Electronic Supplementary Material (ESI) for ChemComm.

Proton coupled electron transfer – a new photochromic performance in host-guest collaborative MOF

Zhichao Shao,[a] Qiong Wu,[a] Xiao Han,[ab] Yujie Zhao,[a] Qiong Xie,[a] Hongfei Wang[a] and Hongwei Hou*,[a]

[a]*College of Chemistry and Molecular Engineering, Zhengzhou University, Zhengzhou, Henan, 450001, P. R. China*

[b]*College of Chemical Engineering & Material, Hebei Key Laboratory of Heterocyclic Compounds, Handan University, Hebei, 056005, P. R. China.*

Author for correspondence:

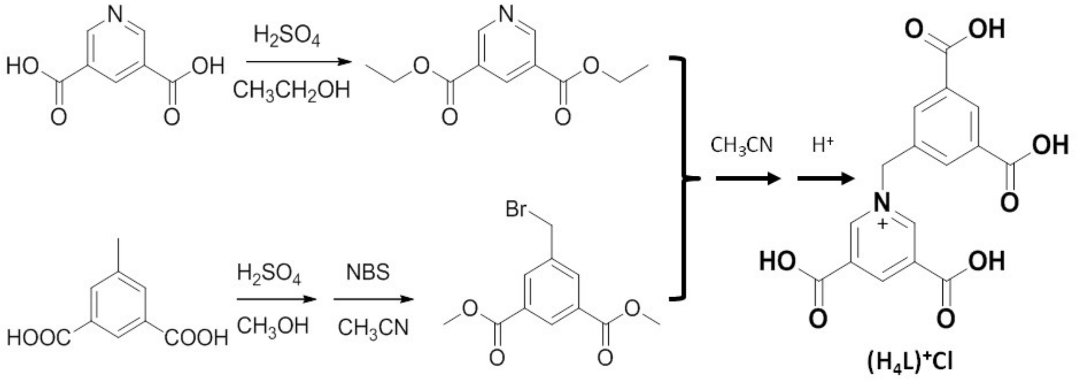
Prof. Hongwei Hou, E-mail: houhongw@zzu.edu.cn.

Supporting Information

Additional experimental details

Materials and physical measurements All the solvents and reagents were purchased from commercial source without further purification. The water used in the experiment is de-ionized water. The data of elemental analyses (C, N and H) were collected by a FLASH EA 1112 elemental analyzer. Thermogravimetric analyses (TGA) were performed on a Netzsch STA 449C thermal analyzer at a heating rate of 10 °C min^{-1} in air. UV-vis spectra were recorded at JASCO-750 UV-vis spectrophotometer. The fluorescence measurements were measured on JASCO FP-8300 spectrophotometer. The Fourier Transform Infra-Red (FT-IR) spectra were carried out on a Bruker Tensor 27 spectrophotometer with KBr pellets in the range of 400-4000 cm^{-1}. The electron paramagnetic resonance (EPR) spectroscopy was detected using a Brucker A300 EPR spectrometer. Powder X-ray Diffraction (PXRD) patterns were obtained by Cu Kα_1 radiation on a PANalytical X'Pert PRO diffractometer. ^{1}H NMR spectrum were conducted on Bruker Avance-600 spectrometers.

Synthesis of $(H_4L)^+Cl$ Diethyl 3,5-pyridinedicarboxylate (1 mmol) and dimethyl 5-(bromomethyl) isophthalate (1.2 mmol) were placed in a 25 ml single-neck round bottom flask, then 15 mL acetonitrile was added as the reaction solvent. The reaction was carried out at 80 °C and the reaction time was determined by TLC. After the completion of the reaction, the column chromatography column was used for separation and purification, and the developing solvent was CH_2Cl_2 to obtain a pure product of the ester in a yield of 90%. The purified ester was dried under vacuum, then transferred to a 25 mL round bottom flask, and then hydrolyzed at 100 °C for 10 h by adding 10 ml concentrated hydrochloric acid, and a white solid appeared in the reaction flask. After the reaction, the cooled reaction liquid was transferred to a beaker, and the product was washed with a large amount of deionized water, and filtered under reduced pressure to obtain a pure ligand $(H_4L)Cl$. The spectra of ^{1}H NMR in ligand synthesis process were showed at Figure S16.



Synthesis of $\{[ZnL(bpe)_{0.5}]\cdot 0.5(H_2bpe)\cdot 3H_2O\}_n$ (1). $(H_4L)^+Cl$ (0.0138g, 0.04mmol), $Zn(NO)_3\bullet 6H_2O$ (0.0119g, 0.04mmol) and 1,4-divinylpyridine (0.0145g, 0.08mmol) were dissolved in a mixture of 2mL N,N-dimethylformamide (DMF), 4 mL de-ionized water and 3 drops concentrated nitric acid. The mixture was sealed in 25mL teflon-lined stainless steel container and kept at 100 ° C for two days (heating process: 3 h to 100 °C, cooling process: 5 °C/h dropped to 50 °C). Pale yellow block crystals were precipitated with the yield of 80% (calculated as Zn). Elemental analysis calculated according to $C_{28}H_{25}N_3O_{11}Zn$, theoretical value (%): C, 52.10%, H, 3.87%, N, 6.51%, actual value (%): C, 52.14%, H, 3.73%, N, 6.36%. Infrared spectrum (KBr, cm^{-1}): 3461(s), 3067(w), 1659(s), 1617(s), 1519(w), 1376(s), 1223(m), 1030(m), 845(s), 723(s).

Single crystal X-ray crystallography. The crystallographic data were collected on a Bruker D8 VENTURE diffractometer with Mo Kα radiation (λ = 0.71073 Å) at 120 K. The integration of the diffraction data and the intensity corrections were performed using the SAINT program.[1] Semiempirical absorption correction was performed using SADABS program.[2] The structures were solved by direct methods and refined with a full matrix least-squares technique based on F^2 with the SHELXL-2014 crystallographic software package.[3] The hydrogen atoms except for those of water molecules were generated geometrically and refined isotropically using the riding model. Crystallographic data and structure processing parameters are summarized in Table S1. Selected bond lengths and bond angles are listed in Table S2.

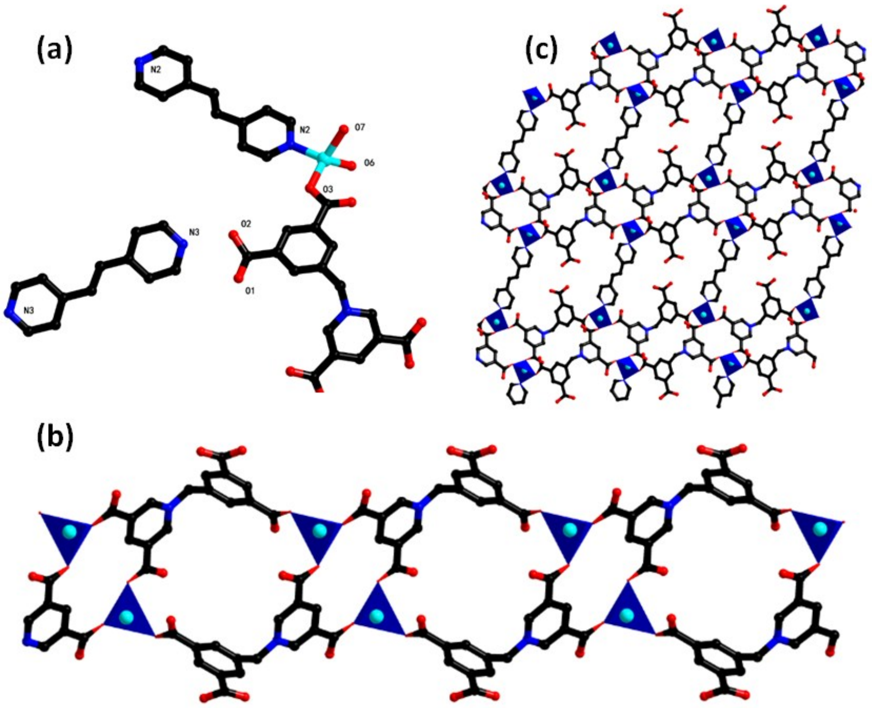


Figure S1. (a) Coordination environment around Zn^{II} in **1**. (b) The one-dimensional chain in **1**. (c) The three-dimensional structure diagram of **1**.

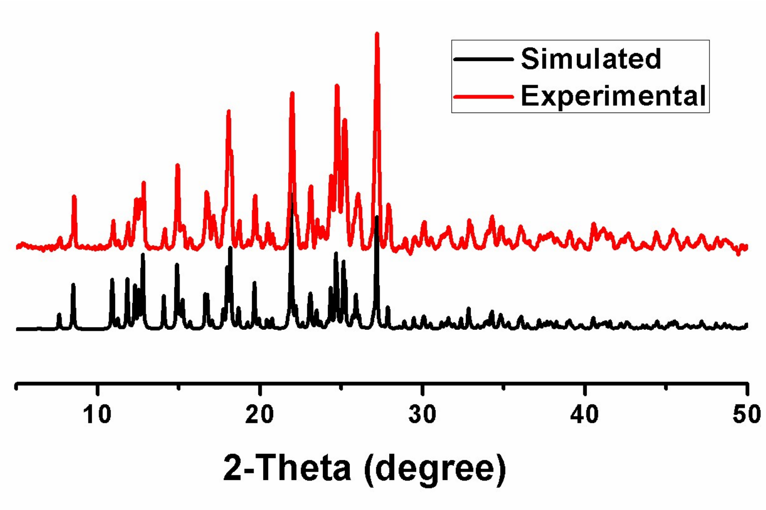


Figure S2 Experimental PXRD pattern of **1**.

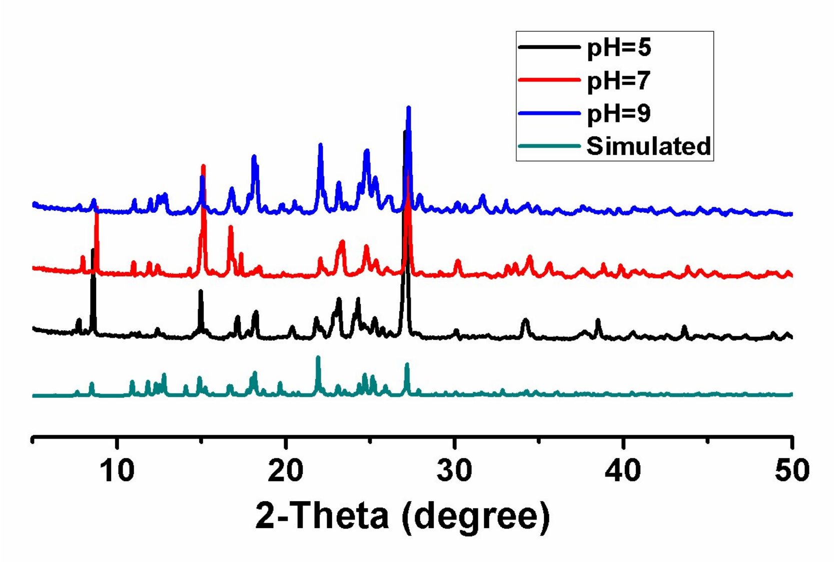


Figure S3 Experimental PXRD data of pH stability for **1**.

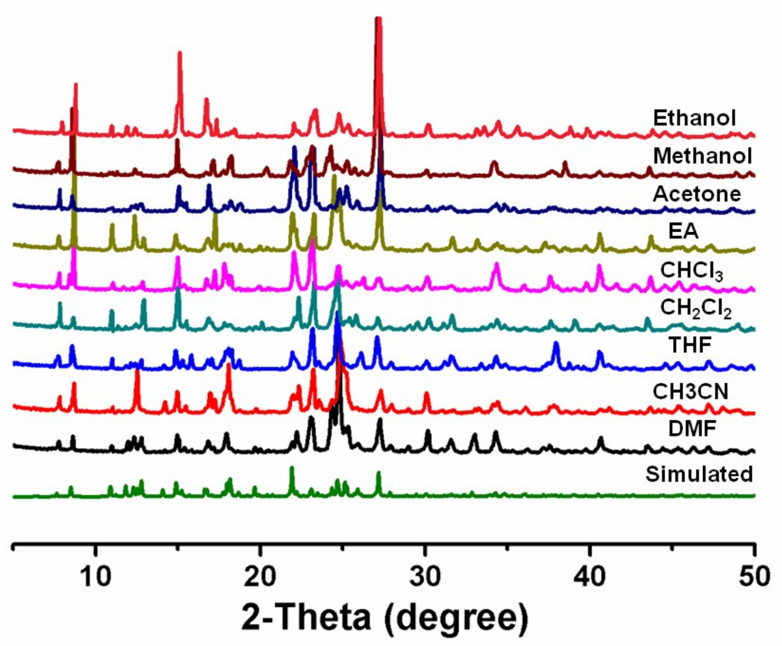


Figure S4 Experimental PXRD data of chemical stability for **1**.

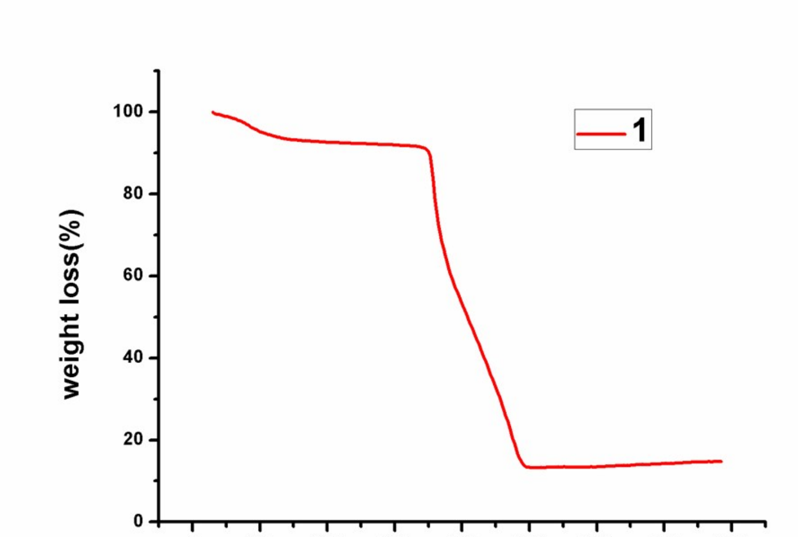


Figure S5 Thermogravimetric analysis of **1**.

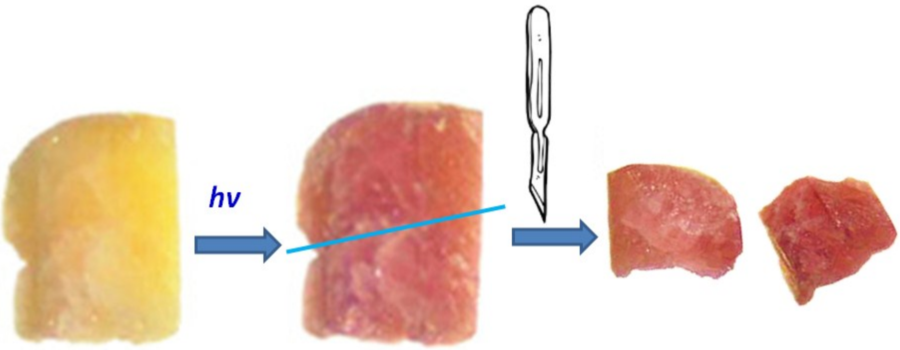


Figure S6 The photographic images of the photochromic effects inside the crystal.

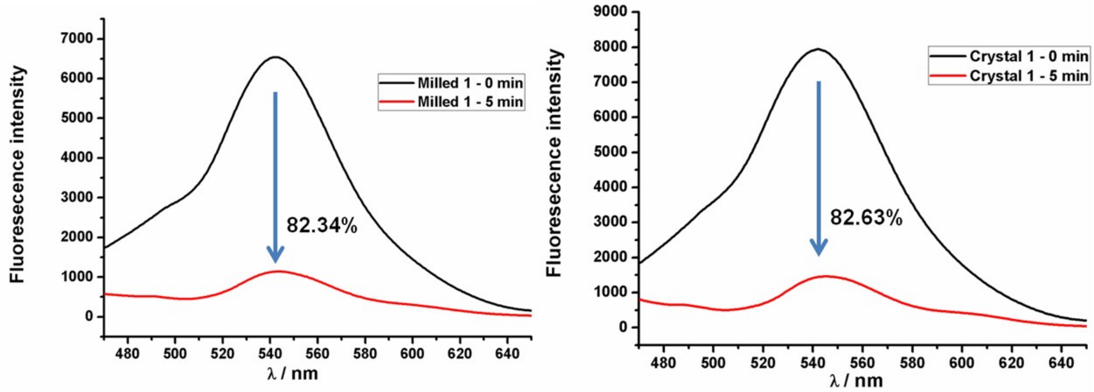


Figure S7 The effect of MOF shape on photochromic behavior.

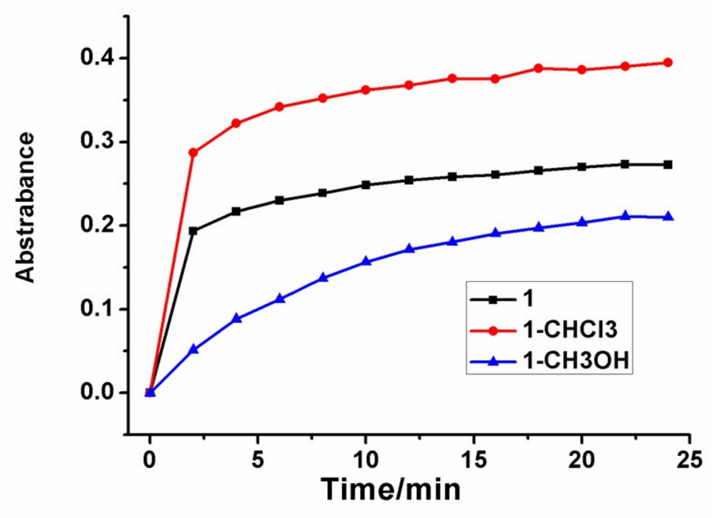


Figure S8 The effect of solvent molecules on the light response rate.

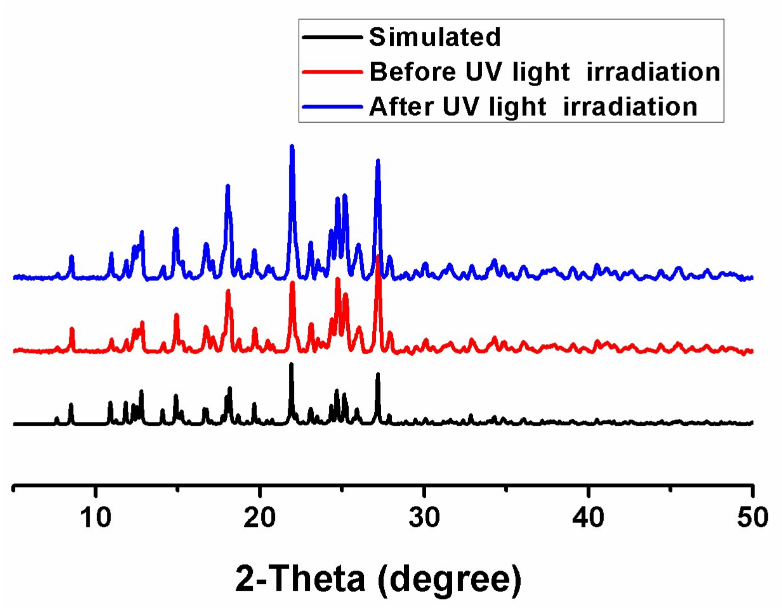


Figure S9 The PXRD spectra before and after illumination.

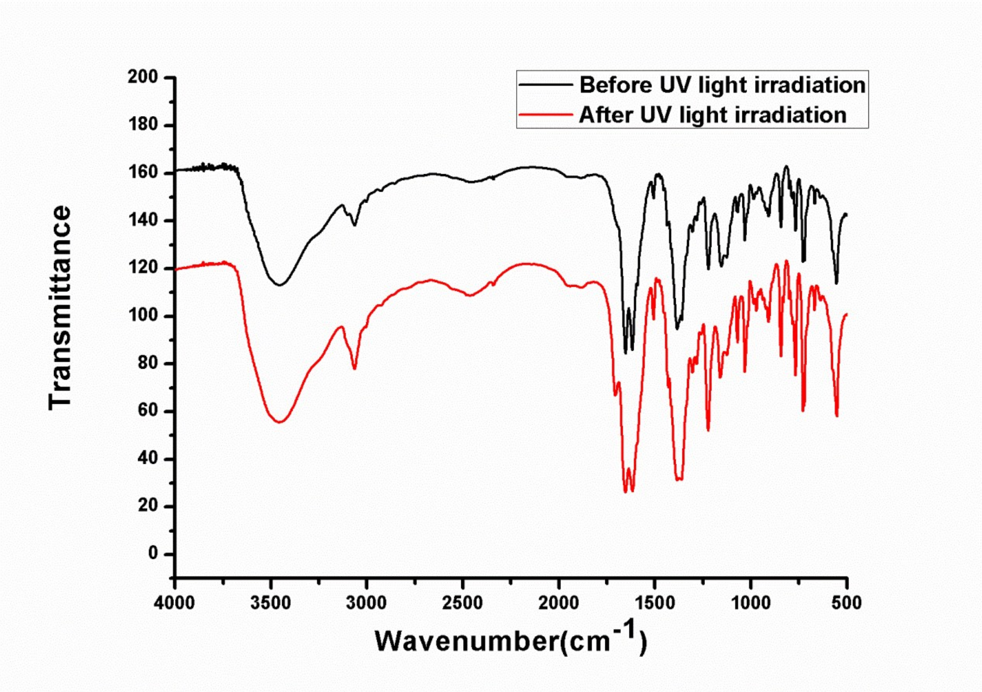


Figure S10. The IR spectra before and after illumination.

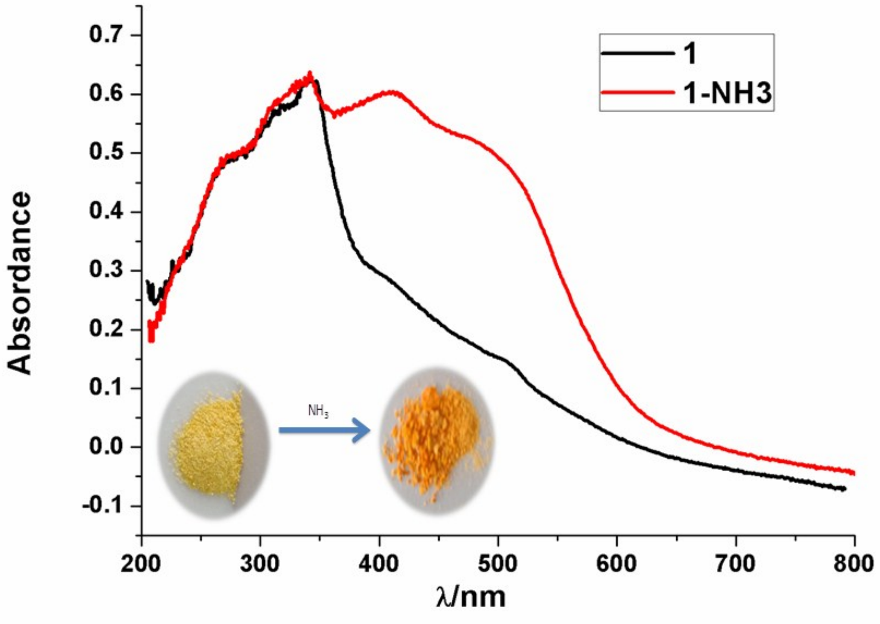


Figure S11 The UV−vis diffuse-reflectance of **1** and **1**-NH$_3$.

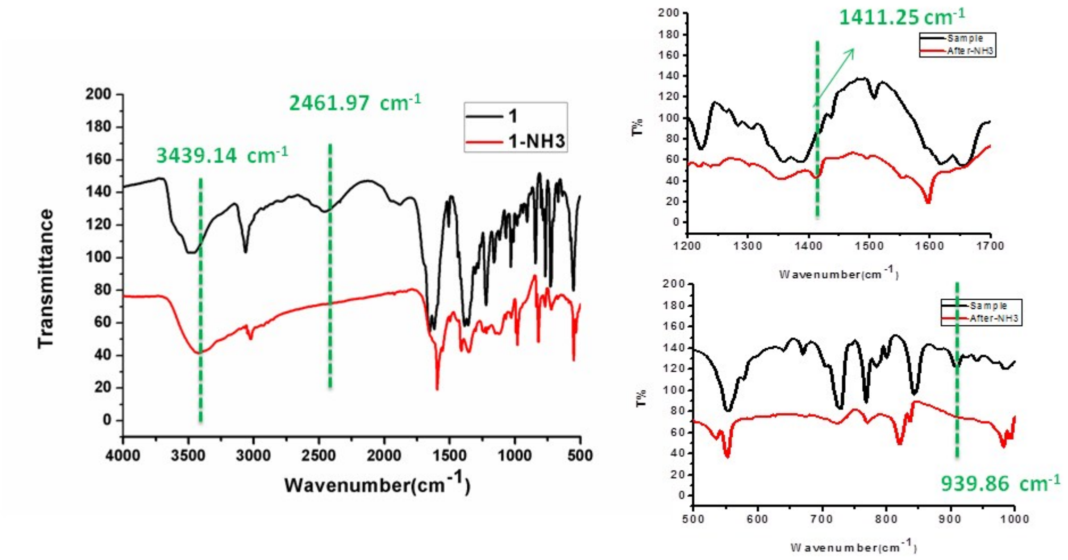


Figure S12 The IR spectra of **1** and **1**-NH_3.

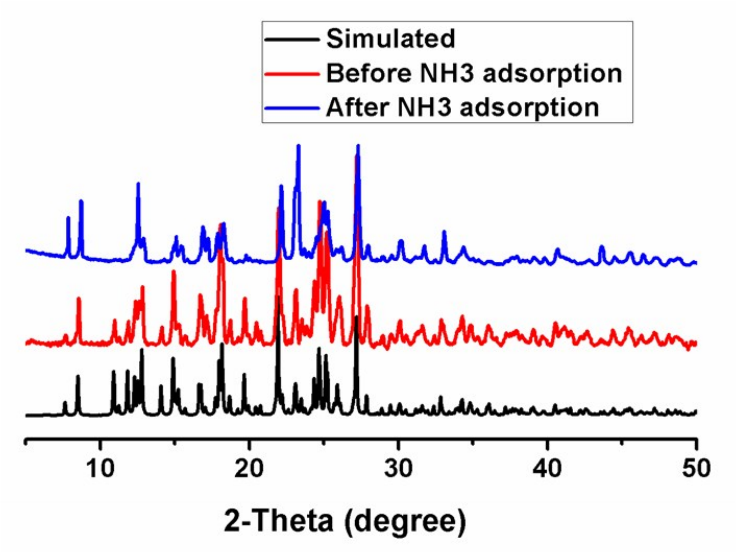


Figure S13 The PXRD spectra of **1** and **1**-NH_3.

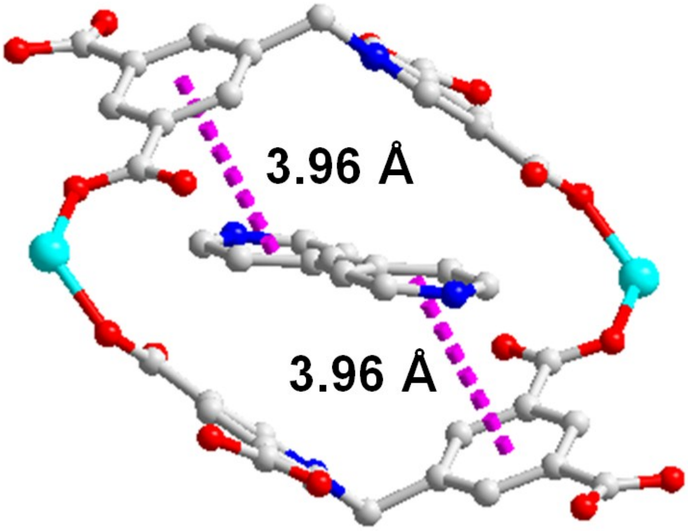


Figure S14 The π-π interaction between the guest molecule and host MOF.

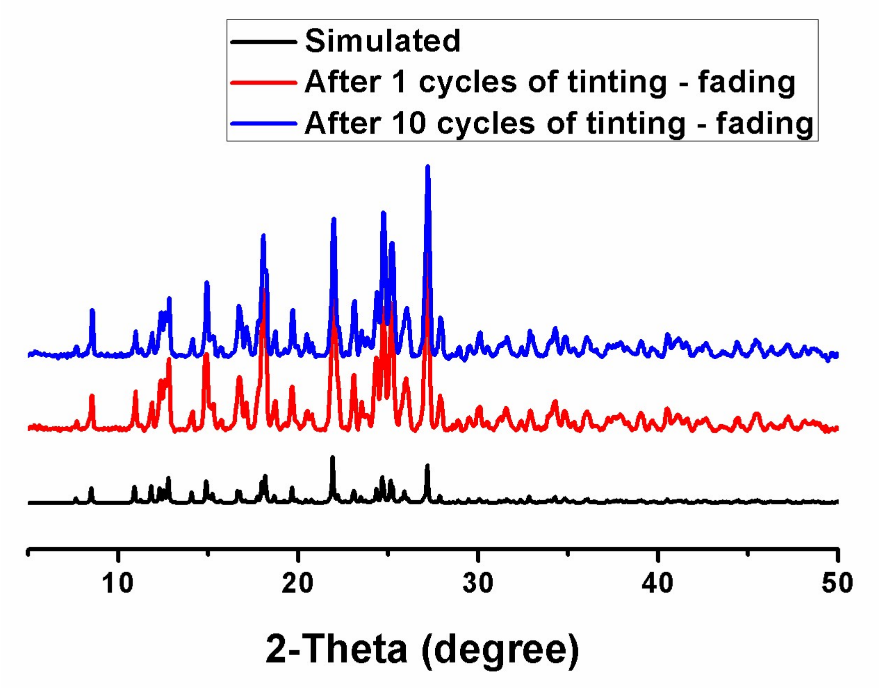


Figure S15. The reusability test of **1**.

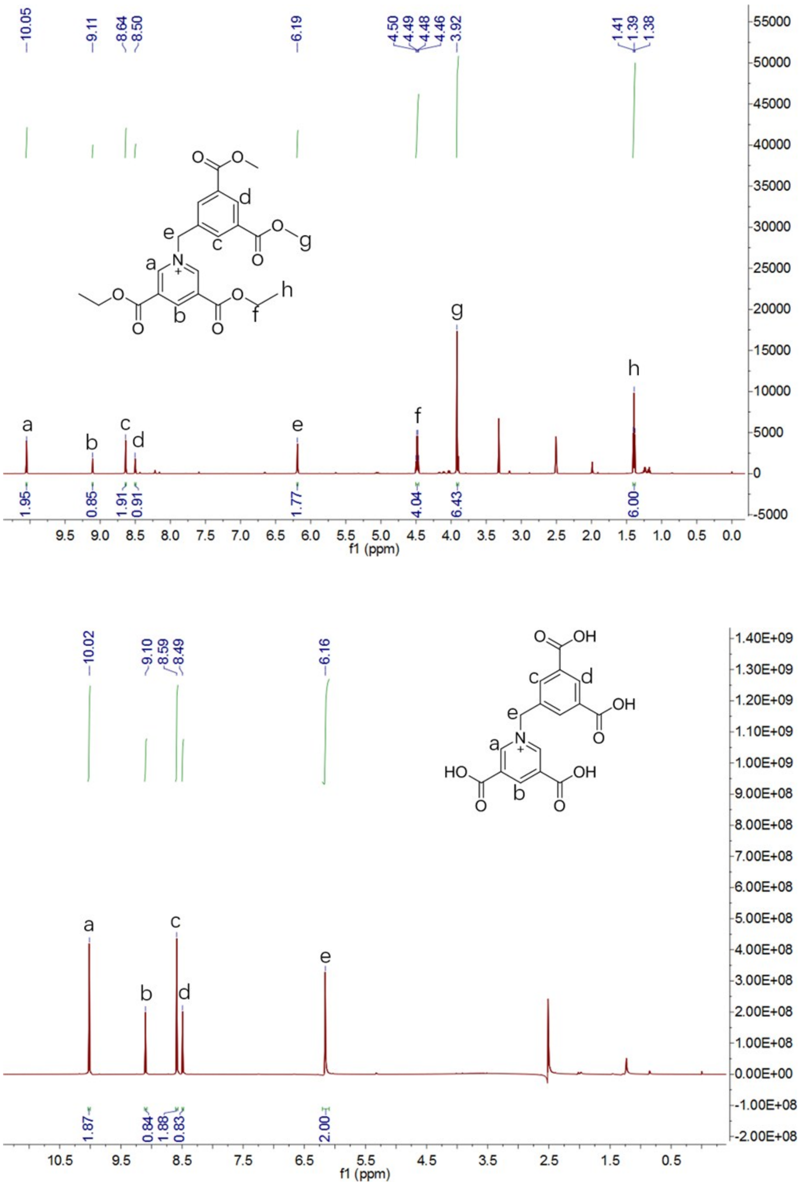


Figure S16. Spectra of ^{1}H NMR in ligand synthesis process.

Table S1 Crystallographic data and structure refinement details for **1**

Compound	**1**
formula	$C_{28}H_{25}N_3O_{11}Zn$
F_w	644.88
T/K	293.15
l (Mo–Ka)/Å	0.71073
Crystsyst	*triclinic*
Space group	*P-1*
a/Å	8.198(7)
b/Å	12.125(9)
c/Å	14.677(11)
α (deg)	72.35(3)
β (deg)	78.63(4)
γ (deg)	82.21(4)
V (Å^3)	1358.5(18)
Z	2
D_{calcd}(g cm^{-3})	1.576
F(000)	664.0
μ (mm^{-1})	0.974
GOF	1.058
R_1 ($I > 2\sigma(I)$)	0.0337
wR_2 ($I > 2\sigma(I)$)	0.0809

Table S2 Selected bond lengths (Å) and bond angles (deg) for crystal structure description.

1			
Zn1-O3	1.9324(18)	Zn1-O6^{2}	1.9612(19)
Zn1-O7^{1}	1.9448(19)	Zn1-N2	2.023(2)
N1-C8	1.509(3)	N1-C3	1.355(3)
N1-C7	1.359(3)	N2-C18	1.346(3)
C5-C4	1.391(3)	N2-C17	1.338(3)
C4-C2	1.395(3)	C2-C1	1.520(3)
C2-C3	1.388(3)	O1-C12	1.221(3)
O3-Zn1-O7^{1}	122.61(8)	O7^{1}-Zn1-O6^{2}	94.32(7)
O3-Zn1-O6^{2}	121.03(7)	O7^{1}-Zn1-N2	107.55(7)
O3-Zn1-N2	99.75(9)	O6^{2}-Zn1-N2	111.48(9)
Symmetry codes:	^{1}-1+X,1+Y,+Z; ^{2}1-X,1-Y,-Z; ^{3}1-X,1-Y,2-Z; ^{4}3-X,-Y,1-Z		

REFERENCES

1. SAINT, Bruker AXS, Inc., Madison, WI, 2001;
2. G. M. Sheldrick, SADABS, University of Göttingen, Germany, 2003.
3. G. M. Sheldrick, A short history of SHELX, Acta Crystallogr., Sect. A: Found. Crystallogr., 2008, 64, 112–122;