

SUPPLEMENTARY INFORMATION

Luminescent lanthanide barcodes based on postsynthetic functionalized nanoscale metal-organic frameworks

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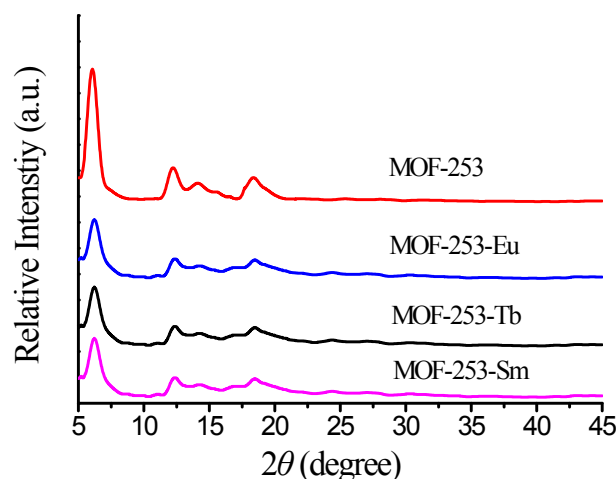


Figure S1 Powder x-ray diffraction patterns for MOF-253, MOF-253-Eu, MOF-253-Tb and MOF-253-Sm, the PXRD of MOF-253 is consistent with reported literature.^{S1}

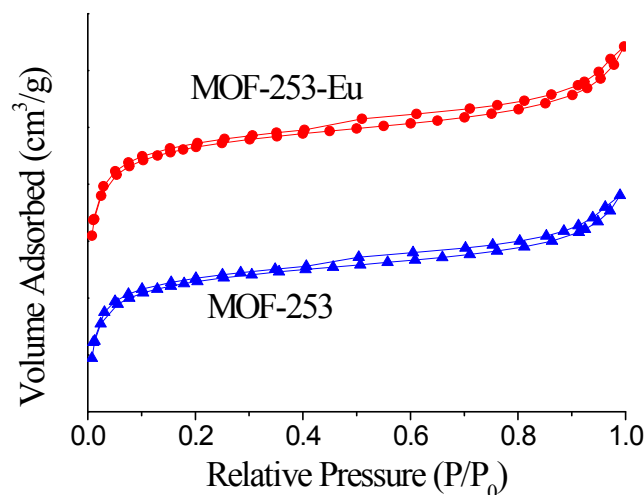


Figure S2 N₂ adsorption-desorption isotherms of MOF-253 and MOF-253-Eu, the Langmuir surface areas of MOF-253 and MOF-253-Eu were calculated to be 1156, and 763 m²/g, the surface areas of as-synthesized MOF-253 was considerably lower than Yaghi's work, but is consistent with other work about MOF-253.^{S2}

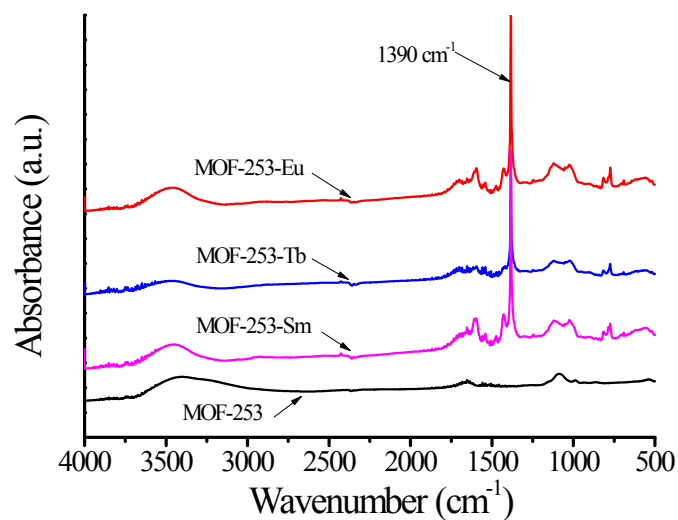


Figure S3 FT-IR spectra of MOF-253, MOF-253-Eu, MOF-253-Tb and MOF-253-Sm.

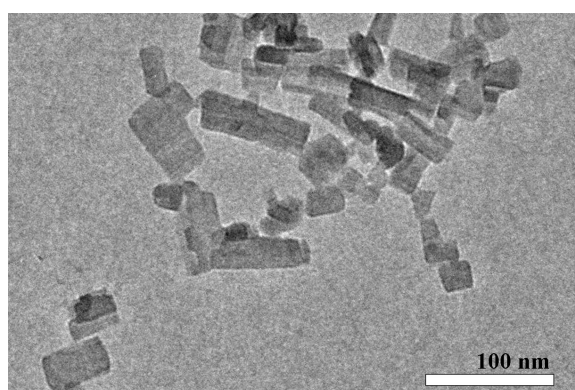


Figure S4 The TEM of MOF-253.

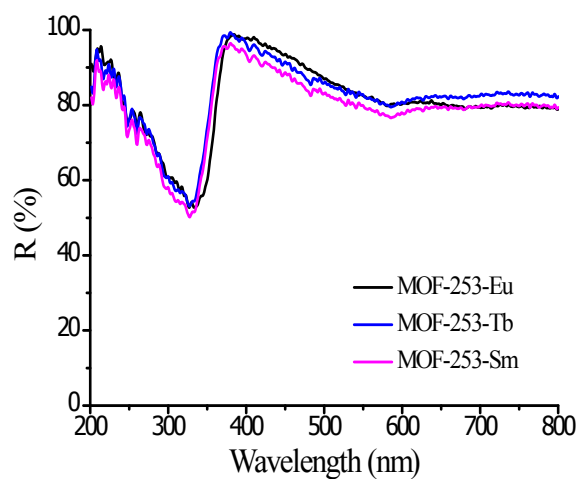


Figure S5 UV-visible diffuse reflectance spectra (DRS) of MOF-253-Ln (Ln = Eu, Tb and Sm).

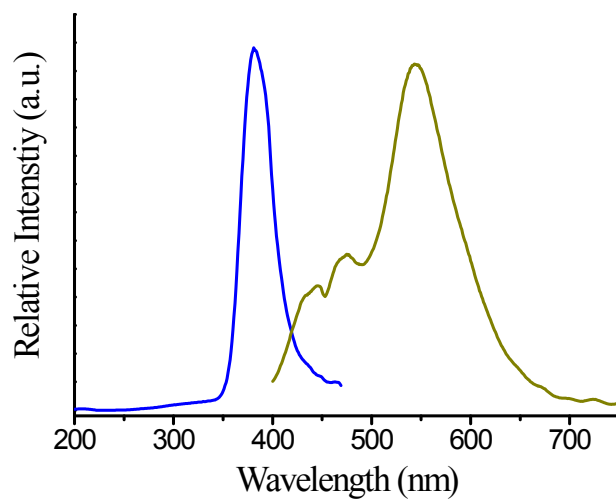


Figure S6 The excitation (blue) and PL spectra (yellow) of MOF-253 ($\lambda_{\text{em}} = 550$ nm and $\lambda_{\text{ex}} = 380$ nm).

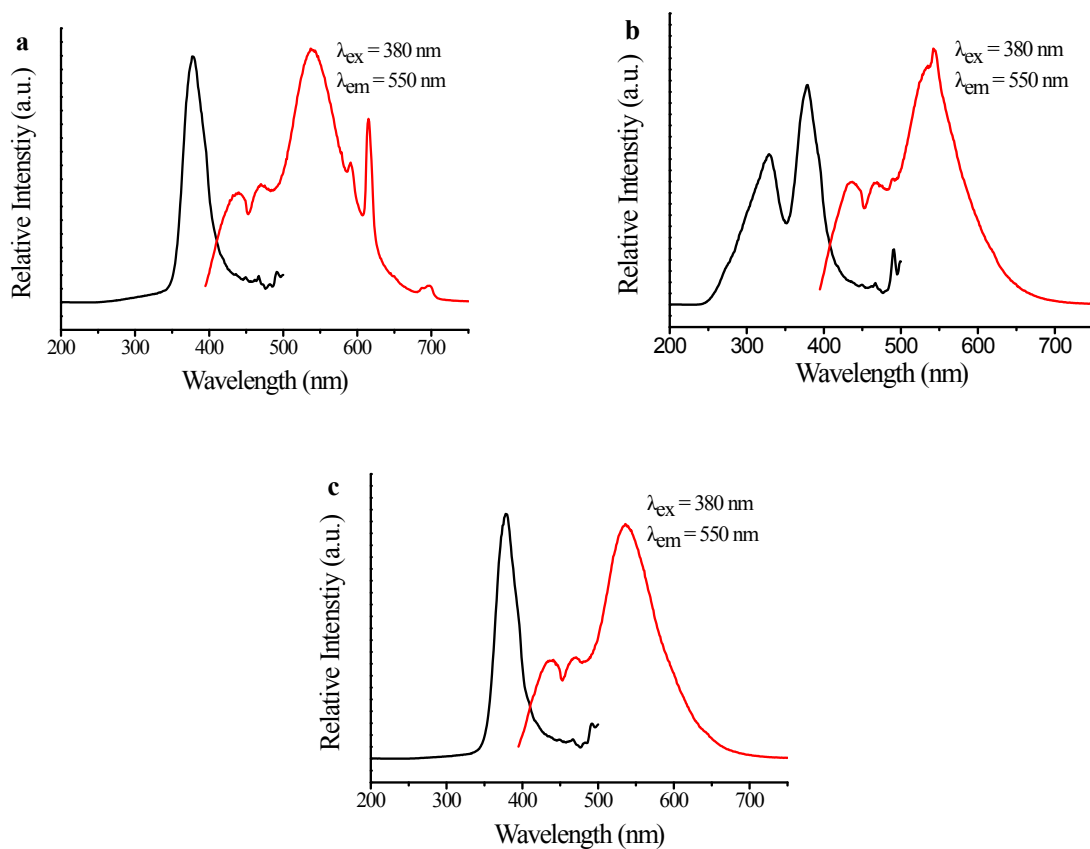


Figure S7 The excitation and emission spectra of MOF-253-Eu (a), MOF-253-Tb (b) and MOF-253-Sm (c) ($\lambda_{\text{em}} = 550$ nm and $\lambda_{\text{ex}} = 380$ nm).

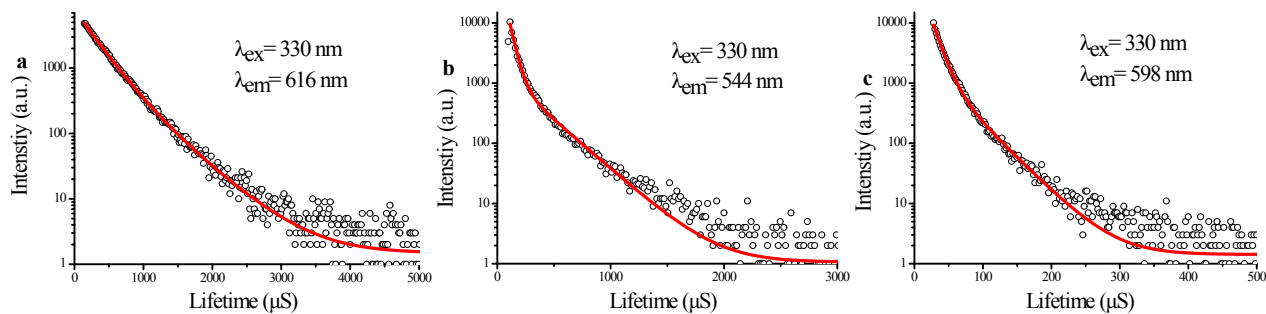


Figure S8 The lifetime decay curve of 5D_0 (Eu^{3+}) for MOF-253-Eu (a) ($\lambda_{\text{ex}} = 330$ nm and $\lambda_{\text{em}} = 616$ nm), 5D_4 (Tb^{3+}) for MOF-253-Tb (b) ($\lambda_{\text{ex}} = 330$ nm and $\lambda_{\text{em}} = 544$ nm) and $^4G_{5/2}$ (Sm^{3+}) for MOF-253-Sm (c) ($\lambda_{\text{ex}} = 330$ nm and $\lambda_{\text{em}} = 598$ nm), respectively.

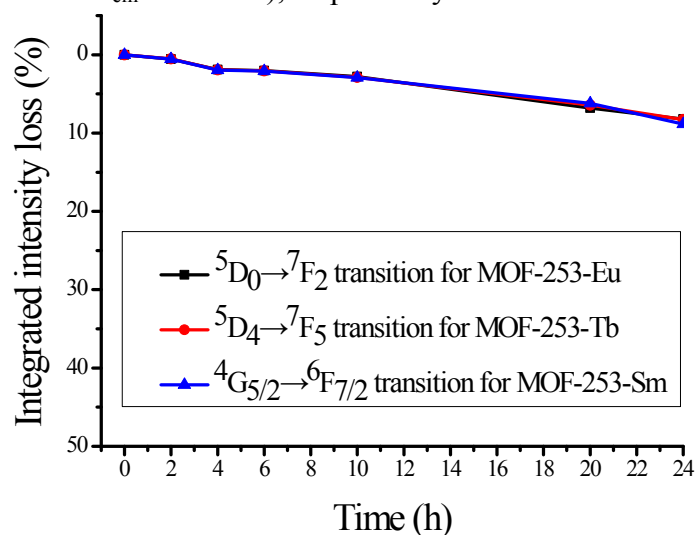


Figure S9 Integrated intensity loss of MOF-253-Ln (Ln = Eu, Tb and Sm) with increasing time of UV ($\lambda = 365$ nm) exposure.

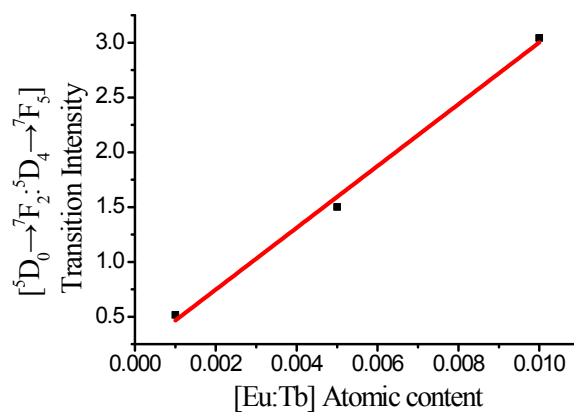


Figure S10 Plot of the ratio of integrated transition intensities of $^5D_0 \rightarrow ^7F_2$ (Eu^{3+} ion) and transition of $^5D_4 \rightarrow ^7F_5$ (Tb^{3+} ion) vs their atomic ratio as measured by ICP.

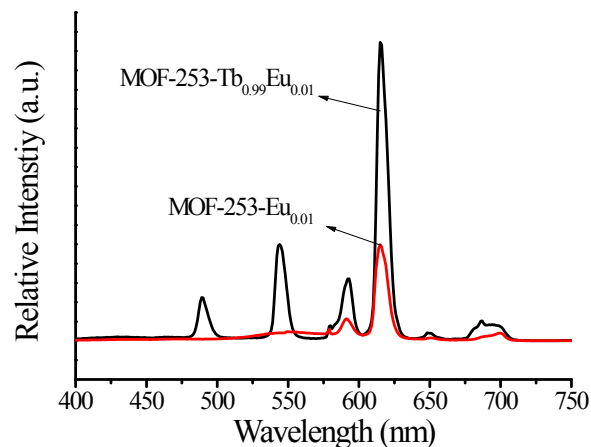


Figure S11 The emission spectra of MOF-253-Tb_{0.99}Eu_{0.01} and MOF-253-Eu_{0.01} under excitation at 330 nm.

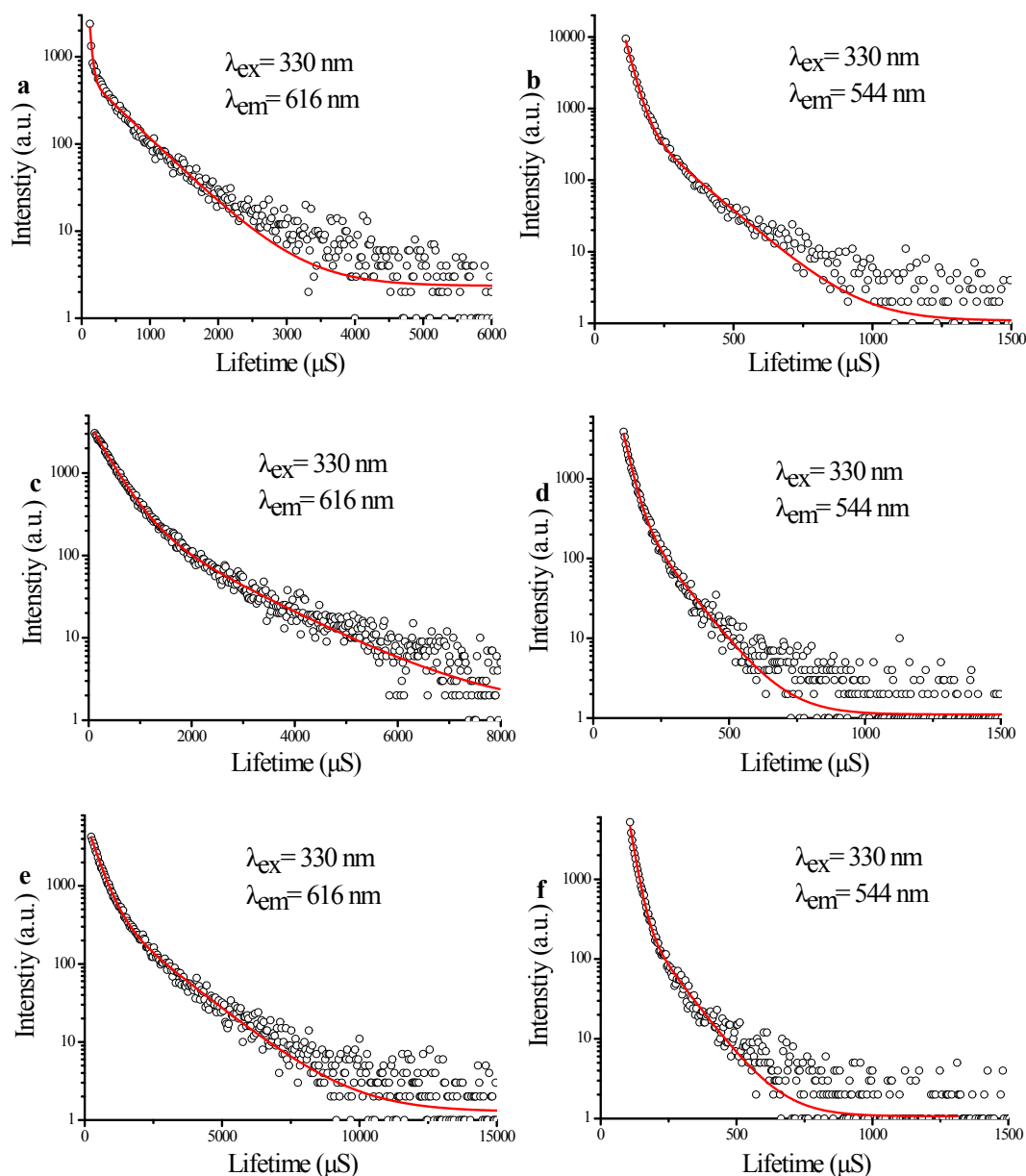


Figure S12 The lifetime decay curve of 5D_0 (Eu^{3+}) for MOF-253-Tb_{0.999}Eu_{0.001} (a) ($\lambda_{\text{ex}} = 330$ nm and $\lambda_{\text{em}} = 616$ nm), 5D_4 (Tb^{3+}) for MOF-253-Tb_{0.999}Eu_{0.001} (b) ($\lambda_{\text{ex}} = 330$ nm and $\lambda_{\text{em}} = 544$ nm), 5D_0 (Eu^{3+}) for MOF-253-Tb_{0.995}Eu_{0.005} (c) ($\lambda_{\text{ex}} = 330$ nm and $\lambda_{\text{em}} = 616$ nm), 5D_4 (Tb^{3+}) for MOF-253-Tb_{0.995}Eu_{0.005} (d) ($\lambda_{\text{ex}} = 330$ nm and $\lambda_{\text{em}} = 544$ nm), 5D_0 (Eu^{3+}) for MOF-253-Tb_{0.99}Eu_{0.01} (e) ($\lambda_{\text{ex}} = 330$ nm and $\lambda_{\text{em}} = 616$ nm) and 5D_4 (Tb^{3+}) for MOF-253-Tb_{0.99}Eu_{0.01} (f) ($\lambda_{\text{ex}} = 330$ nm and $\lambda_{\text{em}} = 544$ nm), respectively.

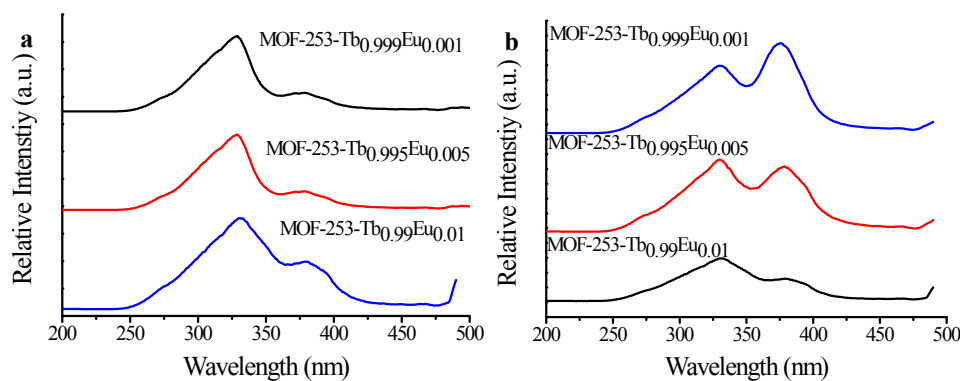


Figure S13 The excitation spectra of MOF-253-Tb_xEu_{1-x}, a is obtained for monitoring characteristic emission of Tb³⁺ ion (544 nm) and b is obtained for monitoring characteristic emission of Eu³⁺ ion (616 nm).

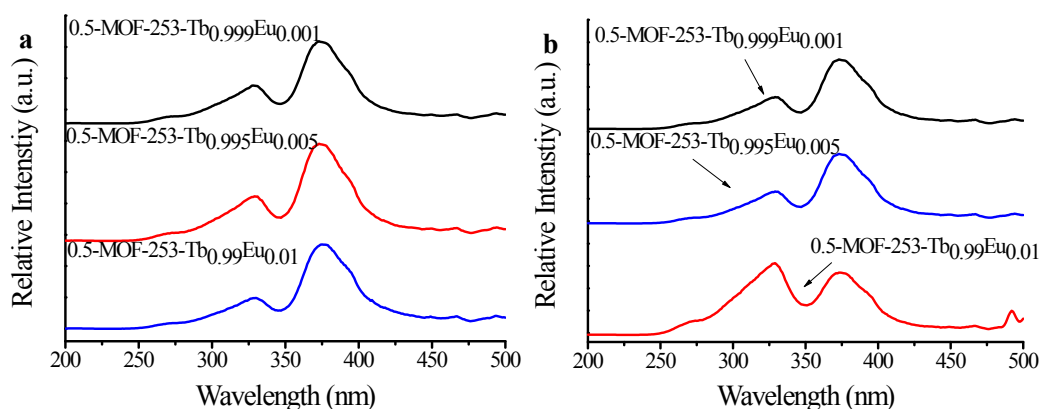


Figure S14 The excitation spectra of 0.5-MOF-253-Tb_xEu_{1-x}, a is obtained for monitoring characteristic emission of Tb³⁺ ion (544 nm) and b is obtained for monitoring characteristic emission of Eu³⁺ ion (616 nm).

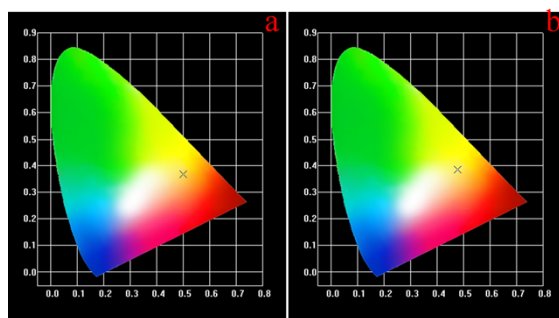


Figure S15 The point of MOF-253-Ln-1 (a) ($X = 0.5012$ and $Y = 0.3675$) and MOF-253-Ln-2 (b) ($X = 0.4782$ and $Y = 0.3846$) in the CIE chromaticity diagram.

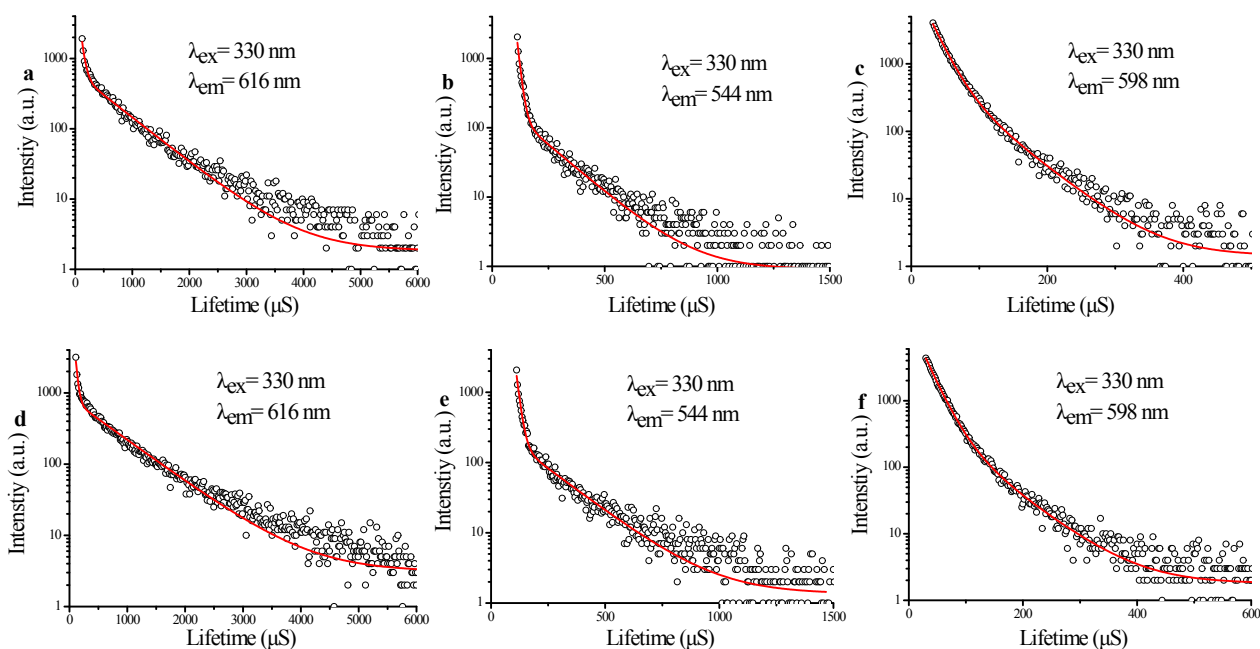


Figure S16 The lifetime decay curve of 5D_0 (Eu^{3+}) for MOF-253-Ln-1 (a) ($\lambda_{\text{ex}} = 330$ nm and $\lambda_{\text{em}} = 616$ nm), 5D_4 (Tb^{3+}) for MOF-253-Ln-1 (b) ($\lambda_{\text{ex}} = 330$ nm and $\lambda_{\text{em}} = 544$ nm), $^4G_{5/2}$ (Sm^{3+}) for MOF-253-Ln-1 (c) ($\lambda_{\text{ex}} = 330$ nm and $\lambda_{\text{em}} = 598$ nm), 5D_0 (Eu^{3+}) for MOF-253-Ln-2 (d) ($\lambda_{\text{ex}} = 330$ nm and $\lambda_{\text{em}} = 616$ nm), 5D_4 (Tb^{3+}) for MOF-253-Ln-2 (e) ($\lambda_{\text{ex}} = 330$ nm and $\lambda_{\text{em}} = 544$ nm) and $^4G_{5/2}$ (Sm^{3+}) for MOF-253-Ln-2 (f) ($\lambda_{\text{ex}} = 330$ nm and $\lambda_{\text{em}} = 598$ nm), respectively.

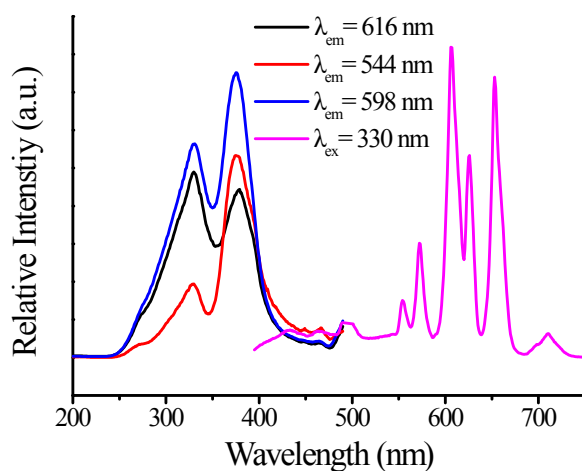


Figure S17 The luminescent spectra of IL-MOF-Ln.

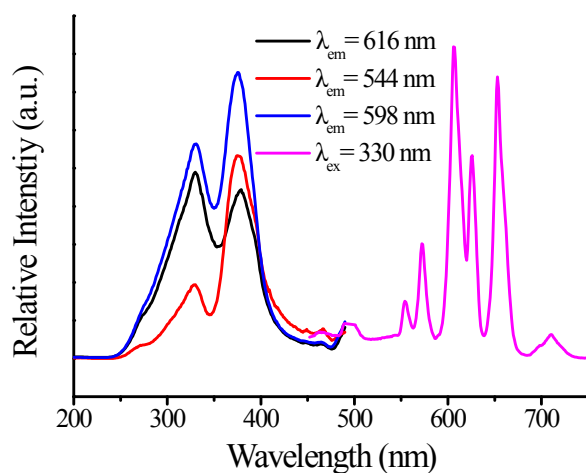


Figure S18 The luminescent spectra of spin coating thin film based on MOF-253-Ln-1.



Figure S19 The photograph of IL-MOF-253-Ln after cooled completely in the room temperature.

Table S1 The lifetime of lanthanide barcoded material based on MOF-253.

	Lifetime of 5D_0 (Eu^{3+}) (μs)	Lifetime of 5D_4 (Tb^{3+}) (μs)	Lifetime of $^4G_{5/2}$ (Sm^{3+}) (μs)
	($\lambda_{\text{ex}} = 330 \text{ nm}$ and $\lambda_{\text{em}} = 616 \text{ nm}$)	($\lambda_{\text{ex}} = 330 \text{ nm}$ and $\lambda_{\text{em}} = 544 \text{ nm}$)	($\lambda_{\text{ex}} = 330 \text{ nm}$ and $\lambda_{\text{em}} = 598 \text{ nm}$)
MOF-253-Eu	347.47	/	/
MOF-253-Tb	/	122.29	/
MOF-253-Sm	/	/	20.76
MOF-253-Tb _{0.99} Eu _{0.01}	814.80	39.07	/
MOF-253-Tb _{0.995} Eu _{0.005}	670.00	49.53	/
MOF-253-Tb _{0.999} Eu _{0.001}	441.74	53.35	/
MOF-253-Ln-1	551.15	75.38	31.02
MOF-253-Ln-2	613.32	98.52	32.89

Table S2 Relative Ln^{3+} content for the MOF-253-Tb_xEu_{1-x} during synthesis (Calcd.) and as determined by ICP analysis of the final product, the sum of lanthanide ion is 100 %.

	Synthesis amount (mmol)		% Tb ³⁺ ion		% Eu ³⁺ ion	
	Tb(NO ₃) ₃	Eu(NO ₃) ₃	Calcd.	ICP	Calcd.	ICP
MOF-253-Tb _{0.99} Eu _{0.01}	0.0990	0.0010	99.000	98.998	1.000	1.002
MOF-253-Tb _{0.995} Eu _{0.005}	0.0995	0.0005	99.500	99.501	0.500	0.499
MOF-253-Tb _{0.999} Eu _{0.001}	0.0999	0.0001	99.900	99.899	0.100	0.101

Table S3 Relative Ln³⁺ content for the MOF-253-Ln-1 and MOF-253-Ln-2 during synthesis (Calcd.) and as determined by ICP analysis of the final product, the sum of lanthanide ion is 100 %.

	Synthesis amount (mmol)			% Tb ³⁺ ion		% Eu ³⁺ ion		% Sm ³⁺ ion	
	Tb(NO ₃) ₃	Eu(NO ₃) ₃	Sm(NO ₃) ₃	Theor.	ICP	Calcd.	ICP	Calcd.	ICP
MOF-253-Ln-1	0.0500	0.0050	0.0495	50.000	49.998	0.500	0.501	49.500	49.501
MOF-253-Ln-2	0.0700	0.0070	0.0293	70.000	69.999	0.700	0.699	29.300	29.302

Reference:

- S1. E. D. Bloch, D. Britt, C. Lee, C. J. Doonan, F. J. Uribe-Romo, H. Furukawa, J. R. Long and O. M. Yaghi, *J. Am. Chem. Soc.*, 2010, **132**, 14382.
- S2. F. Carson, S. Agrawal, M. Gustafsson, A. Bartoszewicz, F. Moraga, X. D. Zou, B. Martin-Matute, *Chem-Eur. J.*, 2012, **18**, 15337.