Supplementary Information

Synthesis, Modulation, and Characterization of Ln³⁺ Ions Doped Metal–Organic Frameworks for WLED Applications

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*Corresponding author: Longcheng Wang Telephone: 86-571-8684326 E-mail: <u>wlongcheng@zstu.edu.cn</u> The supplementary information for the manuscript is given in this section. The PXRD patterns of as-prepared samples are given in Fig. S1.



Fig. S1 The PXRD patterns of bio-MOF-1 and Ln@bio-MOF-1 samples.



SEM images of given samples are shown in Fig. S2.

Fig. S2 The SEM images of: (a) bio-MOF-1, (b) Eu@bio-MOF-1, (c) Tb@bio-MOF-1, and (d) Tb/Eu@bio-MOF-1 (1).



The TG curves of given samples are shown in Fig. S3.

Fig. S3 The TG curves of: (a) bio-MOF-1, (b) Tb@bio-MOF-1, (c) Eu@bio-MOF-1, and (d) Tb/Eu@bio-MOF-1 (1).

In Fig. S3 (a), bio-MOF-1 possesses three mass loss processes: release of water and guest solvent molecules, removal of dimethylammonium cations and collapse of the framework.^{1, 2} All the Ln@bio-MOF-1 samples (Fig. S3 (c)-(d)) have similar mass loss characteristics and the TG curve in Fig. S3 (d) is taken as an example to demonstrate the mass loss process. The first mass loss step (mass loss: 9.27%) was observed between 30 and 306 °C, which might be caused by the removal of water and guest solvent molecules in the framework. Then, in temperature range between 306 and 400 °C, the mass loss might be attributed to the loss of dimethylammonium cation (mass loss: 9.77%). In the temperature range between 400 and 594 °C, the final mass loss process (mass loss: 17.62%) might be caused by the primary framework's breakdown.



Fig. S4 (a) Temperature-dependence emission spectra (λ_{ex} =365 nm), and (b) the relationship between ln (I₀/I-1) and 1/kT of Tb/Eu@bio-MOF-1 (1).

The emission spectra of Tb/Eu@bio-MOF-1 (1) at different temperatures (25-250 °C) are shown in Fig. S4 (a). The emission intensity gradually decreased with increasing temperature, which might be caused by the thermal quenching process. At 150 °C, the emission intensity remained 50.32% of the initial intensity (25 °C). At 250 °C, the emission intensity remained at a relatively good level, 31.71% of the initial intensity (25 °C). The activation energy (E_a) of the Tb/Eu@bio-MOF-1 (1) phosphor is calculated by the Arrhenius equation.³

$$\ln\left(\frac{I_0}{I} - 1\right) = \ln A - \frac{E_a}{kT} \#(1)$$

Where I_0 is the initial integrated emission intensity, I refers to the integrated emission intensity at different temperatures, A is a constant, and k denotes the Boltzmann constant (8.62×10⁻⁵ eV/K). The relationship between ln (I_0/I -1) and 1/kT is demonstrated in Fig. S4 (b). The slope of the fitting line is -0.1298, which indicates activation energy of 0.1208 eV.



Fig. S5 Emission spectra of: (a) x%Tb@bio-MOF-1 (x=5, 10, 20, 30, 40) excited at 322 nm and (b) y%Eu@bio-MOF-1 (y=0.01, 1, 3, 5, 7) excited at 320 nm.

As the molar ratios of Tb³⁺ and Eu³⁺ ions increase, the emission intensity of ligand gradually decreases, and the characteristic emissions intensity of Tb³⁺ and Eu³⁺ ions (Tb³⁺: ${}^{5}D_{4} \rightarrow {}^{7}F_{6, 5, 4, 3}$; Eu³⁺: ${}^{5}D_{0} \rightarrow {}^{7}F_{1, 2}$) gradually increase, which might be caused by the energy transfer process from ligand to Tb³⁺ and Eu³⁺ ions by the "Antenna Effect".

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Sample MOFs	Luminescence lifetime (τ)			ETE (%)
	385 nm	545 nm	615 nm	$Tb^{3+} \rightarrow Eu^{3+}$
bio-MOF-1	3.49 ms			
Tb@bio-MOF-1		5.33 ms		
Eu@bio-MOF-1			4.29 ms	
Tb/Eu@bio-MOF-1 (1)	4.32 ms	4.90 ms	4.21 ms	8.07
Tb/Eu@bio-MOF-1 (2)	4.07 ms	3.97 ms	4.34 ms	25.52
Tb/Eu@bio-MOF-1 (3)	4.51 ms	3.79 ms	4.56 ms	28.88
Tb/Eu@bio-MOF-1 (4)	5.13 ms	3.4 ms	4.62 ms	36.21
Tb/Eu@bio-MOF-1 (5)	4.33 ms	2.8 ms	4.74 ms	47.47

Table S1 Calculated luminescence lifetimes (τ) of LnMOFs and energy transfer efficiency of Tb³⁺ \rightarrow Eu³⁺

References

- 1 J. Y. An, C. M. Shade, D. A.-Czegan, S. Petoud and N. L. Rosi, J. Am. Chem. Soc., 2011, 133, 1220-1223.
- 2 N. Z. Zhang, D. W. Zhang, J. Zhao and Z. G. Xia, Dalton Trans., 2019, 48, 6794-6799.
- 3 S. Bhushan and M. V. Chukichev, J. Mater. Sci. Lett., 1988, 7, 319-321.