

White light emission by a lanthanide doped Sm(III) framework constructed from 4-sulfobenzoate and 1*H*-imidazo[4,5-*f*][1,10]-phenanthroline†

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The 2D isostructural lanthanide–organic frameworks [Ln(4-SBA)-(IP)OH]·1.5H<sub>2</sub>O (Ln = Sm **1**, Eu **2**, Gd **3** and Tb **4**; 4-SBA = 4-sulfobenzoate and IP = 1*H*-imidazo[4,5-*f*][1,10]-phenanthroline) display different luminescent behavior. White light emission was realized by introducing single dopant Eu(III) and codopants Eu(III)/Gd(III) or Eu(III)/Tb(III) into the Sm(III) framework for the first time.

Metal–organic frameworks (MOFs) have attracted considerable attention due to their novel structures and potential applications in catalysis, magnetism, gas storage, and luminescence, *etc.*<sup>1</sup> Research on white light emitting MOFs is currently an expanding field.<sup>2</sup> This is because the white light emitting materials have broad applications in display and lighting.<sup>3</sup> Lanthanide–organic frameworks (LnOFs) display narrow bandwidth and intense emission upon ultraviolet light excitation.<sup>2e,4</sup> Several examples of white light emitting LnOFs have been reported, such as La:Eu,Tb, Gd:Eu,Tb, Gd:Dy, Eu, Gd:Dy, Sm and Gd:Eu co-doped LnOFs for white light emission,<sup>2f-h</sup> where Eu(III), Tb(III), Sm(III) and Dy(III) ions emit metal-centered (MC) red, green, orange and yellow light, respectively. La(III) and Gd(III) frameworks exhibit no MC emission in the visible range, which can provide ligand-centered (LC) blue emission. Thus, white light emission was realized by doping with luminescent Ln(III) ions into the La(III) or Gd(III) framework.

The luminescent LnOFs consist of a central Ln(III) ion and organic ligand as a photosensitizer. 4-Sulfobenzoic acid (4-H<sub>2</sub>SBA) is known as an efficient sensitizer for Ln(III) ions.<sup>5</sup> The 1*H*-imidazo[4,5-*f*][1,10]-phenanthroline (IP) has a large conjugated electron system and it can serve as co-chelating and co-sensitizing ligand. It can shield the coordination sphere of the metal ion from the ingress of water molecules, which is known to quench luminescence efficiency. Furthermore,

the IP has a broad luminescence centered at 460 nm.<sup>2h,6</sup> For the Ln(III) cations, we are more interested in Eu(III), Tb(III), Gd(III) and Sm(III) ions, which display different luminescent behavior due to their quite different energy level diagrams.<sup>7</sup> So, we synthesized the Sm(III), Eu(III), Gd(III) and Tb(III)-frameworks with the bridging 4-H<sub>2</sub>SBA ligand and the terminal IP ligand. For the first time, luminescent Sm(III) framework as matrix, Eu(III) or Gd(III)/Eu(III) and Tb(III)/Eu(III) as dopants are incorporated into the new white light emitting materials, which are distinctly different from the previous reports.<sup>2f-h</sup>

The complexes [Ln(4-SBA)(IP)OH]·1.5H<sub>2</sub>O (Ln = Sm **1**, Eu **2**, Gd **3** and Tb **4**) are isostructural (Table S1–S2, Fig. S1 ESI†) and consist of 2D networks, herein only the structure of **4** will be discussed in detail.‡ The asymmetric unit of **4** comprises one Tb(III) ion, one 4-SBA, one IP and one hydroxyl group. As shown in Fig. 1a, four O atoms from four 4-SBA ligands, two hydroxyl groups, and two N atoms from the IP ligand complete the coordination sphere around the Tb(III) ion in the square-antiprism polyhedra. Tb–O distances range from 2.294(5) to 2.421(5) Å, and Tb–N distances are 2.583(3) and 2.574(4) Å. The 4-SBA ligand bonds to four different Tb(III) ions with the sulfonate and carboxylate groups in a bridging-bidentate fashion, while the IP ligand is chelated to the Tb(III) ion (Scheme S1†). The hydroxyl groups bridge the Tb(III) centers to form [Tb<sub>2</sub>(μ<sub>2</sub>-OH)<sub>2</sub>(IP)<sub>2</sub>]<sup>4+</sup> binuclear units that are connected by sulfonate groups and 4-SBA ligands along the *a* and *b* axis, to

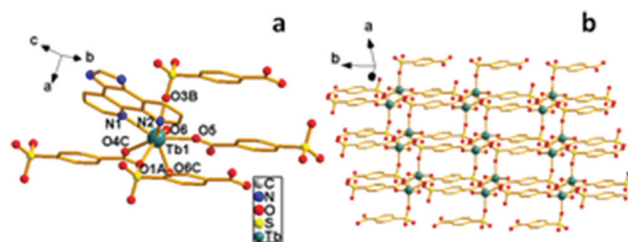


Fig. 1 (a) Coordination environment of the Tb(III) ion in **4** and (b) 2D layer structure. Free water molecules, H atoms and IP ligands are omitted for clarity. Symmetry codes: A: 1 – *x*, 1 – *y*, –*z*; B: –*x*, 1 – *y*, –*z*; C: 1 – *x*, –*y*, –*z*.

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generate a 2D layer structure (Fig. 1b). Short and long Tb...Tb distances are 3.620(5) and 6.877(5) Å, respectively. The layers are stacked in an AA fashion *via* interlayer hydrogen bonds (Table S3†), resulting in a 3D network, intercalated by free water molecules (Fig. S2 ESI†). The comparison of crystal data (Table S2 ESI†) in the complexes **1–4** shows that the average distances of Ln–O, Ln–N and Ln...Ln decrease successively, respectively, in agreement with lanthanide contraction.

The excitation spectra (Fig. S3†) and emission spectra of the complexes **1–4** in the solid state were investigated at room temperature. The lowest excited state  $^6P_{7/2}$  of Gd(III) is at high energy level (around 32 150 cm<sup>-1</sup>), there is no Gd(III) emission in the visible range, and the luminescence observed is due to the ligand part in the complex.<sup>7</sup> When excited at 365 nm, the Gd(III) framework (**3**) produces a large broad emission centered at 542 nm in the green spectral region (410–580 nm) (Fig. 2a), which can be assigned to the LC luminescence from intra-ligand  $\pi^*-\pi$  transition. A significant red-shift in the emission maxima and an enhancement in the intensity are observed compared to the bands of the free ligands (467 nm for IP and 428 nm for 4-SBA, Fig. S4 ESI†), which may be attributed to metal–ligand coordination and its structure.<sup>6</sup> For the Sm(III) framework (**1**), under excitation at 365 nm, the narrow emission bands at 558, 597 and 640 nm are attributed to  $^4G_{5/2} \rightarrow ^6H_{5/2}$ ,  $^4G_{5/2} \rightarrow ^6H_{7/2}$  and  $^4G_{5/2} \rightarrow ^6H_{9/2}$  transitions of the Sm(III) ion, respectively (Fig. 2b). An intense broad emission band centered at 468 nm with a shoulder at 492 nm is observed, which arises from LC luminescence.<sup>8</sup> The quantum yield of **1** is about 2.41%, and the luminescence lifetime is  $\tau_1 = 4.15 \mu\text{s}$  and  $\tau_2 = 14.91 \mu\text{s}$  (Fig. S5a ESI†).

The excitation spectra of **2** and **4** have a band maximum around 347 nm for **2** and 364 nm for **4** (Fig. S3c, d ESI†), confirming that the energy transfer takes place from the ligand to the Eu(III)/Tb(III) ions. Under excitation at 347 nm, the complex **2** exhibits the characteristic emission of the Eu(III)

ion (Fig. 2c). The strongest emission band splits into two peaks at 612 and 623 nm, corresponding to the  $^5D_0 \rightarrow ^7F_2$  transition. The emission peaks at 578, 590, 649 and 696 nm correspond to  $^5D_0 \rightarrow ^7F_0$ ,  $^5D_0 \rightarrow ^7F_1$ ,  $^5D_0 \rightarrow ^7F_3$  and  $^5D_0 \rightarrow ^7F_4$  transitions, respectively. In addition, a very weak LC luminescence at 420–520 nm is observed in **2**. Compared with the emission of **1**, the intensity of the LC band in **2** is weaker, indicating that a sizable energy transfer from the ligands to the  $^5D_0$  level of Eu(III) occurs.<sup>4c</sup> The intensity ratio of 1.06 for  $I(^5D_0 \rightarrow ^7F_2) : I(^5D_0 \rightarrow ^7F_1)$  indicates that the Eu(III) ion does not locate on an inversion center. When the complex **4** was excited at 364 nm, it reveals emission bands at 490, 546, 584 and 619 nm corresponding to  $^5D_4 \rightarrow ^7F_J$  ( $J = 6-3$ ) transitions of Tb(III), respectively. The strongest emission band at 546 nm corresponds to the  $^5D_4 \rightarrow ^7F_5$  transition (Fig. 2d). The LC band in **4** is not observed, which suggests that a complete energy transfer occurs from the ligands to the  $^5D_4$  level of Tb(III). The quantum yields are 20.78% for **2** and 9.28% for **4** and the luminescence lifetimes are 464.04  $\mu\text{s}$  for **2** and 258.62  $\mu\text{s}$  for **4** (Fig. S5b and c, ESI†), which are higher than those of **1** because the Eu(III) and Tb(III) ions have fewer excited states and ground states in contrast to Sm(III).

It is noteworthy that the Sm(III) framework provides blue (462 nm), green (558), orange (597 nm) and red (640 nm) emission. It is possible to achieve white light emission by adjusting the blue to red intensity ratio. Thus, Ln(III)-doped materials were prepared and their phase purity was verified by powder X-ray diffraction (PXRD) analysis (Fig. S1 ESI†). The photoluminescent properties were investigated and the quality of the white light is quantified by CIE chromaticity coordinates, color rendering index (CRI) and correlated color temperature (CCT). The Sm<sub>99.83</sub>Eu<sub>0.17</sub> doped sample shows the MC characteristic emission at 579, 591, 613, 650 and 694 nm for Eu(III) and at 558 nm for Sm(III), while a broad LC emission band centered at 468 and 492 nm appears in the emission spectrum (Fig. 3a).

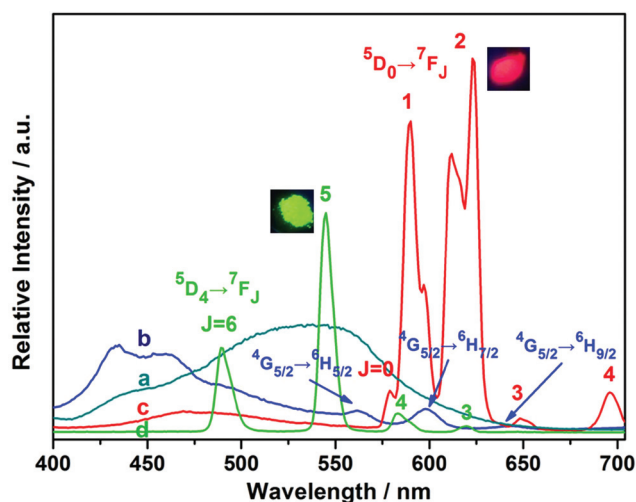


Fig. 2 Emission spectra of the complexes **3** (a) ( $\lambda_{\text{ex}} = 365$  nm), **1** (b) ( $\lambda_{\text{ex}} = 365$  nm), **2** (c) ( $\lambda_{\text{ex}} = 347$  nm) and **4** (d) ( $\lambda_{\text{ex}} = 364$  nm). Inset: image of **2** and **4** by 365 nm light.

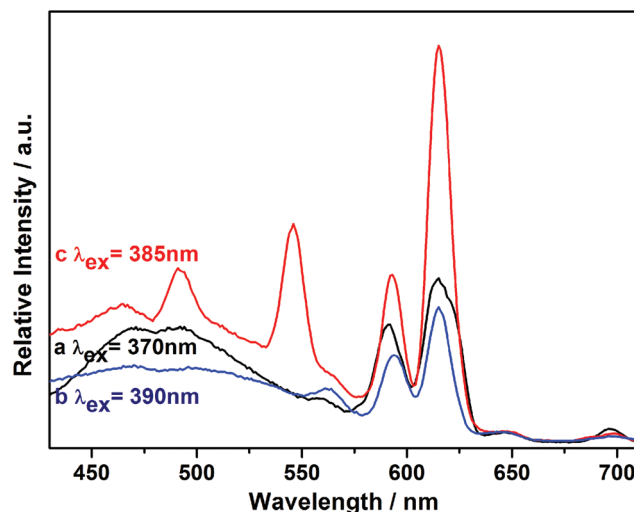


Fig. 3 Emission spectra of the doped complexes Sm<sub>99.83</sub>Eu<sub>0.17</sub> (a), Sm<sub>41.26</sub>Gd<sub>44.72</sub>Eu<sub>14.02</sub> (b) and Sm<sub>27.93</sub>Tb<sub>53.13</sub>Eu<sub>18.94</sub> (c).

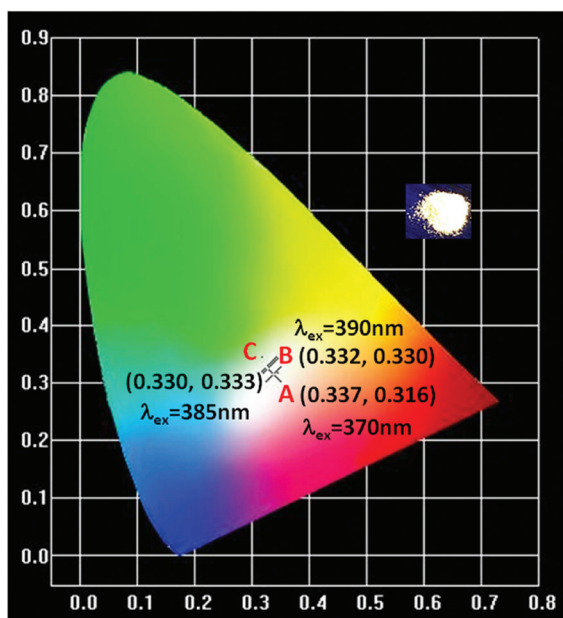


Fig. 4 The CIE chromaticity coordinate diagram of the doped complexes  $\text{Sm}_{99.83}\text{Eu}_{0.17}$  (A),  $\text{Sm}_{41.26}\text{Gd}_{44.72}\text{Eu}_{14.02}$  (B) and  $\text{Sm}_{27.93}\text{Tb}_{53.13}\text{Eu}_{18.94}$  (C). Inset: image of doped complexes by 365 nm light.

The peaks at 597 and 640 nm of  $\text{Sm}(\text{III})$  are overlapped with the peaks at 591 and 650 nm of  $\text{Eu}(\text{III})$ , respectively. The CIE chromaticity coordinates change from (0.356, 0.325) to (0.314, 0.318) excited at 330–380 nm falling within the white light region (Fig. S6a, Table S4 ESI†). The coordinate (0.337, 0.316) (Fig. 4A) (CRI 66, CCT 5259 K) excited at 370 nm is very close to the standard white light (0.333, 0.333) according to 1931 CIE coordinate diagram and its quantum yield is 3.40%. As a result, the  $\text{Sm}(\text{III})$  and  $\text{Eu}(\text{III})$  frameworks generates a novel two-component white light emission for the first time.

The  $\text{Gd}(\text{III})$  framework affords a green emission. As a consequence, white light emission can be obtained by introducing  $\text{Gd}(\text{III})/\text{Eu}(\text{III})$  dopants into the  $\text{Sm}(\text{III})$  framework and by varying the amount of  $\text{Eu}(\text{III})$ ,  $\text{Gd}(\text{III})$  and  $\text{Sm}(\text{III})$  ions. The emission spectrum (Fig. 3b) of the  $\text{Sm}_{41.26}\text{Gd}_{44.72}\text{Eu}_{14.02}$  doped material is similar to that of the  $\text{Sm}_{99.83}\text{Eu}_{0.17}$  doped material. For the  $\text{Sm}_{41.26}\text{Gd}_{44.72}\text{Eu}_{14.02}$  doped material that is a white light emitter with color coordinates (0.345, 0.355) to (0.321, 0.328) excited at 340–395 nm (Fig. S6b, Table S4 ESI†). The coordinate (0.332, 0.330) (Fig. 4B) (CRI 81, CCT 5523 K) excited at 390 nm is pure white light emission and its quantum yield is 2.23%.

Obviously, white light emission can be realized by introducing codopant  $\text{Tb}(\text{III})/\text{Eu}(\text{III})$  into the  $\text{Sm}(\text{III})$  framework. The emission spectrum (Fig. 3c) of the  $\text{Sm}_{27.93}\text{Tb}_{53.13}\text{Eu}_{18.94}$  doped material shows emission bands of ligands,  $\text{Sm}(\text{III})$  and  $\text{Eu}(\text{III})$ , which are similar to those in  $\text{Sm}_{99.83}\text{Eu}_{0.17}$  doped material. The characteristic emission bands at 490 and 546 nm from  $\text{Tb}(\text{III})$  are also observed. The peaks at 584 and 619 nm of  $\text{Tb}(\text{III})$  are overlapped with the peaks at 593 and 619 nm of  $\text{Eu}(\text{III})$ , respectively. White light emission is achieved with CIE

coordinates (0.349, 0.359) to (0.285, 0.315) excited at 340–395 nm (Fig. S6c, Table S4 ESI†). The CIE coordinate (0.330, 0.333) (Fig. 4C) (CRI 86, CCT 5595 K) excited at 385 nm is ideal for white light emission and its quantum yield is 2.71%. This approach further improves the color properties such as CRI, CCT and chromaticity to approach the requirements for solid-state lighting. The CRI value is up to 80, which corresponds to a warm-white light.

In order to demonstrate the potential of doped materials with respect to colour tuning, a series of doped materials with different doping ratios were synthesized and their photoluminescent properties were investigated (Fig. S7 ESI†). The emission intensity of the  $\text{Ln}(\text{III})$  ion varies with the  $\text{Ln}(\text{III})$  concentration. For  $\text{Sm}:\text{Eu}$  doped materials (ratios from 90 : 10 to 40 : 60) and  $\text{Sm}:\text{Tb},\text{Eu}$  doped materials (ratios from 40 : 25 : 35 to 40 : 45 : 15), the luminescence intensity of  $\text{Sm}(\text{III})$  or  $\text{Eu}(\text{III})$  and  $\text{Tb}(\text{III})$  ions increases as the  $\text{Sm}(\text{III})$  or  $\text{Eu}(\text{III})$  and  $\text{Tb}(\text{III})$  concentration increase. However, the emission intensity of the  $\text{Eu}(\text{III})$  ion in  $\text{Sm}:\text{Gd},\text{Eu}$  doped materials (ratios from 45 : 40 : 15 to 45 : 20 : 35) decreases as the  $\text{Eu}(\text{III})$  concentration increases, which shows a concentration quenching effect.

## Conclusion

We have reported the design, synthesis and characterization of new LnOFs constructed from the 4- $\text{H}_2\text{SBA}$  and IP ligands. New white light emitting materials were realized by introducing single dopant  $\text{Eu}(\text{III})$ , codopants  $\text{Gd}(\text{III})/\text{Eu}(\text{III})$  or  $\text{Tb}(\text{III})/\text{Eu}(\text{III})$  into the  $\text{Sm}(\text{III})$  framework as matrix. This is the first example of white light emitting materials for  $\text{Sm}$ -based LnOFs doped with  $\text{Ln}(\text{III})$ .  $\text{Tb}(\text{III})/\text{Eu}(\text{III})$ -codoped material shows a good quality of white light.

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## Notes and references

† Crystallographic data for 4:  $\text{C}_{40}\text{H}_{32}\text{N}_8\text{O}_{15}\text{S}_2\text{Tb}_2$ ,  $M_r = 1246.70$ , triclinic, space group  $P\bar{1}$ ,  $Z = 1$ ,  $a = 6.8766(7)$  Å,  $b = 10.1482(10)$  Å,  $c = 15.1965(15)$  Å,  $\alpha = 83.857(2)^\circ$ ,  $\beta = 78.023(2)^\circ$ ,  $\gamma = 77.275(2)^\circ$ ,  $V = 1009.83(17)$  Å<sup>3</sup>,  $D = 2.050$  g cm<sup>-3</sup>,  $T = 293(2)$  K,  $R_{\text{int}} = 0.0358$ ,  $R_{[\sigma > 2\sigma(f)]} = 0.0456$ ,  $wR_{2[\sigma > 2\sigma(f)]} = 0.0983$ ,  $R_{\text{all data}} = 0.0574$ ,  $wR_{2\text{all data}} = 0.1042$ .

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