Electronic Supplementary Information

Bifunctional photo- and vapochromic behaviors of a novel porous zwitterionic metal-organic framework

Li Li, Yang Hua, Yu Guo, Hai-Yu Wang, Xiao-Nan Li and Hong Zhang*

Institute of Polyoxometalate Chemistry, Department of Chemistry, Northeast Normal University, Changchun, Jilin 130024, PR China.
Fax:+86-0431-85098827; Tel:+86-0431-85099372; E-mail: hope20130122@163.com

Contents:

1. Experimental Section

1.1 Materials.

H_3CbdcPCl (**Scheme S1**, ESI†) was prepared as reported.[1] Other chemicals and solvents of reagent grade quality were obtained commercially and used as received without further purification.

1.2 Methods.

1) Single crystal X-ray diffraction analysis of Zn-MOF

Single-crystal X-ray diffraction data for **Zn-MOF** was collected at 296 K on a Bruker SMART APEX II CCD diffractometer equipped with a graphite monochromator Mo-Kα radiation (λ = 0.71073 Å) by using the Φ/ω scan technique. The structure was solved and refined by full-matrix least squares on F^2 using the SHELXL-97 software package[2] with anisotropic thermal parameters for all non-hydrogen atoms. The hydrogen atoms of the organic ligands were generated theoretically and refined with isotropic thermal parameters. The hydrogen atoms of the free water molecules were theoretically generated by using the O–H distance restrained to a target value of 0.85 Å. The entry of CCDC-1850764 contains the supplementary crystallographic data for **Zn-MOF**.

2) Theoretical calculations

Total and partial densities of states (DOS) of **Zn-MOF** were calculated based on density functional theory (DFT) using the CASTEP package.[3] Electrostatic potential surfaces of **Zn-MOF** ware obtained the Gaussian 09 package.[4] Before photo irradiation, Electrostatic potential surface of **1a** was obtained using DFT method (6-31g(d,p)). After accepting electron, Electrostatic potential surface of **1b-P** was obtained using DFT method (6-31g(d,p) for C H N O; Lanl2dz for Zn). The results were analyzed by Multiwfn.[5]

3) FT-IR spectroscopy

The FT-IR spectra were measured by a Mattson Alpha-Centauri spectrometer over the scope 4000–400 cm^{-1} with the pure KBr pellets as the references.

4) Powder X-ray diffraction (PXRD) analysis

A Rigaku D_{max} 2000 X-ray diffractometer with graphite monochromatized Cu $K\alpha$ radiation (λ = 0.15418 nm) was used to measure the PXRD data for **1** and **2** at 293 K. Simulated PXRD patterns were derived from the Mercury Version 1.4.2 software using the X-ray single crystal diffraction data.

5) Thermogravimetric (TG) analysis

TG analyses of **Zn-MOF** was performed on a Perkin-Elmer model TG-7 analyzer from room temperature to 800 °C under nitrogen at a heating rate of 10 °C min^{-1}.

6) Elemental analyses

Elemental analyses of C, H, and N were performed on an Elementar Vario EL III microanalyzer.

7) Ultraviolet–visible (UV–vis) absorption

UV–Vis absorption spectra were measured in the reflectance mode at room temperature on a Perkin-Elmer Lambda 900 UV/vis/NIR spectrophotometer with an integrating sphere attachment and $BaSO_4$ as a reference.

8) Electron spin resonance (ESR)

ESR spectra were recorded at X-band frequency (9.867 GHz) on a Bruker ELEXSYS E500 spectrometer.

9) Light source

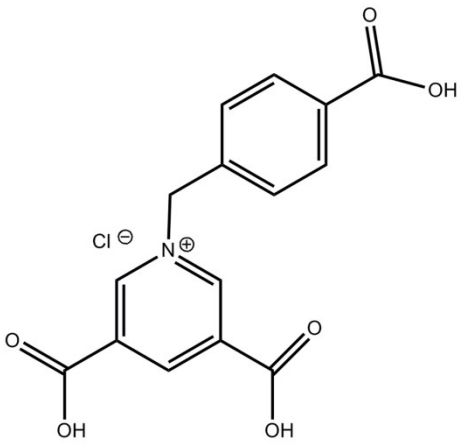
A PLSSXE300C 300 W xenon lamp (ca. 2.4 W/cm^2) system was used to illuminate samples for achieving various spectra.

1.3 Synthesis.

1.3.1 $[Zn(Cbdcp)(4,4'\text{-bipy})_{0.5}]\cdot 2H_2O$ (Zn-MOF)

Zn-MOF was obtained by a hydrothermal reaction of 4,4′-bipy (7.8 mg, 0.05 mmol), H_3cbdcpcl (16.4 mg, 0.05 mmol), $Zn(NO_3)_2\cdot 6H_2O$ (29.7 mg, 0.1mmol), 1 mol/L NaOH (0.6 mL), *N*,*N*-dimethyl formamide (DMF; 2.0 mL) and H_2O (4.0 mL) in a 25 mL Teflon-lined stainless steel autoclave at 120 ºC for 96 h. Colorless crystals were collected by filtration, washed by water, and dried at room temperature. The yield of **Zn-MOF** based on the H_3cbdcpcl was 47.81%. Elem. Anal. calcd for C_{20} H_{17} N_2 O_8 Zn (%): C 50.13, H 3.55, N 5.85. Found (%): C 50.11, H 3.54, N 5.83.

2. Graphics.



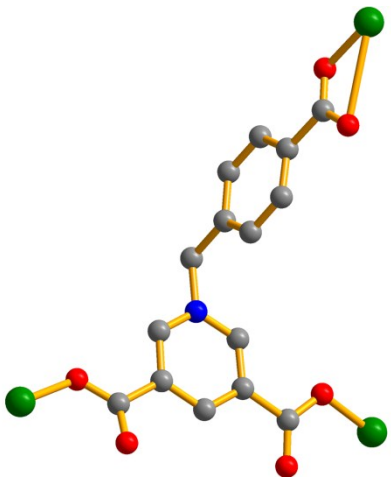


Fig. S1 Lewis structure of ligand H3CbdcpCl (left) and coordination modes exhibited by H3CbdcpCl as observed in **Zn-MOF**. Color scheme: Zn(II), Green; carbon, grey; nitrogen, blue; oxygen, red.

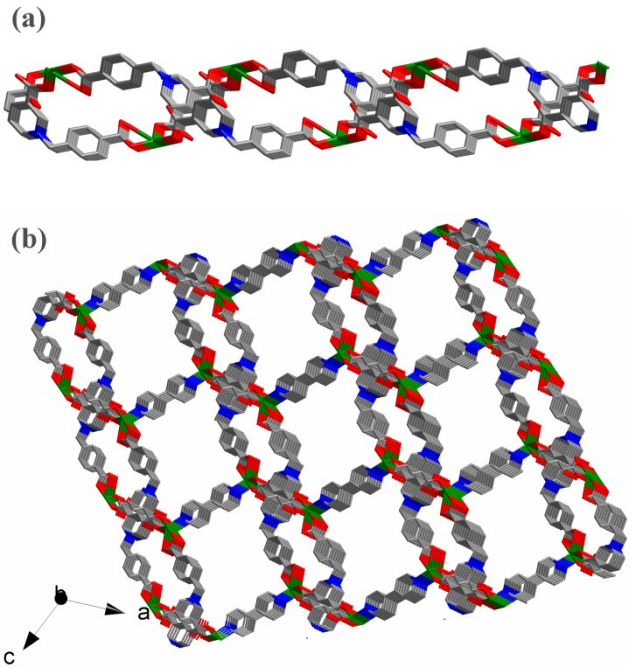


Fig. S2 (a) Neighboring Zn^{2+} ions are linked together by sharing three bridging carboxylate (COO^{-}) to form an infinite 3d framework; (b) The addition of 4,4′-bipy, **Zn–MOF** generate two different holes.

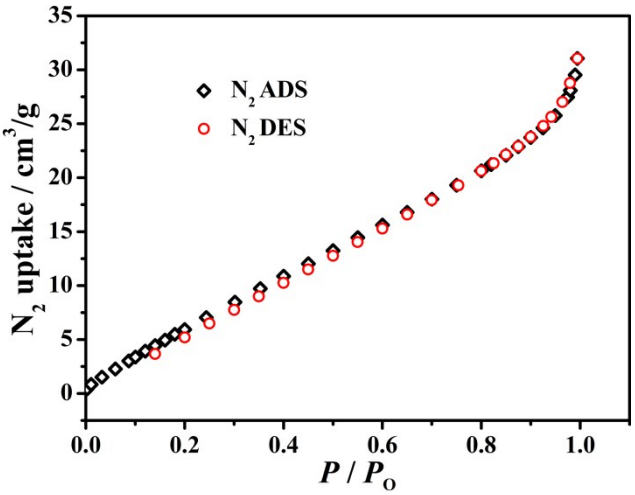


Fig. S3 N_2 adsorption isotherms of **Zn-MOF** measured at 77 K.

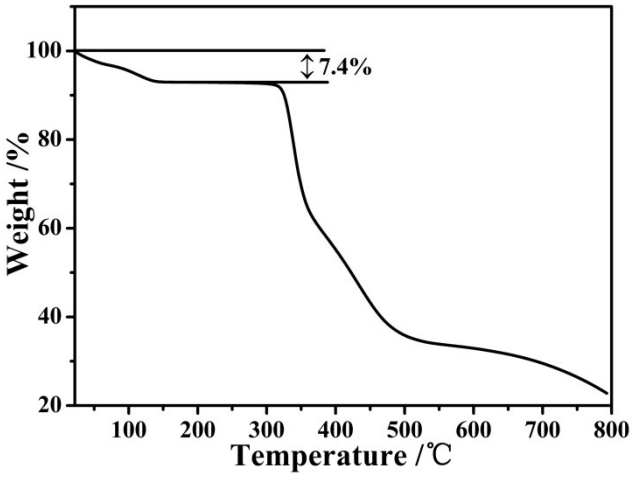


Fig. S4 TGA curve of **Zn–MOF** was investigated using powder samples under N_2. The weight loss is 7.4% (calcd 7.5%) up to 138 °C corresponding to the loss of two free H_2O.

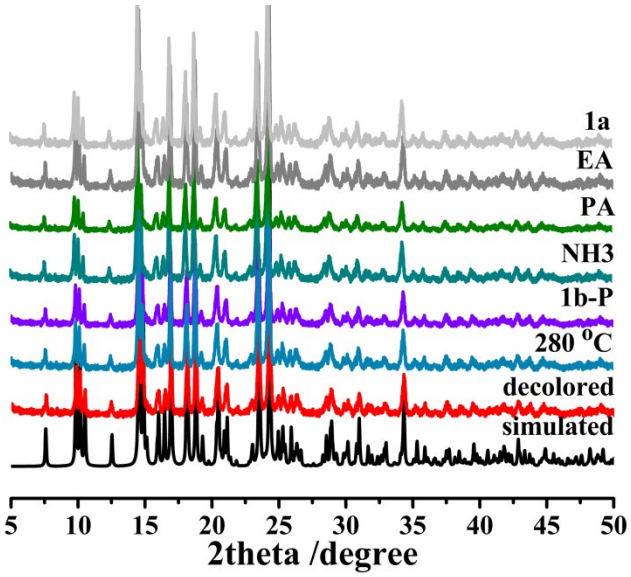


Fig. S5 PXRD patterns of **Zn–MOF**. **Labels**: **1a**, before irradiation; **1b-P**, after photo irradiation; **EA, PA**, **NH3,** 1a exposed to ethamine, n-propylamine, NH3 vapor respectively in the solid state at room temperature; **simulated**, simulated patterns from single-crystal X-ray structure data; **decolored**, after being kept in the dark for two week at room temperature in air; 280 °C, 1a Heated at 280 °C for 2 h.

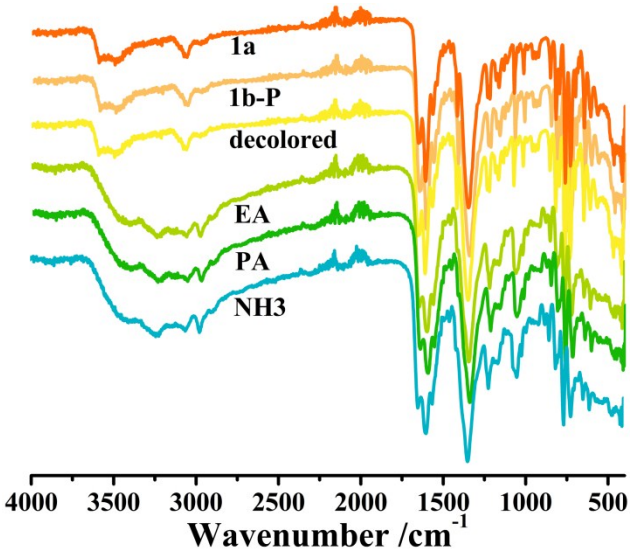


Fig. S6 FT-IR spectra of **Zn–MOF**. **Labels**: **1a**, before irradiation; **1b-P**, after photo irradiation; **EA, PA, NH3, 1a** exposed to ethamine, n-propylamine, NH3 vapor respectively in the solid state at room temperature; **decolored**, after being kept in the dark for two week at room temperature in air.

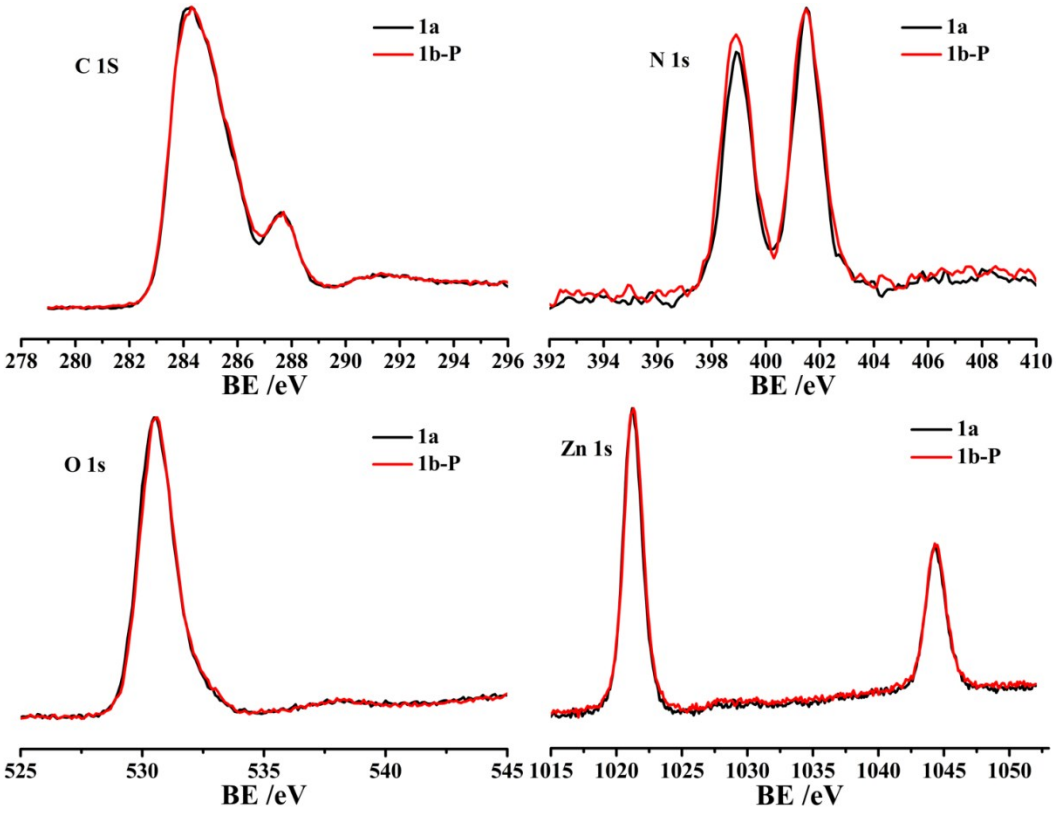


Fig. S7 XPS (Al-Kα) core-level spectra of **Zn–MOF** before and after photo irradiation. Labels: **1a**, before irradiation; **1b-P**, after photo irradiation.

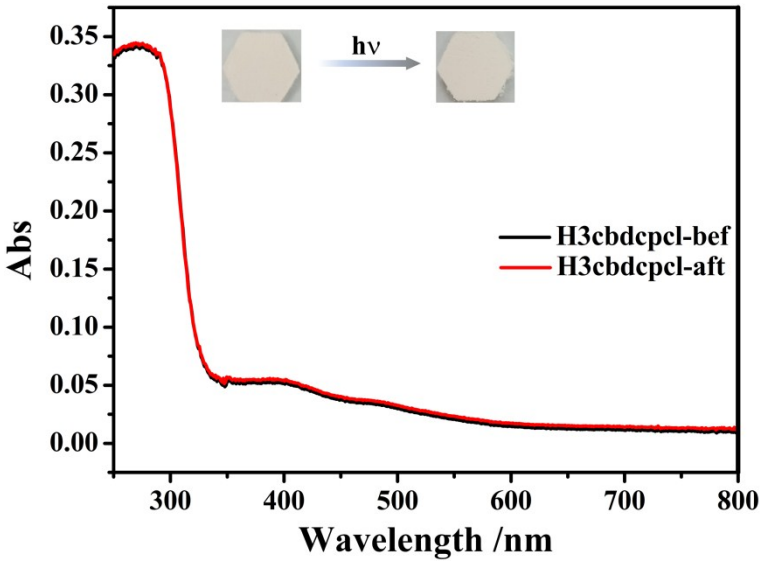


Fig. S8 UV–Vis diffuse reflectance spectra of H3cbdcpcl. The colors change was shown in the inset before and after photo-irradiation.

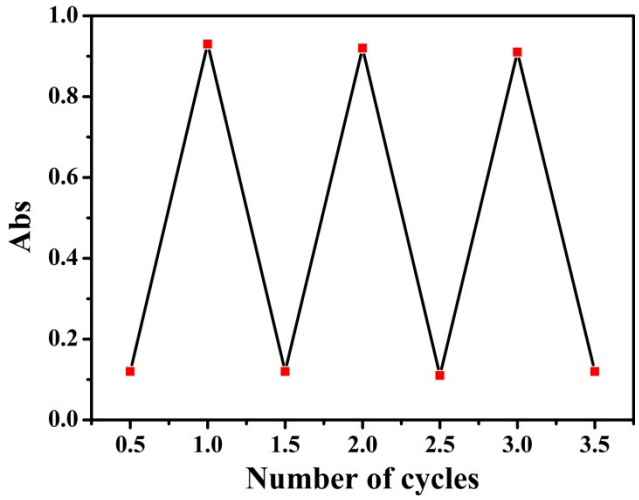


Fig. S9 Variation of the absorbance at λ = 372 nm in the repeated vapochromic response cycles to EA vapor.

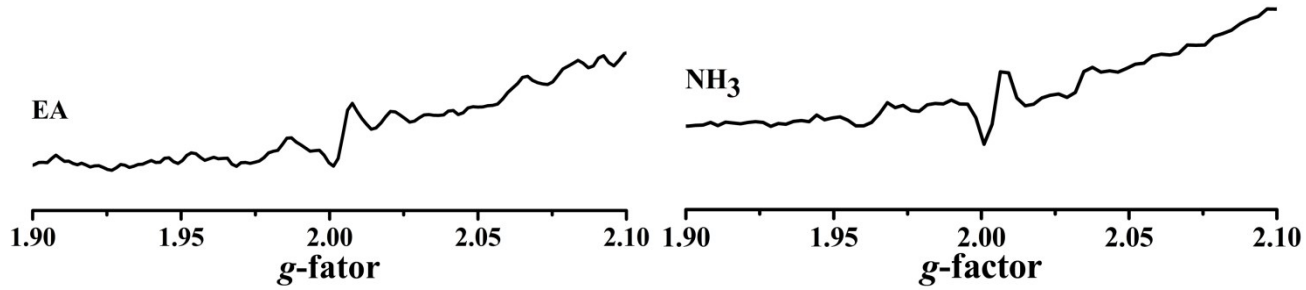


Fig. S10 ESR spectra of the EA-treated (left) and NH_3-treated sample (right).

3. Tables.

Table S1. Crystal Data and Structure Refinements for **Zn-MOF**

Empirical formula	C_{20} H_{17} N_2 O_8 Zn **(1)**
Formula weight	478.75
Temperature /K	296
Crystal system	Monoclinic
Space group	*P*2(1)/c
a /Å	12.7736(12)
b /Å	14.1120(14)
c /Å	12.1366(12)
α /deg	90
β /deg	114.364(2)
γ /deg	90
Volume /Å^3	1992.9(3)
Z	4
D_c /g·cm^{-3}	1.596
Absorption coefficient /mm^{-1}	1.285
Goodness-of-fit on F^2	1.034
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0524$, $wR_2 = 0.1190$
R indices (all data)	$R_1 = 0.0893$, $wR_2 = 0.1384$

$^aR_1 = \sum||F_o|-|F_c||/\sum|F_o|$, $^bwR_2 = \{\sum w[(F_o)^2-(F_c)^2]^2/\sum w[(F_o)_2]^2\}^{1/2}$.

Table S2. Selected bond lengths (Å) and angles (deg) for **Zn-MOF**

bond lengths (Å)		**angles (deg)**	
Zn(1)-O(6)#1	1.948(5)	O(6)#1-Zn(1)-O(1)	109.46(19)
Zn(1)-N(2)	2.040(4)	O(1)-Zn(1)-N(2)	102.92(15)
N(1)-C(15)	1.350(6)	C(14)-N(1)-C(1)	119.9(4)
N(2)-C(9)	1.332(6)	N(1)-C(1)-C(5)	112.7(4)
C(2)-C(4)	1.378(7)	C(3)-C(5)-C(1)	117.3(5)
O(5)-Zn(1)#4	1.962(3)	O(6)-C(20)-C(8)	114.6(7)
O(4)-C(20)	1.226(9)	C(19)-O(5)-Zn(1)#4	117.0(3)

References:

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