Electronic Supplementary Material (ESI) for Dalton Transactions.

Electronic Supplementary Information

Benzotrithiophene based MOFs: interchromophoric interaction affected Ln(III) crystallization selectivity and optoelectronic property

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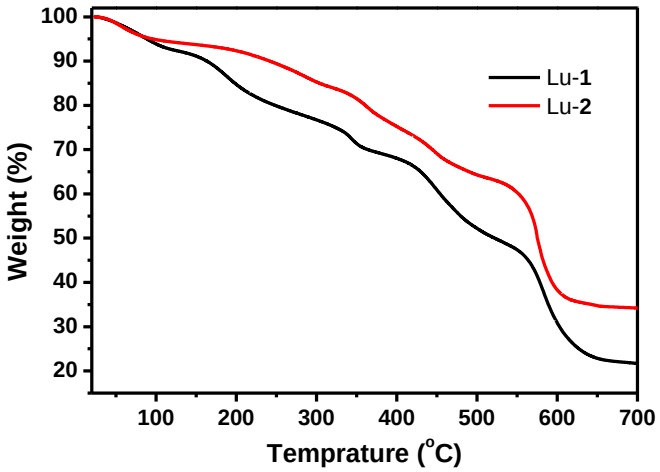

Fig. S1 TGA curves of as-prepared Lu-**1** and Lu-**2** in air atmosphere. The overall weight losses of Lu-**1** and Lu-**2** from room temperature to 700 °C are 78.33% and 65.81%, respectively, which could be assigned to the loss of all H_2O molecules and organic components (calcd. 78.58% for Lu-**1** and 65.88% for Lu-**2**).

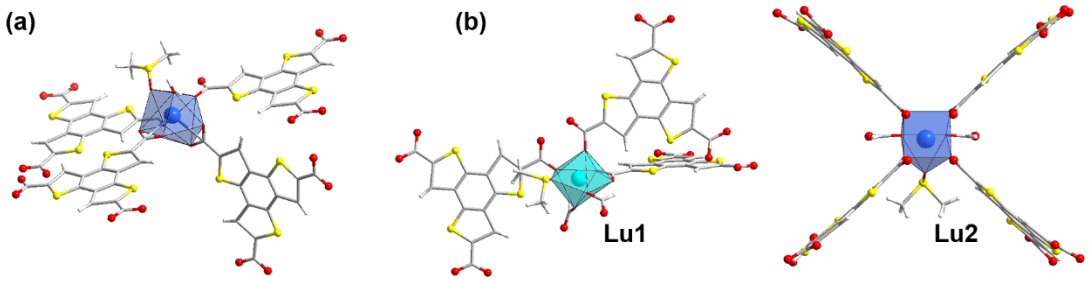

Fig. S2 Coordination environments of Lu^{3+} ions in (a) Lu-**1** and (b) Lu-**2**.

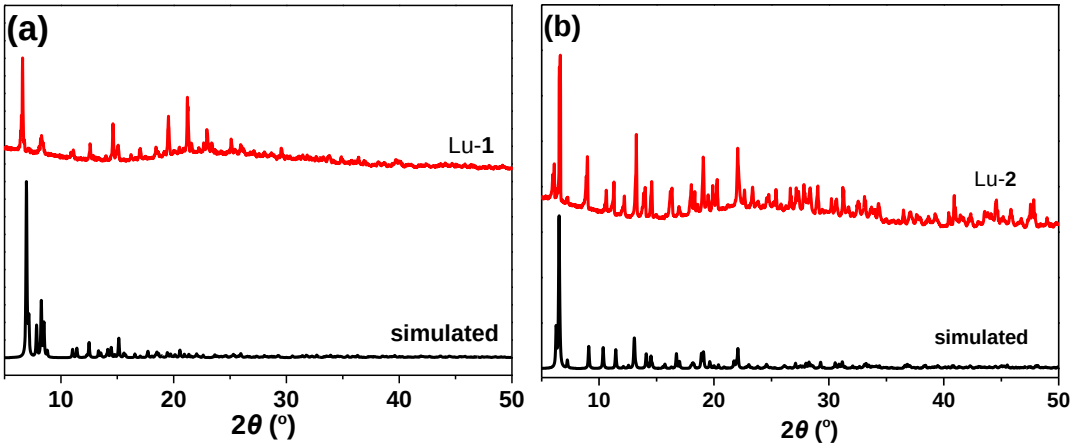

Fig. S3 PXRD patterns of as-prepared (a) Lu-**1** and (b) Lu-**2** samples.

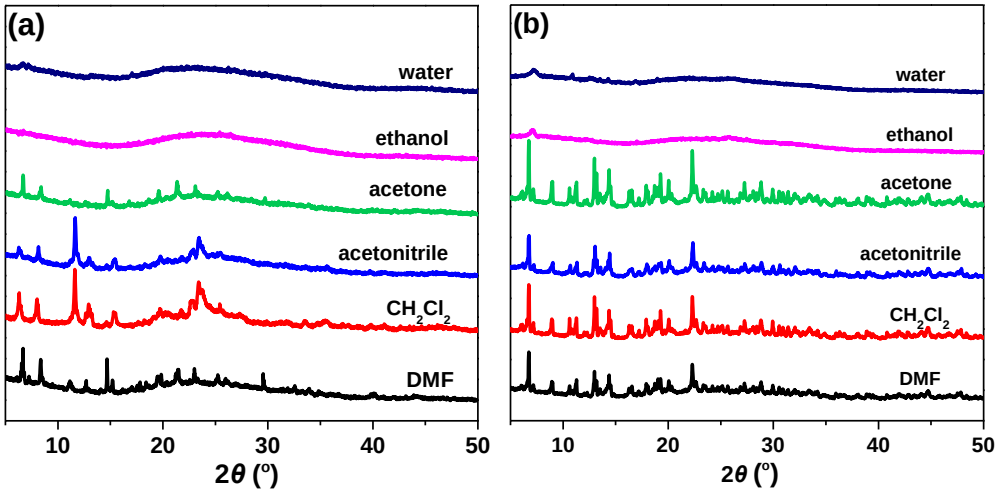

Fig. S4 PXRD patterns of (a) Lu-**1** and (b) Lu-**2** samples after 12 hours of shaking in different solvents.

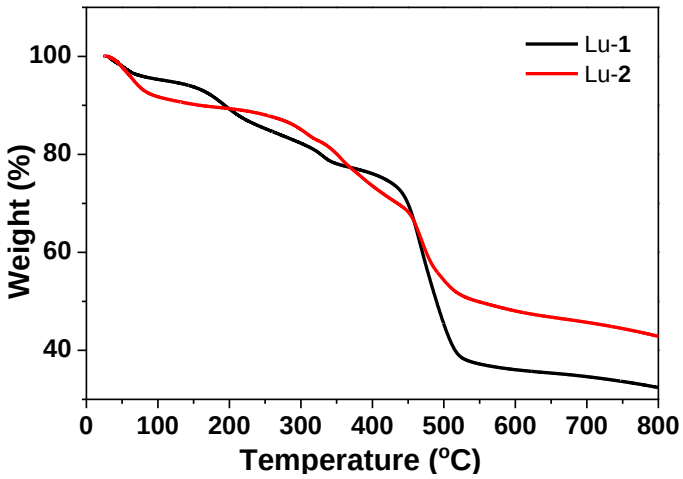

Fig. S5 TGA traces of Lu-**1** and Lu-**2** in N_2 atmosphere. Before measurement, the samples were exchanged with CH_2Cl_2 for 72 h and then dried in vacuum at 40 °C to remove the solvent guests in channels.

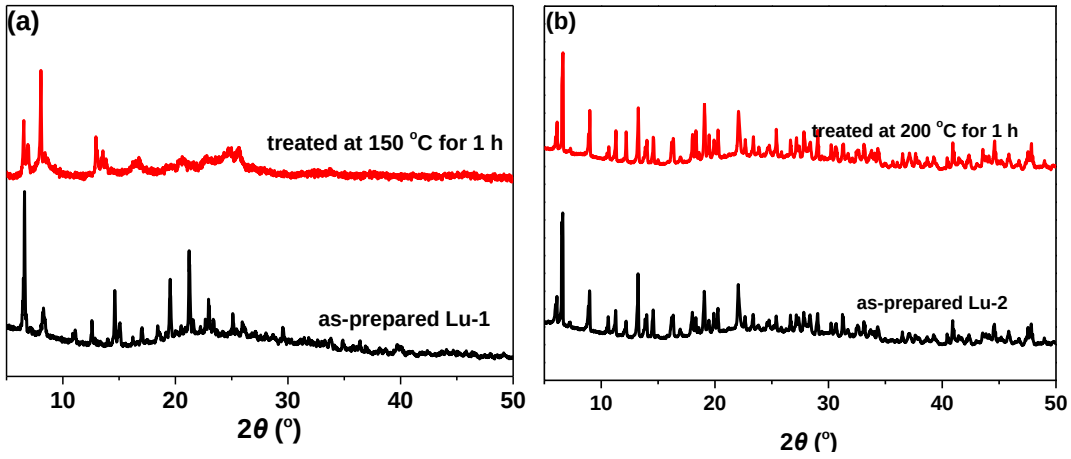

Fig. S6 PXRD patterns of (a) Lu-**1** and (b) Lu-**2** before and after thermal treatment.

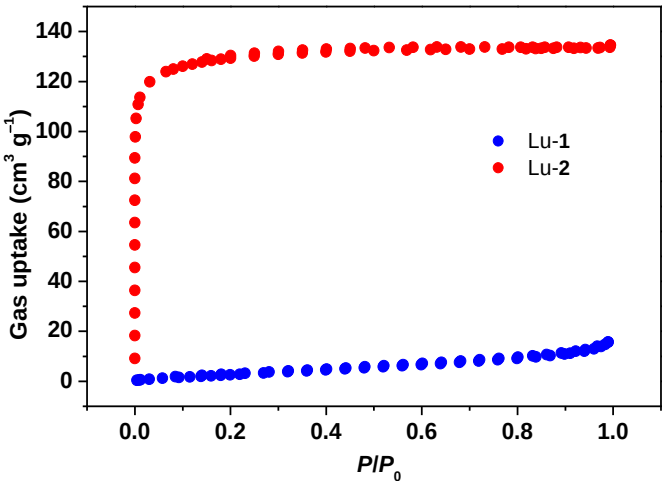

Fig. S7 N_2 sorption isotherms for Lu-**1** and Lu-**2** at 77 K. Before measurement, the samples were exchanged with CH_2Cl_2 for 72 h and then dried in vacuum at 40 °C to remove the solvent guests in channels.

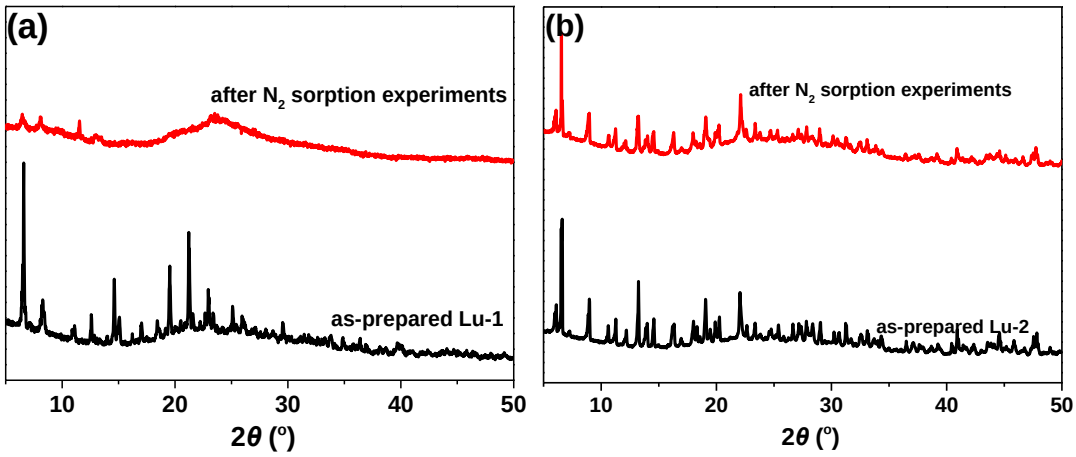

Fig. S8 PXRD patterns of (a) Lu-**1** and (b) Lu-**2** before and after N_2 sorption experiments.

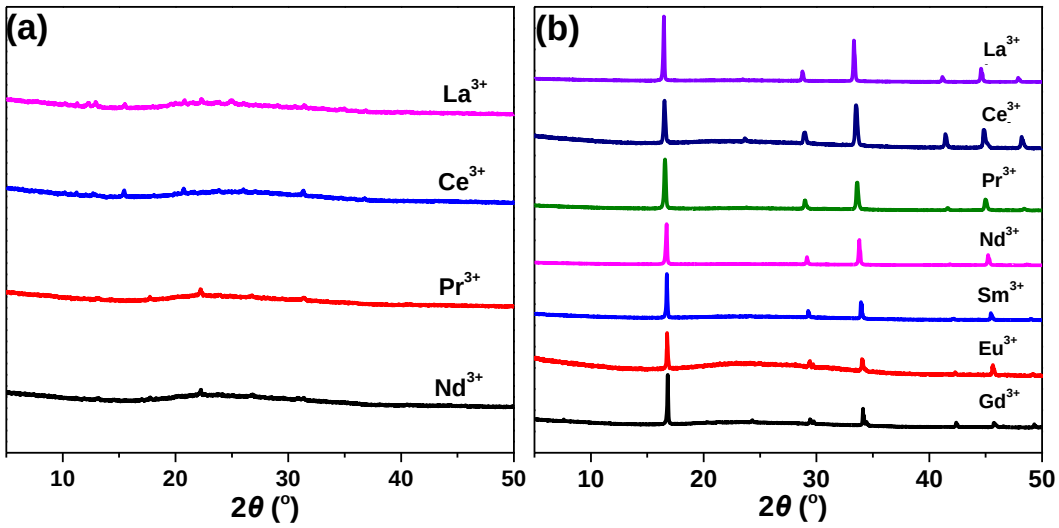

Fig. S9 PXRD patterns of the samples obtained from the replacement of Lu^{3+} (a) by La^{3+}–Nd^{3+} in the synthetic conditions of Lu-**1** and (b) by La^{3+}–Gd^{3+} in the synthetic conditions of Lu-**2**.

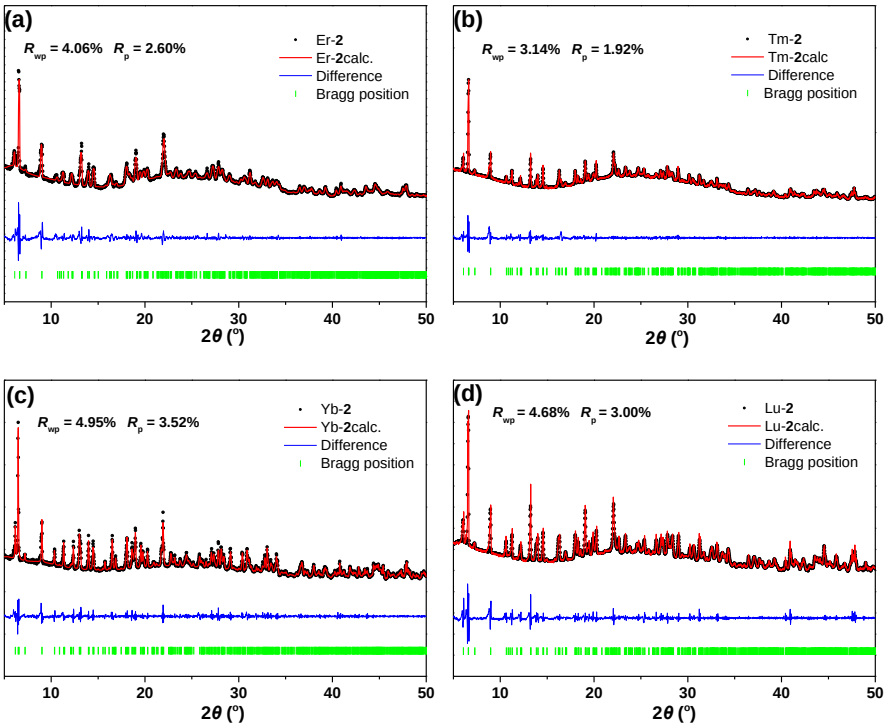

Fig. S10 Pawley refinements (using the Material Studio 8.0 program) of the recorded PXRD data of (a) Er-, (b) Tm-, (c) Yb- and (d) Lu-**2**s.

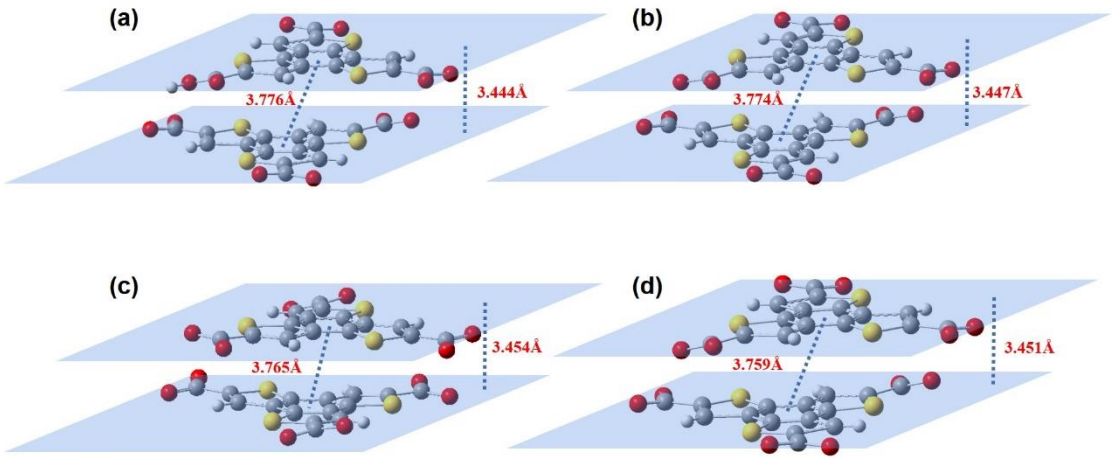

Fig. S11 Anti-parallel arrangement of $BTTC^{3-}$ ligands in (a) Er-**2**, (b) Tm-**2**, (c) Yb-**2** and (d) Lu-**2**.

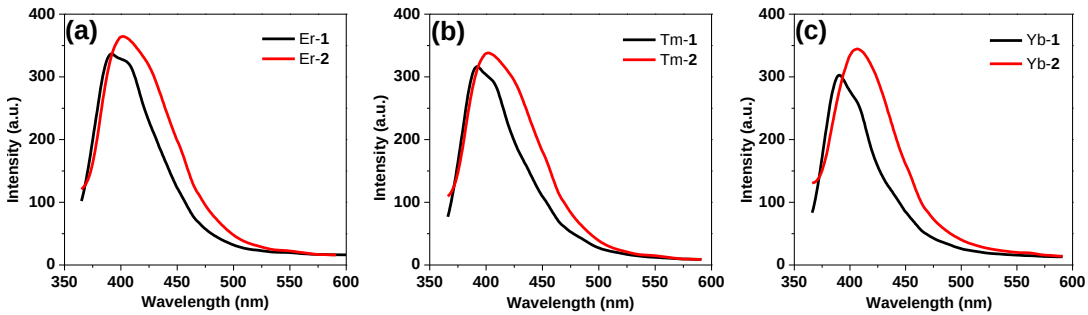

Fig. S12 Photoluminescence spectra of (a) Er-**1**/**2**, (b) Tm-**1**/**2** and (c) Yb-**1**/**2** (λ_{ex} = 304nm).

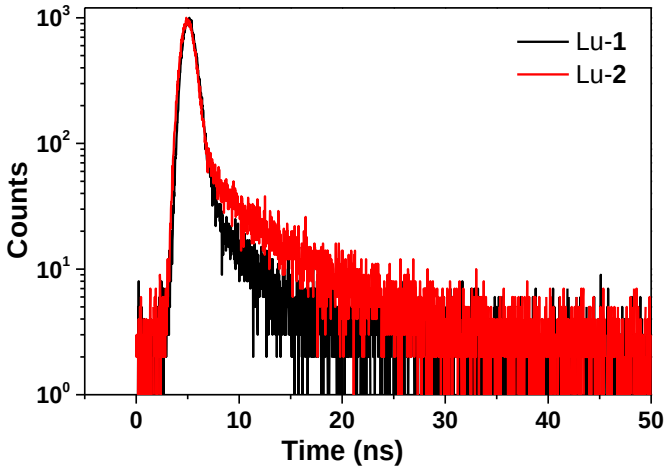

Fig. S13 Time-resolved decays of the emission bands at 400 nm for Lu-**1** and Lu-**2**.

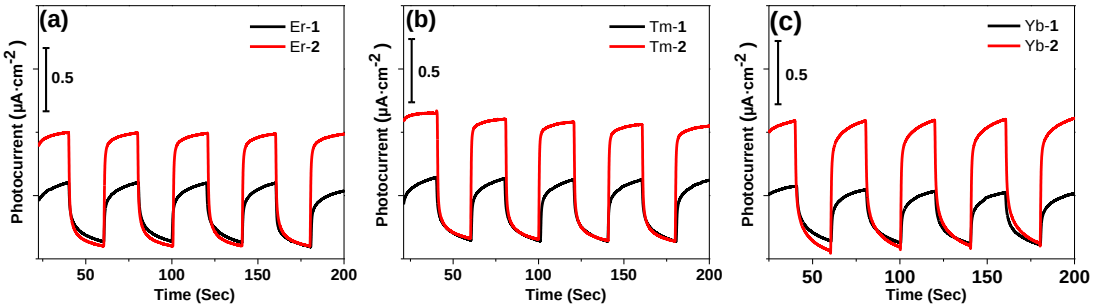

Fig. S14 Photocurrent responses of (a) Er-**1**/**2**, (b) Tm-**1**/**2** and (c) Yb-**1**/**2**.

Table S1 Crystal data and structure refinement for Ln-**1** and Ln-**2**

	Er-**2**	Tm-**2**	Yb-**2**	Lu-**2**	Lu-**1**
Empirical formula	$C_{80}H_{78}O_{50}S_{19}Er_6$	$C_{80}H_{78}O_{50}S_{19}Tm_6$	$C_{80}H_{78}O_{50}S_{19}Yb_6$	$C_{80}H_{78}O_{50}S_{19}Lu_6$	$C_{48}H_{66}O_{24}S_{15}Lu_2$
Formula weight	3452.15	3462.17	3486.89	3498.41	1857.58
T(K)	100	100	100	100	100
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073	1.54184
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	I2/m	I2/m	I2/m	I2/m	*C*2/*c*
a (Å)	15.0482(4)	15.0000(8)	14.9644(3)	14.9505(4)	24.5391(10)
b (Å)	28.3988(5)	28.3529(10)	28.2692(5)	28.1937(6)	15.4070(9)
c (Å)	17.0500(5)	17.0305(9)	17.0535(4)	17.1041(6)	26.8983(9)
α (°)	90	90	90	90	90
β (°)	115.635(3)	115.549(6)	115.487(3)	115.237(3)	113.341(5)
γ (°)	90	90	90	90	90
V (Å^3)	6569.1(3)	6534.7(6)	6512.1(3)	6521.4(4)	9337.3(8)
Z	2	2	2	2	4
*ρ*calc (g/cm^3)	1.745	1.759	1.778	1.781	1.321
μ (mm^{-1})	4.168	4.410	4.647	4.879	7.548
F (000)	2902.0	2916.0	2928.0	2940.0	2344.0
Ref. collected	16669	16084	21802	21702	18776
Independent ref.	5869 (R_{int} = 0.0226)	5836 (R_{int} = 0.0285)	8198 (R_{int} =0.0197)	8393 (R_{int} = 0.0186)	8214 (R_{int} = 0.0558）
Completeness	99.4% (ϑ = 25.0°)	99.4% (ϑ = 25.0°)	99.1% (ϑ = 30.15°)	99.0% (ϑ = 30.45°)	98.7% (ϑ =67.0°)
Data/restraints/ parameters	5869/595/457	5836/554/469	8198/612/493	8393/611/484	8214/82/325
Gof	1.045	1.047	1.030	1.045	1.095
Final *R* indices [*I*>2σ(*I*)]	R_1 = 0.0525, wR_2 = 0.1283	R_1 = 0.0465, wR_2 = 0.1199	R_1 = 0.0445， wR_2 = 0.1033	R_1 = 0.0260， wR_2 = 0.0719	R_1 = 0.0810, wR_2 = 0.2462
R indices (all data)	R_1 = 0.0556, wR_2 = 0.1308	R_1 = 0.0519, wR_2 = 0.1244	R_1 = 0.0463, wR_2 = 0.1043	R_1 = 0.0286, wR_2 = 0.0731	R_1 = 0.0937, wR_2 = 0.2558

Table S2 Crystallization electivity of 7- and 6-coordinated Ln-MOFs towards Ln^{3+} ions

MOF	Coordinated numbers	Applicable Ln^{3+} ions	Ref.
$[Ln(HCOO)(D\text{-cam})]_n$	7	Dy^{3+}, Ho^{3+}, Er^{3+}	1
CPM-29	7	Tb^{3+}, Dy^{3+}, Ho^{3+}, Er^{3+}, Tm^{3+}, Yb^{3+}, Lu^{3+}	2
CPM-66B	6	Er^{3+}, Tm^{3+}, Yb^{3+}, Lu^{3+}	3
$Ln(C_9H_9O_6)$	6	Er^{3+}, Tb^{3+}	4
Ln-**2**	7	Er^{3+}, Tm^{3+}, Yb^{3+}, Lu^{3+}	This work

References

1. M.-L. Sun, X. Zhang, Y.-Y. Huang, Q.-P. Lin, Y.-Y. Qin and Y.-G. Yao, *New J. Chem.*, 2014, **38**, 55−58.
2. X. Zhao, M. Wong, C. Mao, T. X. Trieu, J. Zhang, P. Feng and X. Bu, *J. Am. Chem. Soc.*, 2014, **136**, 12572−12575.
3. H. Yang, F. Peng, D. E. Schier, S. A. Markotic, X. Zhao, A. N. Hong, Y. Wang, P. Feng and X. Bu, *Angew. Chem. Int. Ed.*, 2021, **60**, 11148−11152.
4. D. T. de Lill and C. L. Cahill, *Chem. Commun.*, 2006, **47**, 4946−4948.