Electronic Supplementary Material (ESI) for CrystEngComm.

Electronic Supplementary Information (ESI)

A series of isostructural lanthanide metal-organic frameworks: effective fluorescence sensing for Fe^{3+}, 2,4-DNP and 4-NP

Qianlan Hu, Tong Xu, Jiaming Gu, Lirong Zhang* and Yunling Liu*
State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, College of Chemistry, Jilin University, Changchun 130012, P. R. China, E-mail: zlr@jlu.edu.cn; yunling@jlu.edu.cn

S1. Calculation of quenching efficiency, Stern-Volmer (S-V) equation and LOD.

Quenching efficiency:

quenching efficiency = $(I0 - I)/I0 \times 100\%$

I_0 is the fluorescence intensity values of JLU-MOF201-Y and JLU-MOF201-Tb. *I* is the fluorescence intensity value after adding the Fe^{3+}.

Stern-Volmer (S-V) equation:

$I0/I = 1 + Ksv[\mathrm{C}]$

I_0 is the fluorescence intensity values of JLU-MOF201-Y and JLU-MOF201-Tb. *I* is the fluorescence intensity value after adding the Fe^{3+}. K_{sv} is Stern–Volmer quenching constant. [C] is the concentration of the analyte.

LOD:

$L = 3\mathrm{Sb}/K$

S_b is standard deviation for compounds and K is slope of the Stern-Volmer.

S1. Supporting Figures.

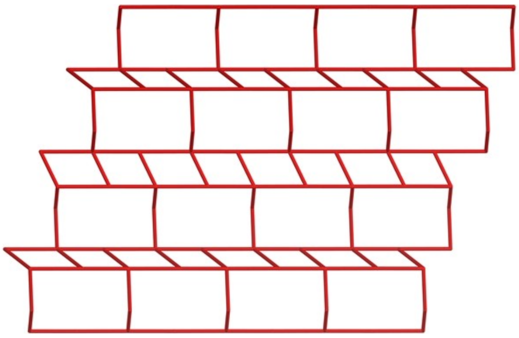

Fig. S1 3,4L83 topology of JLU-MOF201-Y.

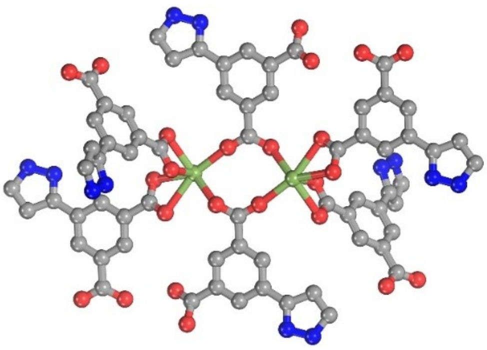

Fig. S2 Binuclear SBUs in JLU-MOF201-Y. Color scheme: carbon = gray, nitrogen = blue, oxygen = red, yttrium = green. (All H atoms and guest molecules are omitted for clarity)

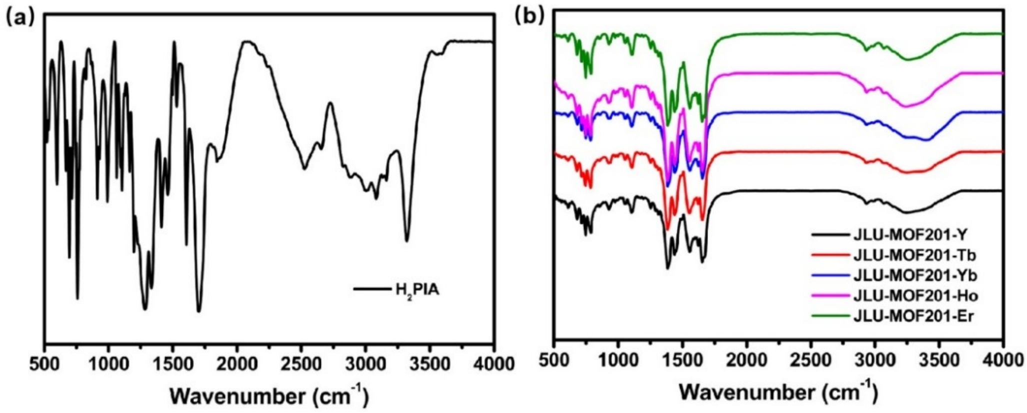

Fig. S3 The IR spectra of (a) H_2PIA and (b) JLU-MOF201-Ln.

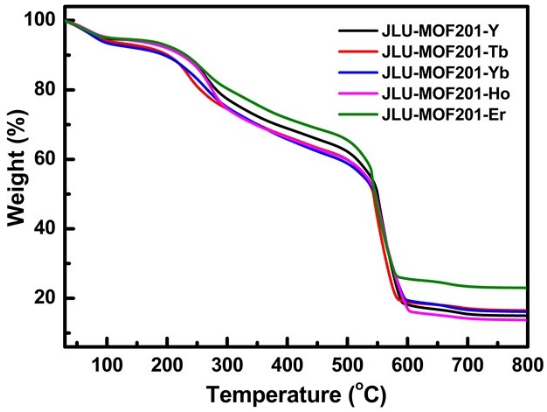

Fig. S4 Thermogravimetric analysis curves of JLU-MOF201-Ln for the as-synthesized samples.

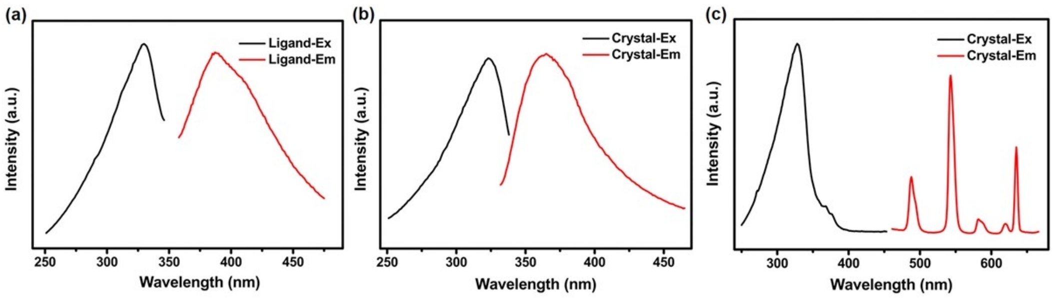

Fig. S5 Excitation and emission spectra of (a) H_2PIA, (b) JLU-MOF201-Y and (c) JLU-MOF201-Tb.

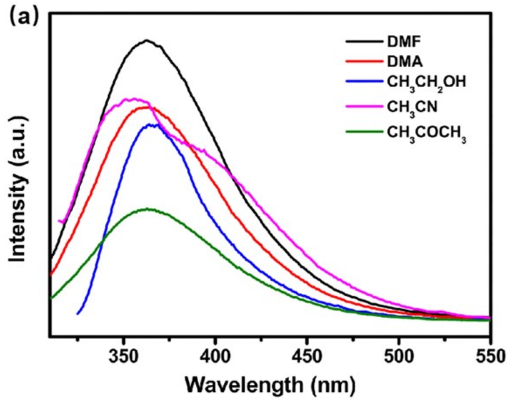

Fig. S6 Emission spectra of compounds (a) JLU-MOF201-Y and (b) JLU-MOF201-Tb in different solvents.

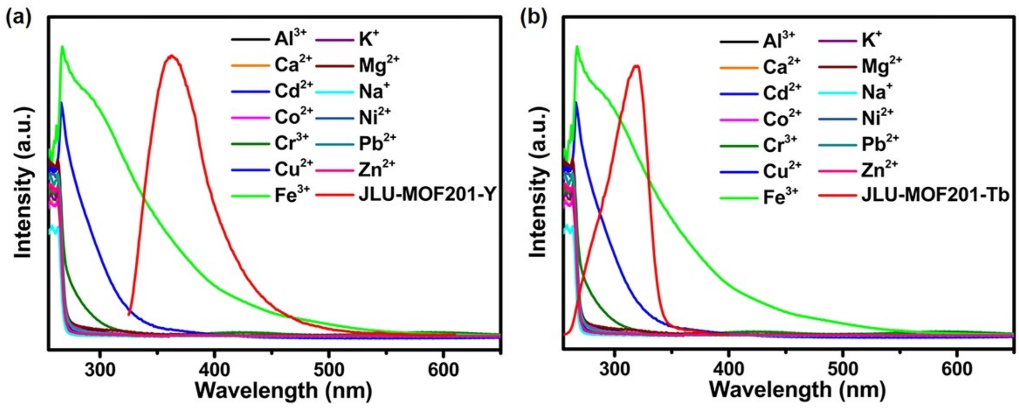

Fig. S7 UV-vis absorption spectra of different metal ions in DMF solution (5×10^{-4} mol·L^{-1}), emission spectrum of (a) JLU-MOF201-Y and excitation spectrum of (b) JLU-MOF201-Tb in DMF solution (2 mg·mL^{-1}).

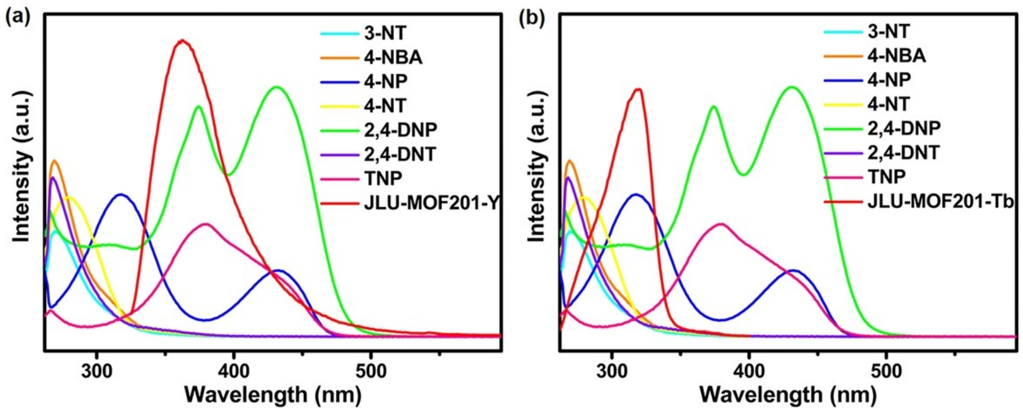

Fig. S8 UV-vis absorption spectra of different NAEs in DMF solution (1×10^{-4} M) and emission spectrum of (a) JLU-MOF201-Y and (b) JLU-MOF201-Tb in DMF solution (2 mg·mL^{-1}).

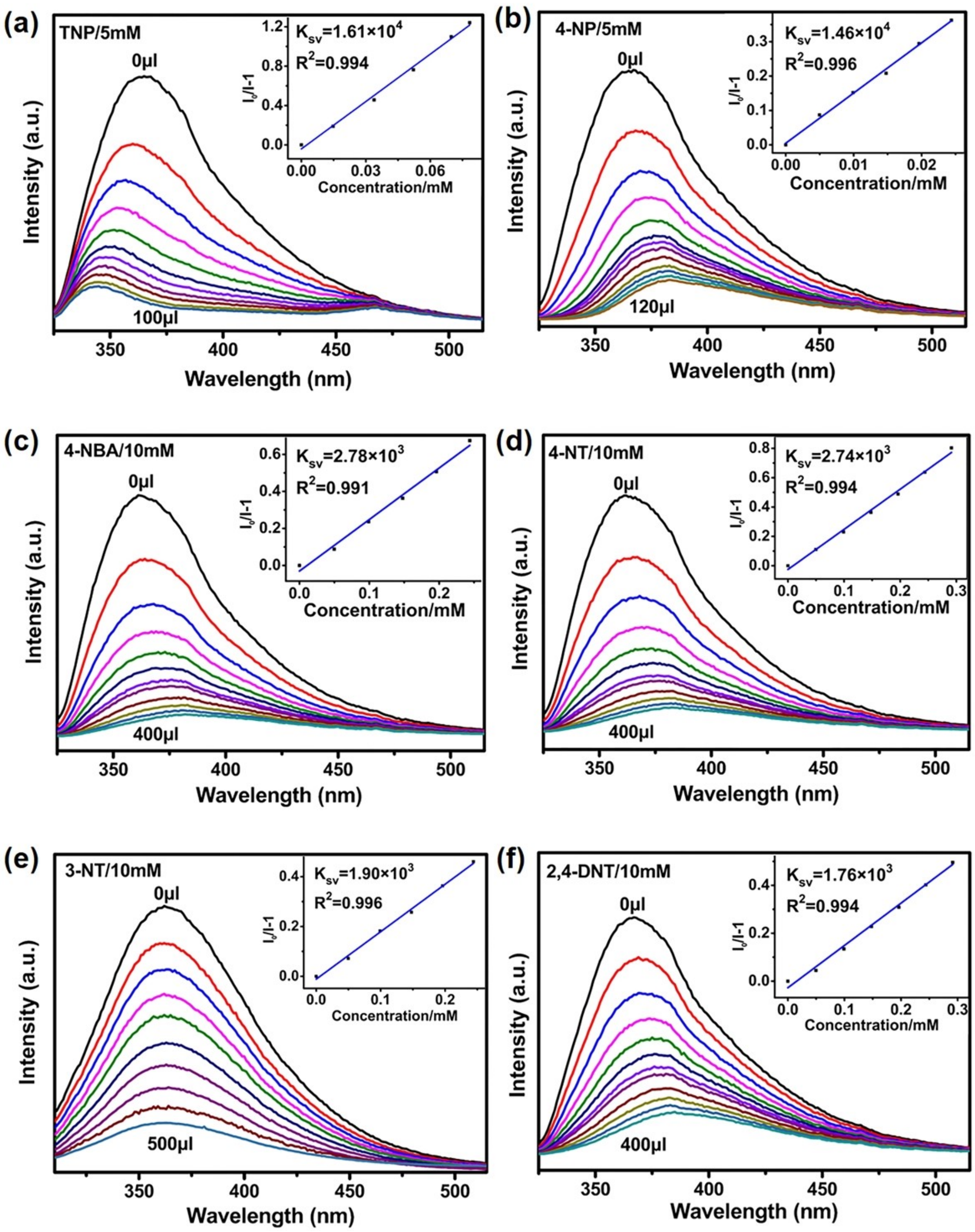

Fig. S9 Influence on the emission spectra of JLU-MOF201-Y decentralized in DMF by gradual addition of (a) TNP, (b) 4-NP, (c) 4-NBA, (d) 4-NT, (e) 3-NT and (f) 2,4-DNT solution.

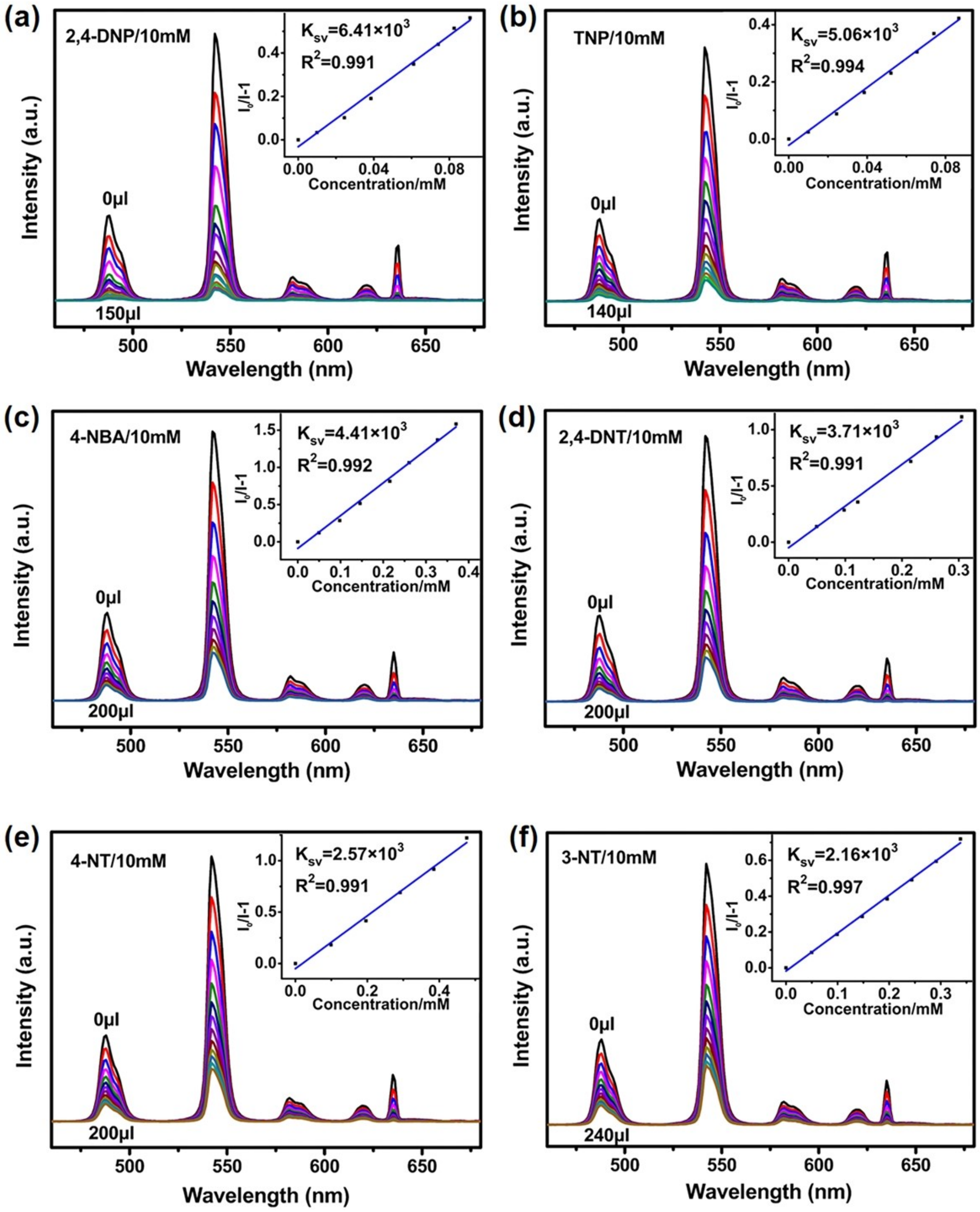

Fig. S10 Influence on the emission spectra of JLU-MOF201-Y decentralized in DMF by gradual addition of (a) 2,4-DNP, (b) TNP, (c) 4-NBA, (d) 2,4-DNT, (e) 4-NT and (f) 3-NT solution.

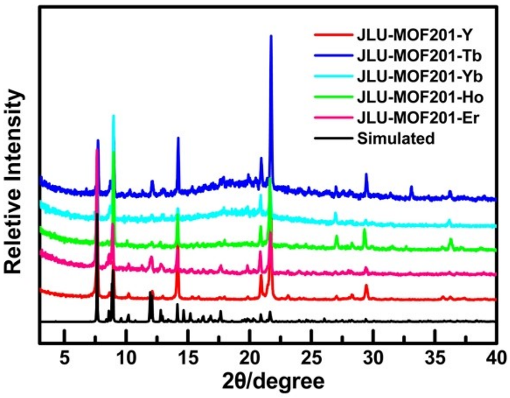

Fig. S11 PXRD patterns of JLU-MOF201-Y for simulated and as-synthesized samples of JLU-MOF201-Ln.

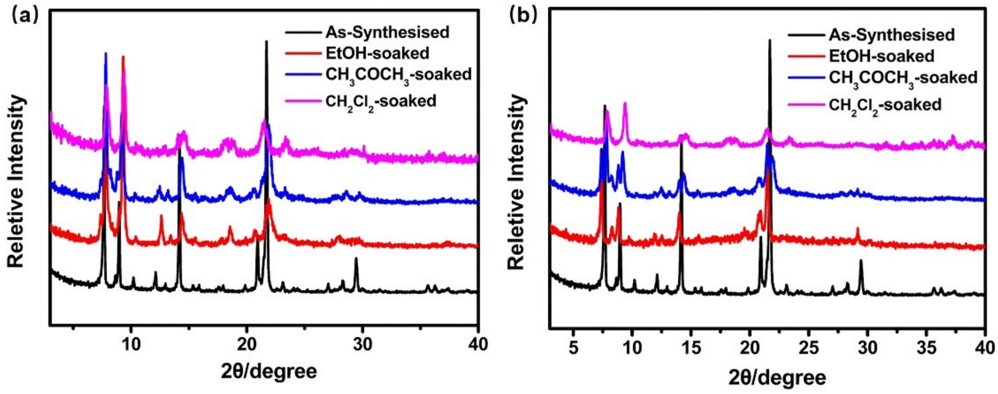

Fig. S12 PXRD patterns of (a) JLU-MOF201-Y and (b) JLU-MOF201-Tb as-synthesized and after soaking in different organic solvents.

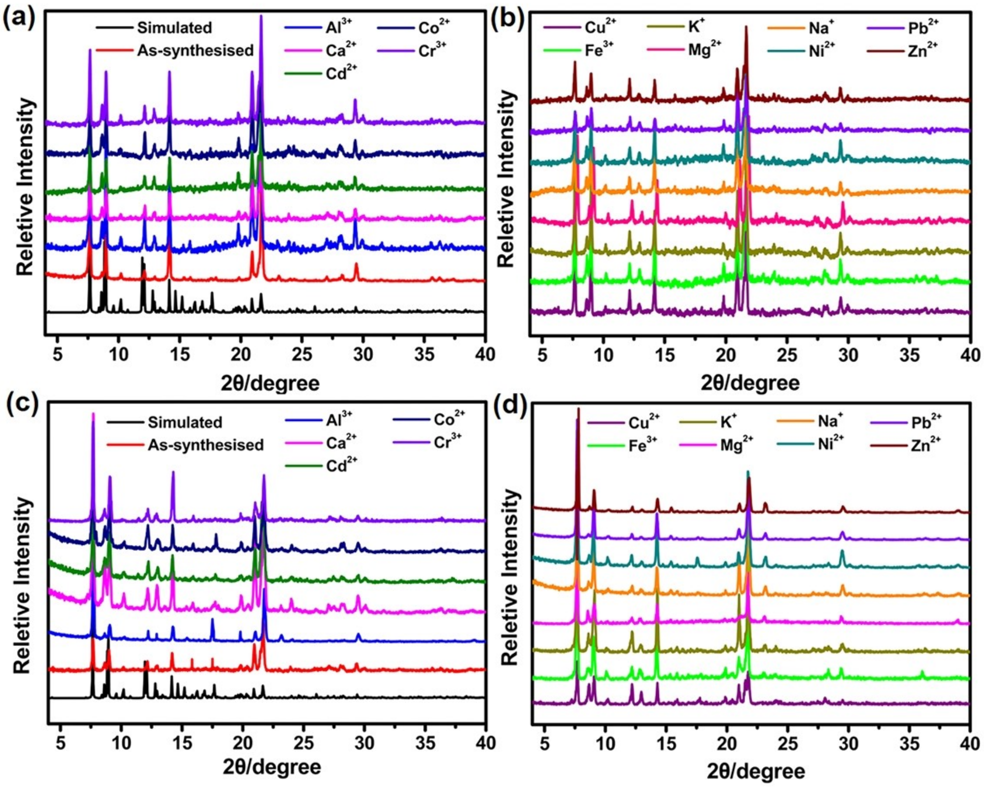

Fig. S13 PXRD patterns of JLU-MOF201-Y (a, b) and JLU-MOF201-Tb (c, d) as-synthesized and after soaking in

DMF solutions with different metal ions.

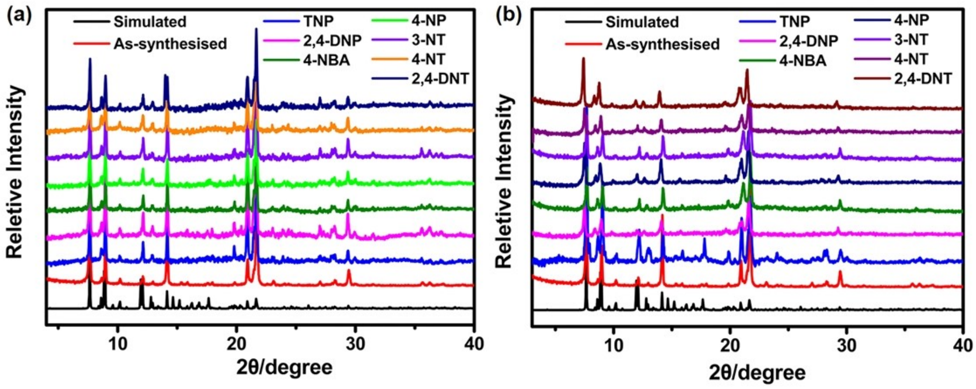

Fig. S14 PXRD patterns of as-synthesized JLU-MOF201-Y and samples after soaking in different NAEs DMF solution.

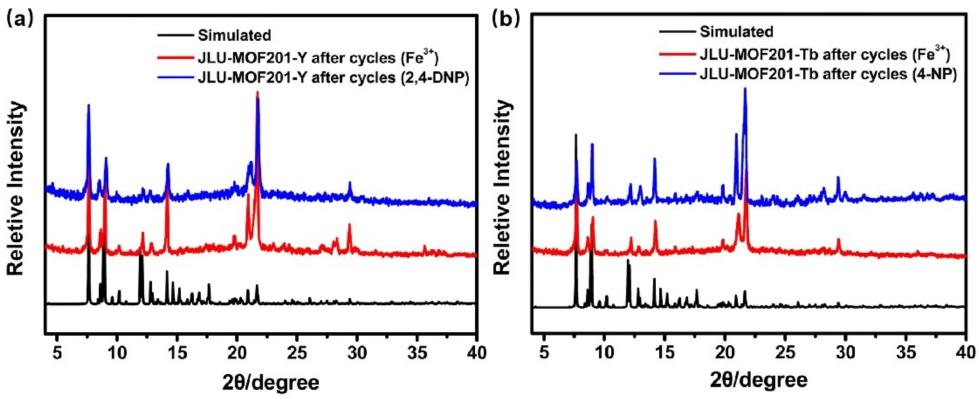

Fig. S15 PXRD patterns of JLU-MOF201-Y (a) and JLU-MOF201-Tb (b) as-synthesized and after four quenching-recovery cycles.

S1. Supporting Tables.

Table S1. Crystal data and structure refinements for the JLU-MOF201-Y.

Parameters	**JLU-MOF201-Y**
Formula	$C_{43}H_{42}N_9O_{16}Y_2$
Formula weight	1118.67
Temperature(K)	297.8
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	*C2/c*
a (Å)	44.809(4)
b (Å)	10.8964(9)
c (Å)	25.255(2)
α (°)	90.00
B (°)	113.735(2)
γ (°)	90.00
volume (Å^3)	11287.9(17)
Z, D_x (g/cm^3)	8, 1.317
F(000)	4552.0
ϑ range (deg)	2.39-24.26
reflns collected/unique	4927/10254
R_{int}	0.1071
data/restraints/params	10254/779/638
GOF on F^2	1.069
R_1, wR_2 (I>2σ(I))	0.0837/0.1975
R_1, wR_2 (all data)	0.1466/0.2258

Table S2. Unit cell data for the JLU-MOF201-Ln.

	JLU-MOF201-Y	JLU-MOF201-Tb	JLU-MOF201-Yb	JLU-MOF201-Ho	JLU-MOF201-Er
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
a (Å)	44.81	45.21	45.77	44.93	45.02
b (Å)	10.90	10.98	11.06	10.90	10.91
c (Å)	25.26	25.34	25.73	25.23	25.26
α (°)	90.00	90.00	90.00	90.00	90.00
β (°)	113.74	113.76	113.44	113.73	113.45
γ (°)	90.00	90.00	90.00	90.00	90.00
volume ($Å^3$)	11287	11514	11950	11309	11387

Table S3. A comparison of K_{sv} and LODs values of luminescent MOFs for Fe^{3+} detection.

MOFs	K_{sv} (M^{-1})	LOD (μM)	Ref.
$[Zr_6O_6(OH)_2(CF_3COO)_2(C_{11}H_5NO_4)_4(H_2O)_4]$	2.25×10^7	1.70×10^{-3}	1
$[Zn_2Na_2(TPHC)(4,4\text{-}Bipy)(DMF)]\cdot 8H_2O$	5.57×10^4	6.40	2
$[EuDTTA(DMF)_3]NO_3$	3.63×10^4	4.14	3
$\{[Cd(tptb)(H_2DOBDC)(H_2O)]\cdot DMF\}_n$	3.00×10^4	1.67×10^{-5}	4
$[Tb(L_2)(H_2O)(DMF)]_n$	2.89×10^4	0.91	5
$\{[Eu(L)(H_2O)]\cdot 4H_2O\}_n$	1.88×10^4	0.57	6
$\{[Tb(L)(H_2O)]\cdot 7H_2O\}_n$	1.48×10^4	1.26	7
$[Tb_2(PIA)_3(DMF)_3(CH_3OH)]$	**8.83×10^4**	**2.49**	**This work**
FJI-C8 (Zn)	8.25×10^3	23.3	8
$[Y_2(PIA)_3(DMF)_3(CH_3OH)]$	**7.67×10^3**	**2.21**	**This work**
534-MOF-Tb(L11)	5.51×10^3	130	9
$[Zn_2(cptpy)(btc)(H_2O)]_n$	5.46×10^3	4.33	10
$[Zr_6O_4(OH)_4(C_8H_2O_4S_2)_6]\cdot DMF\cdot 18H_2O$	4.41×10^3	1.26	11
$[Zn(3\text{-}bpmh)(HEA)\cdot H_2O]_n$	4.14×10^3	0.89	12
$\{[Eu(BIPATC)_{0.5}(DMA)_2(NO_3)]\cdot DMA\cdot H_2O\}_n$	3.89×10^3	-	13
$[Zn(HBCPBA)(tpim)]\cdot H_2O$	3.57×10^3	-	14
$\{[Eu(TMCA)(DEF)(H_2O)]\cdot(CH_3CN)\}_n$	1.84×10^3	30.10	15

Table S4. A comparison of K_{sv} and LODs values of luminescent MOFs for 2,4-DNP detection.

MOFs	K_{sv} (M^{-1})	LOD (μM)	Ref.
$[Cd_2(TPA)_2(BIYB)_2]_n$	1.60×10^5	0.13	16
$[Zn_5(DpImDC)_2(DMF)_4(H_2O)_3]\cdot H_2O\cdot DMF$	8.70×10^4	-	17
$[Cd(TTPBA\text{-}4)_2(OH)_2\cdot H_2O]_n$	4.10×10^4	9.50×10^{-3}	18
$[Y_2(PIA)_3(DMF)_3(CH_3OH)]$	**3.63×10^4**	**0.46**	**This work**
Sc-EBTC	2.85×10^4	4.30×10^{-5}	19
$[Zn_2(TCPE)(tta)_2]\cdot 2DMF\cdot 4H_2O\cdot 2Me_2NH^{2+}$	2.60×10^4	6.12×10^{-5}	20
$\{[(CH_3)_2NH_2]_6[Cd_5(L)_4]\cdot H_2O\cdot 3DMF\}_n$	2.37×10^4	4.57×10^{-3}	21
$\{(NH_2(CH_3)_2)[Zn_4(ddn)_2(COO)(H_2O)_4]\cdot solvent\}_n$	0.89×10^4	8.75×10^{-3}	22

Table S5. A comparison of the values of K_{sv} and LODs of luminescent MOFs for the detection of 4-NP.

MOFs	K_{sv} (M^{-1})	LOD (μM)	Ref.
$[Eu_{0.5}Tb_{0.5}(L)(H_2O)_3]_n$	7.50×10^6	-	23
$\{[Tb(HL)]\cdot 3DMF\cdot 3H_2O\}_n$	3.60×10^5	2.33×10^{-8}	24
$\{[Cd_{3.5}(\mu_3\text{-}OH)(TCPB)_2(bimb)(H_2O)_3]\cdot 0.5dioxane\cdot 0.5H_2O\}$	3.80×10^4	0.49×10^{-3}	25
$[Tb_2(PIA)_3(DMF)_3(CH_3OH)]$	**1.89×10^4**	**1.01**	**This work**
Eu-CP	1.38×10^4	3.00×10^{-9}	26
$[Cd(L)(phen)_2]\cdot 5H_2O$	5.13×10^3	1.15×10^{-5}	27

Table S6. The K_{sv} and LODs values of JLU-MOF201-Y and JLU-MOF201-Tb for the detection of NAEs.

	JLU-MOF201-Y		JLU-MOF201-Tb	
NAEs	K_{sv} (M^{-1})	LOD (μM)	K_{sv} (M^{-1})	LOD (μM)
2,4-DNP	3.36×10^4	0.46	6.41×10^3	2.99
4-NP	1.46×10^4	1.15	1.89×10^4	1.01
TNP	1.16×10^4	1.04	5.06×10^3	3.79
4-NBA	2.78×10^3	6.05	4.41×10^3	4.35
3-NT	1.90×10^3	8.85	2.16×10^3	8.87
4-NT	2.74×10^3	6.14	2.57×10^3	7.46
2,4-DNT	1.76×10^3	9.60	3.71×10^3	5.17

Table S7. The ICP data of JLU-MOF201-Y and Fe^{3+}@JLU-MOF201-Y.

Compounds	Y^{3+} (ppm)	Fe^{3+} (ppm)
JLU-MOF201-Y	17.96	-
Fe^{3+}@ JLU-MOF201-Y	23.95	0.11

Table S8. The ICP data of JLU-MOF201-Tb and Fe^{3+}@JLU-MOF201-Tb.

Compounds	Tb^{3+}	Fe^{3+}
JLU-MOF201-Tb	18.24	-
Fe^{3+}@ JLU-MOF201-Tb	25.83	0.19

References

1. C. Gogoi and S. Biswas, *Dalton Trans.*, 2018, **47**, 14696-14705.
2. C. Yu, X. Sun, L. Zou, G. Li, L. Zhang and Y. Liu, *Inorg. Chem.*, 2019, **58**, 4026-4032.
3. Y. Zhang, L. Wu, M. Feng, D. Wang and C. Li, *J. Solid State Chem.,* 2021, **294**, 121868.
4. Y. P. Li, S. F. Li, X. Geng, R. D. Wang, L. C. He, S. Y. Wang, L. Du and Q. H. Zhao, *Inorg. Chem. Commun.*, 2021, **128**, 108604.
5. X. Mi, D. Sheng, Y. Yu, Y. Wang, L. Zhao, J. Lu, Y. Li, D. Li, J. Dou, J. Duan and S. Wang, *ACS. Appl. Mater. Interfaces*, 2019, **11**, 7914-7926.
6. B. Li, J. P. Dong, Z. Zhou, R. Wang, L. Y. Wang and S. Q. Zang, *J. Mater. Chem. C*, 2021, **9**, 3429-3439.
7. J. P. Dong, B. Li, Y. J. Jin and L. Y. Wang, *CrystEngComm*, 2021, **23**, 1677-1683.
8. C. H. Chen, X. S. Wang, L. Li, Y. B. Huang and R. Cao, *Dalton Trans.*, 2018, **47**, 3452-3458.
9. M. Chen, W. M. Xu, J.-Y. Tian, H. Cui, J. X. Zhang, C.-S. Liu and M. Du, *J. Mater. Chem. C*, 2017, **5**, 2015-2021.
10. H. Chen, P. Fan, X. Tu, H. Min, X. Yu, X. Li, J. L. Zeng, S. Zhang and P. Cheng, *Chem. Asian. J*., 2019, **14**, 3611-3619.
11. R. Dalapati, U. Kokcam-Demir, C. Janiak and S. Biswas, *Dalton Trans.*, 2018, **47**, 1159-1170.
12. Y. Wang, Y. Zhao, H. Yu, Z.-Q. Liu, L.-J. Wang, R.-Y. Huang, W. Xu and J.-F. Wu, *J. Solid State Chem*., 2020, **288**, 121404.
13. X. Wang, Y. Wang, X. Wang, K. Lu, W. Jiang, P. P. Cui, H. Hao and F. Dai, *Dalton Trans.*, 2020, **49**, 15473-15480.
14. X. Liu, L. Zhao, C. Zhao, L. Meng and C. Liu, *Journal of Molecular Structure*, 2019, **1188**, 238-243.
15. G. M. Liang, S. Wang, M. Y. Xu, H.-L. Chen, G. Y. Liang, L. C. Gui and X. J. Wang, *CrystEngComm*, 2020, **22**, 6161-6169.
16. X. Wang, Y. Han, X. X. Han, X. Hou, J.-J. Wang and F. Fu, *New J. Chem.,* 2018, **42**, 19844-19852.
17. J. Li, X. Luo, Y. Zhou, L. Zhang, Q. Huo and Y. Liu, *Cryst. Growth Des.,* 2018, **18**, 1857-1863.
18. I. E. Khalil, T. Pan, Y. Shen and W. Zhang, *Inorg. Chem. Commun.,*2020, **120**, 108170.
19. D. Zhan, A. Saeed, Z. Li, C. Wang, Z. Yu, J. Wang, N. Zhao, W. Xu and J. Liu, *Dalton Trans.*, 2020, **49**, 17737-17744.
20. X. Zhang, G. Ren, M. Li, W. Yang and Q. Pan, *Cryst. Growth Des.*, 2019, **19**, 6308-6314.
21. L. Lu, J. Wu, J. Wang, J. Q. Liu, B. H. Li, A. Singh, A. Kumar and S. R. Batten, *CrystEngComm*, 2017, **19**, 7057-7067.
22. A. Ma, J. Wu, Y. Han, F. Chen, B. Li, S. Cai, H. Huang, A. Singh, A. Kumar and J. Liu, *Dalton Trans.*, 2018, **47**, 9627-9633.
23. X. Cheng, J. Hu, J. Li and M. Zhang, *J. Lumin.*, 2020, **221**, 117100.
24. Z. G. Lin, F. Q. Song, H. Wang, X. Q. Song, X. X. Yu and W. S. Liu, *Dalton Trans.*, 2021, **50**, 1874-1886.
25. J. Zhang, L. Gao, Y. Wang, L. Zhai, X. Niu and T. Hu, *New J. Chem*., 2019, **43**, 16853-16859.
26. Y. Liu, J. Ma, C. Xu, Y. Yang, M. Xia, H. Jiang and W. Liu, *Dalton Trans*., 2018, **47**, 13543-13549.
27. S. S. Chen, Z. Y. Zhang, R. B. Liao, Y. Zhao, C. Wang, R. Qiao and Z. D. Liu, *Inorg. Chem.*, 2021, **60**, 4945-4956.