Electronic Supplementary Material (ESI) for Dalton Transactions.
This journal is © The Royal Society of Chemistry 2017

[Supporting information]

The mixed-ligand strategy to assemble a microporous anionic metal-organic framework: Ln^{3+} post-functionalization, sensors and selective adsorption of dyes

Mingming Guo,[a] Sixu Liu,[a] Huadong Guo,[a]* Yingying Sun,[a] Xianmin Guo[a]* and Ruiping Deng[b]*

[a] Department of Chemistry, Changchun Normal University, Changchun, 130032, P. R. China. Fax: +86-431-86168210; Tel: +86-431-86168210; E-mail: hdxmguo@163.com; xian_min@hotmail.com
[b] Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, 5625 Renmin Street, Changchun City, Jilin Province, P.R. China, 130022. Fax: +86-431-85698041; Tel: +86-431-85262414; E-mail: dengrp@ciac.jl.cn

Table 1. Crystal and Structure Refinement Data for Compounds **1**.

param	**1**
formula	$C_{102}H_{106}N_{12}O_{20}SZn_2$
fw	1982.78
space group	*P*-1
a	13.563(5)
b	15.831(5)
c	24.582(5)
α (deg)	93.410(5)
β(deg)	95.780(5)
γ (deg)	104.908(5)
V	5054(3)
Z	2
D_{calcd} (g cm^{-3})	1.303
F(000)	2076
GOF on F^2	1.033
R_1/wR_2[I≥2sigma(I)]	0.0687/0.1901
R_1/wR_2 (all data)	0.1038/0.2095

Table S2. selected bond lengths [Å] and angles [°] for **1**.

Zn(1)-N(1)	2.044(4)	Zn(1)-O(7)	1.951(4)
Zn(1)-O(4)#3	1.950(4)	Zn(1)-O(12)#1	1.923(4)
Zn(2)-O(1)	1.948(4)	Zn(2)-O(10)	1.968(4)
Zn(2)-O(5)#2	2.188(6)	Zn(2)-O(6)#2	2.217(6)
O(12)#1-Zn(1)-O(4)#3	115.23(17)	O(12)#1-Zn(1)-O(7)	127.00(18)
O(7)-Zn(1)-O(4)#5	107.74(17)	O(12)#1-Zn(1)-N(1)	98.60(18)
O(4)#2-Zn(1)-N(1)	97.96(18)	O(7)-Zn(1)-N(1)	104.8(2)
O(1)-Zn(2)-O(10)	105.0(3)	O(10)-Zn(2)-N(4)#3	101.7(2)
O(1)-Zn(2)-O(5)#4	105.3(2)	O(10)-Zn(2)-O(5)#4	146.4(2)
N(4)#3-Zn(2)-O(5)#4	89.4(2)	O(1)-Zn(2)-O(6)#4	111.9(2)
O(10)-Zn(2)-O(6)#4	95.3(2)	N(4)#3-Zn(2)-O(6)#4	140.8(2)
O(5)#4-Zn(2)-O(6)#4	59.1(3)		

Symmetry transformations used to generate equivalent atoms: #1 x,y-1,z; #2 x,y+1,z; #3 x-1,y,z+1; #4 x-1,y,z-1.

Table S3. The ICP results of Ln^{3+}@**1** (Ln = Eu, Tb, Sm, Dy)

Compounds	Zn^{3+} (ppm)	Ln^{3+} (ppm)	Zn^{3+}/ Ln^{3+}
Eu^{3+}@**1**	96470	25780	1:0.2681
Tb^{3+}@**1**	89840	23420	1:0.2607
Sm^{3+}@**1**	85800	22830	1:0.2661
Dy^{3+}@**1**	90410	24250	1:0.2682

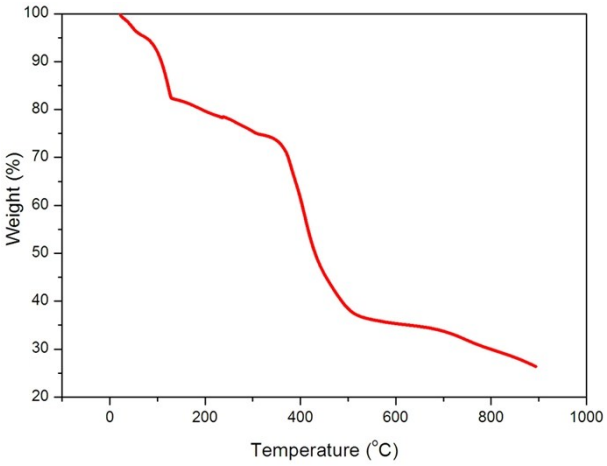

Fig. S1. The TGA curves of **1**. To characterize the thermal stabilities of compounds **1**, its thermal behavior was investigated by TGA. The experiments were performed on samples consisting of numerous single crystals of **1** under nitrogen atmosphere with a heating rate of 10°C/min. The weight loss in the range of 25-350°C is attributed to the release of free DMF molecules and $Me_2NH_2^+$ (obsd 26.5%, calcd 26.8%). The destruction of the framework occurs at ca. 365°.

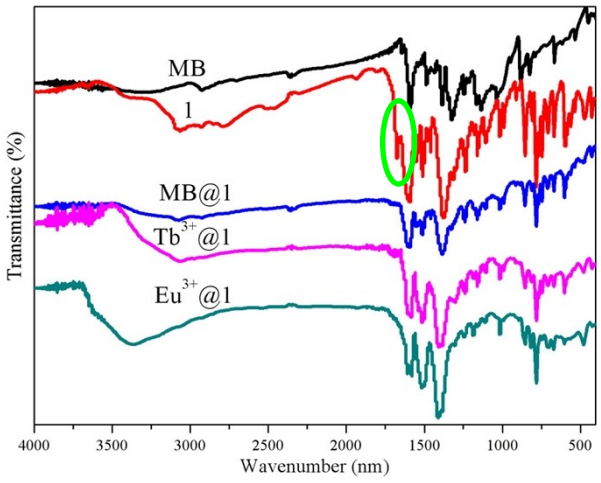

Fig. S2. FT-IR spectrum of MB, **1**, MB@**1**, Tb^{3+}@**1** and Eu^{3+}@**1**. Comparing to the spectra of **1**, the disappearance of absorption band located at 1670 cm^{-1} (assigned to the asymmetric stretching vibrations of C=O) in MB@**1**, Tb^{3+}@**1** and Eu^{3+}@**1,** indicates the weak interactions between uncoordinated C=O from carboxylates and cationic ions.

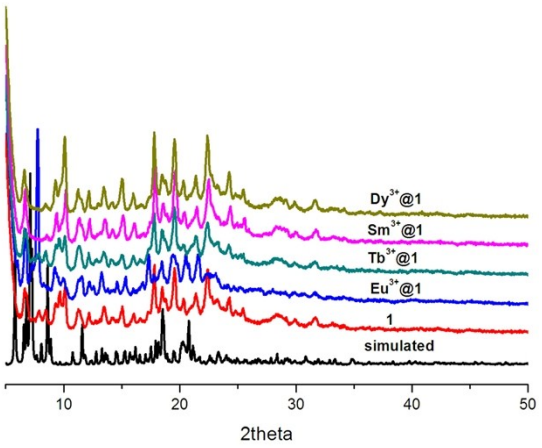

Fig. S3. PXRD patterns of the as-synthesized **1** and Ln^{3+}@**1** (Ln = Eu, Tb, Sm, Dy).

Table S4. Comparison of MB adsorption capacity for MOF-based adsorbents.

MOF-type Adsorbents	Uptake capacity (mg g^{-1})	Ref
FJI-C_2	1323	1
$[Cd_2(H_2O)_2L]\cdot 5H_2O\cdot 0.5DMF$	1008	2
$[Ca(HDCPP)_2(H_2O)_2]_n(DMF)_{1.5n}$	952	3
ZJU-24	902	4
$[Mg(HDCPP)_2(DMF)_2]_n\cdot(H_2O)_7$ n	862	3
DUT-23(Cu)	814	5
Amino-MIL-101-Al	762	6
MIL-100 (Fe)	736	7
Co-MOF	725	8
Ni-MOF	708	8
UMCM-150 flower-like	560	9
1	348	this work
$Cu_3(BTC)_2$	243	10

Reference

[1] X.-S. Wang, J. Liang, L. Li, Z.-J. Lin, P. P. Bag, S.-Y. Gao, Y.-B. Huang and R. Cao, *Inorg. Chem*., 2016, **55**, 2641.
[2] Y.-F. Hui, C.-L. Kang, T. Tian, S. Dang, J. Ai, C. Liu, H.-R. Tian, Z.-M. Sun and C.-Y. Gao *CrystEngComm*, 2017, **19**, 1564.
[3] Y. Hou, J. Sun, D. Zhang, D. Qi, and J. Jiang, *Chem. Eur. J.*, 2016, **22**, 6345.
[4] Q. Zhang, J. Yu, J. Cai, R. Song, Y. Cui, Y. Yang, B. Chen and G. Qian, *Chem. Commun.*, 2014, **50**, 14455.
[5] Z.-P. Qi, J.-M. Yang, Y.-S. Kang, F. Guo and W.-Y. Sun, *Dalton Trans.*, 2016, **45**, 8753.
[6] E. Haque, V. Lo., A. I. Minett, A. T. Harris and T. L. Church, *J. Mater. Chem. A*., 2014, **2**, 193.
[7] 22. M. Tong, D. Liu, Q. Yang, D.-V. Sabine, G. Maurin and C. Zhang, *J. Mater. Chem. A*., 2013, **1**, 8534.
[8] Z. Zhu, Y.-L. Bai, L. Zhang, D. Sun, J. Fang, S. Zhu, *Chem. Commun.*, 2014, **50**, 14674.
[9] J.-M. Yang, Q. Liu, Y.-S. Kang and W.-Y. Sun, *CrystEngComm*, 2015, **17**, 4825.
[10] X. Zhao, S. Liu, Z. Tang, H. Niu, Y. Cai, W. Meng, F. Wu and J. P. Giesy, *Scientific reports*, 2015, **5**, 11849.