-NH₂. The procedure was the same as that for **UPC-38(Eu)-H**, except for H₃**L-H** instead of H₃**L-NH**₂. **UPC-38(Eu)-NH**₂ was obtained in 75.8% yield. Anal. calcd for $C_{13.5}H_{15}Eu_{0.5}N_{1.5}O_5$: C, 45.77; H, 4.26; N, 5.93. Found: C, 45.37; H, 4.21; N, 5.64. IR data (KBr, cm⁻¹): 3334(s), 2928(m), 2563(w), 2170(w), 1950(w), 1592(s), 1412(s), 1365(s), 1090(m), 868(m), 779(s), 738(m), 662(m), 545(w).

Synthesis of UPC-38(Eu)-CH₃. The procedure was the same as that for **UPC-38(Eu)-H**, except for H₃**L-H** instead of H₃**L-CH**₃. **UPC-38(Eu)-CH**₃ was obtained in 76.4% yield. Anal. calcd for C₁₄H_{15.5}Eu_{0.5}NO₅: C, 47.53; H, 4.41; N, 3.96. Found: C, 47.66; H, 4.49; N, 4.02. IR data (KBr, cm⁻¹): 3251(s), 2928(m), 2866(w), 2177(w), 1943(w), 1585(s), 1406(s), 1178(m), 1096(m), 868(m), 786(s), 724(m), 662(m), 545(w).

Synthesis of UPC-38(Eu)-OCH₃. The procedure was the same as that for **UPC-38(Eu)-H**, except for H₃L-H instead of H₃L-**OCH**₃. **UPC-38(Eu)-OCH**₃ was obtained in 78.8% yield. Anal. calcd for C_{14.5}H₁₄Eu_{0.5}NO_{5.5}: C, 47.55; H, 3.85; N, 3.82. Found: C, 47.06; H, 3.24; N, 4.03. IR data (KBr, cm⁻¹): 3382(s), 2927(w), 2872(w), 1950(w), 1660(s), 1537(s), 1406(s), 1227(m), 1089(m), 1006(m), 868(m), 786(s), 724(s), 662(m), 545(w).

Synthesis of doped bimetallic UPC-38(Eu_xTb_{1-x})-OCH₃ MOFs. Microcrystalline powders of the codoped bimetallic complex UPC-38(Eu_xTb_{1-x})-OCH₃ were synthesized according to similar procedures mentioned above only with changing the stoichiometric ratios of RE(NO₃)₃·6H₂O. Powder X-ray diffraction (PXRD) proved the isostructural structures of the doped complexes and the UPC-38 complex. Inductively coupled plasma (ICP) spectroscopy was executed to determine the relative molar ratios within the doped MOFs.

Conflicts of interest

The authors declare no competing financial interest.

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