Porous Framework Based on Tetrakis(4-pyridyloxy methyl)methane Fine-tuned by Metal Ions: Synthesis, Crystal Structures and Adsorption Properties

Zhao Li, [a] Xi Chen, [a] Min Su, [a] Bi-quan Zhang, [a] Fan Yu,[b] Bao Li, [b,*] Tian-le Zhang

[a] College of Chemistry and Chemical Engineering, Huazhong University of Science and Technology, Wuhan, Hubei 430074, P. R. China; E-mail: libao@hust.edu.cn

[b] Hubei Key Laboratory of Industrial Fume & Dust Pollution Control, Jianghan University, Wuhan, 430056, P.R. China

Materials and General Methods. All reagents were purchased from commercial sources and were used without further purification. FT–IR spectra were recorded as KBr pellets with an Equinox 55 FT–IR spectrophotometer (4000–400 cm^{-1}). Thermal gravimetric analyses (TGA) were performed under N_2 atmosphere (100 ml/min) with a heating rate of 4°C/min between ambient temperature and 500°C using a Pyris1 thermogravimetric analyzer. Powder X-ray diffraction (PXRD) data were collected over the 2θ range 5~60° using a X'Pert PRO automated diffractometer at room temperature, with a step size of 0.02° in 2θ ang. Photoluminescence spectra were recorded using an F-280 fluorescence spectrophotometer.

Synthesis of $\{[Co_2(TPOM)(oba)_2(H_2O)_4]\}_n$ (1): A mixture of TPOM (22.2 mg，0.05 mmol), $Co(NO_3)_2$•$6H_2O$ (29.1 mg，0.1 mmol) and 4-(4-Carboxyphenoxy)benzoic acid (25.8 mg, 0.1 mmol) was dissolved in 4 mL DMF, and 8 mL H_2O in 18-mL Teflon reactor. The mixture was stirred at room temperature for 5 min, and then heated at 110℃ for 3 days. After the mixture was cooled to room temperature at 5℃/h, red crystals of **1** were obtained from the filtrate. Yield: 40%. IR (KBr, cm^{-1}): 3064.5 2930.2 1598.9 1573.3 1415.3 1274.9 1241.1 1161.4 1011.6 876.9 776.5 698.6 Calcd for dyhydrated $C_{53}H_{48}Co_2N_4O_{16}$: C, 57.31%, H, 3.99%, N, 5.04%; found C, 57.83%, H,

4.45%, N, 5.67%. . According to the TGA results, the possible formula should be $\{[Co_2(TPOM)(oba)_2(H_2O)_4]\cdot(H_2O)_6\}_n$.

Synthesis of $\{[Zn_2(TPOM)(oba)_2]\}_n$ (2): A mixture of TPOM (22.2 mg，0.05 mmol), $Zn(NO_3)_2$•$6H_2O$ (29.7 mg，0.1 mmol) and 4-(4-Carboxyphenoxy)benzoic acid (25.8 mg, 0.1 mmol) was dissolved in 6 mL DMF, 6 mL H_2O and 1 mL MeOH in 18-mL Teflon reactor. The mixture was stirred at room temperature for 5 min, and then heated at 110℃ for 3 days. After the mixture was cooled to room temperature at 3℃/h, colorless square-like crystals of **2** were obtained from the filtrate. IR (KBr, cm^{-1}): 3445.6 1614.2 1510.3 1372.6 1296.2 1234.9 1213.8 1162.7 1033.63 877.3 784.0 662.6. Calcd for dyhydrated $C_{53}H_{40}N_4O_{14}Zn_2$: C, 58.53%, H, 3.71%, N, 5.15%; found C, 57.96%, H, 3.45%, N, 5.67%. According to the TGA results, the possible formula should be $\{[Zn_2(TPOM)(oba)_2]\cdot(DMF)_2(H_2O)_8\}_n$.

Synthesis of $\{[Cd_2(TPOM)(oba)_2(H_2O)_4]\}_n$ (3): A mixture of TPOM (22.2 mg，0.05 mmol), $Cd(NO_3)_2$•$4H_2O$ (30.8 mg，0.1 mmol) and 4-(4-Carboxyphenoxy)benzoic acid (25.8 mg, 0.1 mmol) was dissolved in 9 mL DMF, and 3 mL H_2O in 25-mL glass vial. The mixture was stirred at room temperature for 5 min, and then heated at 80℃ for 3 days. And colorless crystals of 3 were obtained from the filtrate. IR (KBr, cm^{-1}): 3073.0 2952.5 1292.0 1603.2 1506.9 1396.4 1291.4 1162.6 1030.8 875.9 780.2 661.2. Anal. Calcd for dyhydrated $C_{53}H_{48}Cd_2N_4O_{16}$: C, 52.27%, H, 3.64%, N, 4.60%; found C, 52.55%, H, 3.86%, N, 5.11%. According to the TGA results, the possible formula should be $\{[Cd_2(TPOM)(oba)_2(H_2O)_4]\cdot(H_2O)_8\}_n$

X-Ray Structural Determination. Suitable single crystals were selected and mounted onto the end of a thin glass fiber. X-ray intensity data were measured on Bruker APEX-II CCD or Oxford Gemini S Ultra for **1**-3. The structure was solved by direct methods and refined by full-matrix least squares using the *SHELXTL* crystallographic software package.[1-2] Anisotropic displacement parameters were applied to all non-hydrogen atoms. The hydrogen atoms were included and were generated geometrically. Structure refinement after modification of the data for the non-coordinate lattice solvent molecules with the SQUEEZE routine of PLATON[3] led to better refinement and data convergence for 1-3. CCDC 1404387 (1), CCDC 1404388 (2) and CCDC 1404388 (3) contain the supplementary crystallographic data for this paper. The data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html.

1 SMART and SAINT, Area Detector Software Package and SAX Area Detector Integration

Program; Bruker Analytical X-Ray; Madison, WI, USA, 1997.

2 G. M. Sheldrick, SHELXTL-PLUS, Crystal Structure Analysis Package; Bruker Analytical X-Ray; Madison, WI, USA, 1997.

3 PLATON program: A. L. Spek, Acta Crystallogr. Sect. A, 1990, **46**, 194.

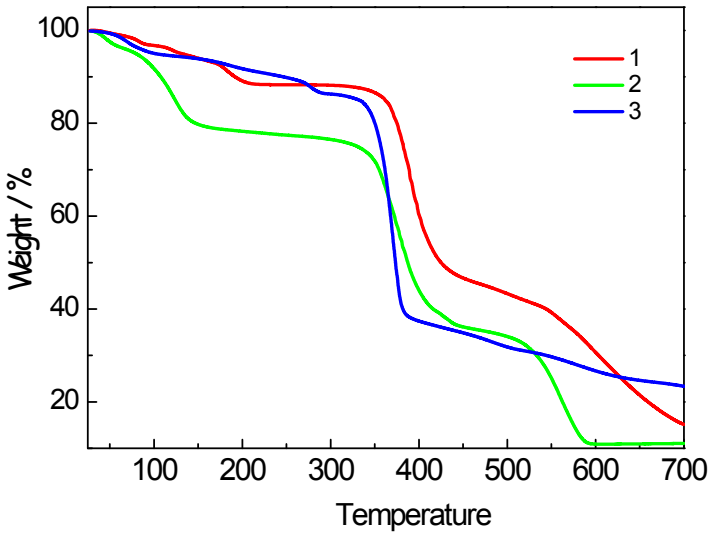


Figure S1 TGA curves of 1-3

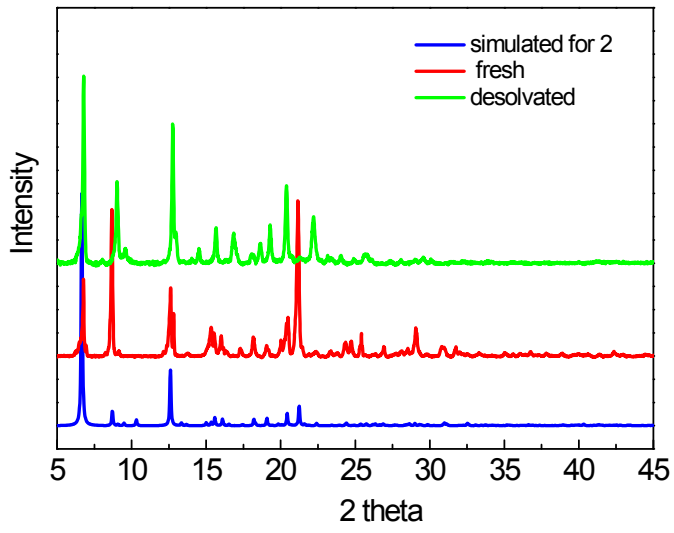


Figure S2 XRD spectra of 2

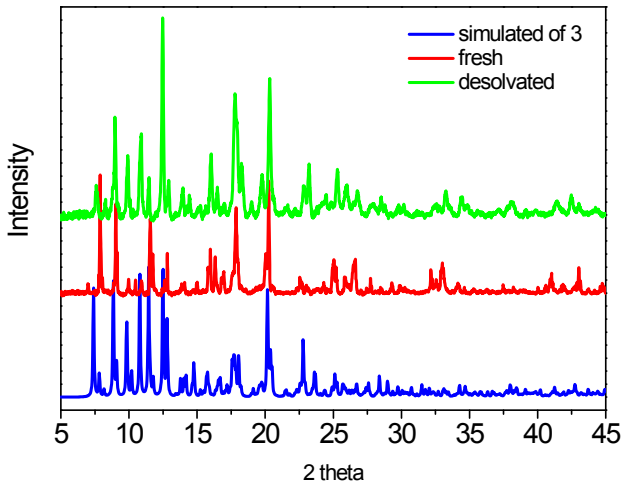


Figure S3 XRD spectra of 3

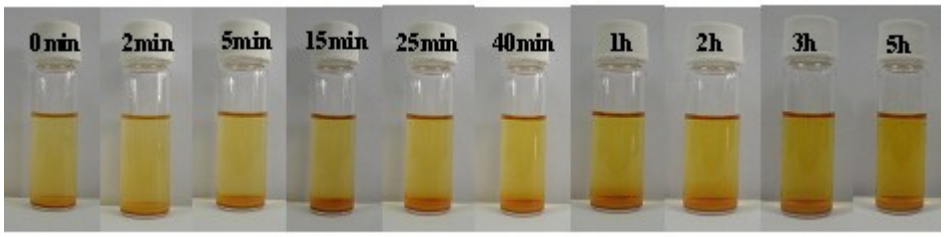


Figure S4. Photographs of the color changes of 2@ I_2 in methanol solution.

Soaked experimets: The fresh sample of 2 were activated by heating, and immersed in different solvents or cyclohexane containg iodine or CH_2Cl_2 containg different dyes. After two days, the solid samples were filtered and washed by the pure solvents, then carried out the corresponding measurments.

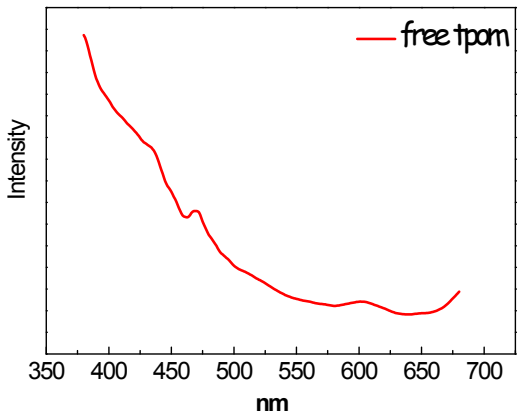
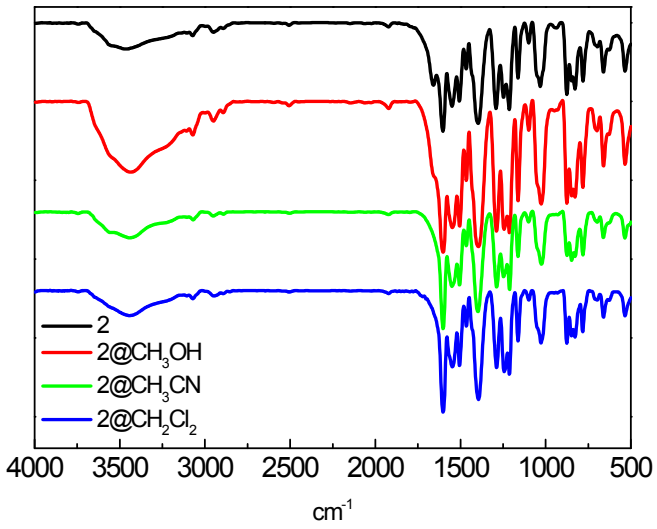
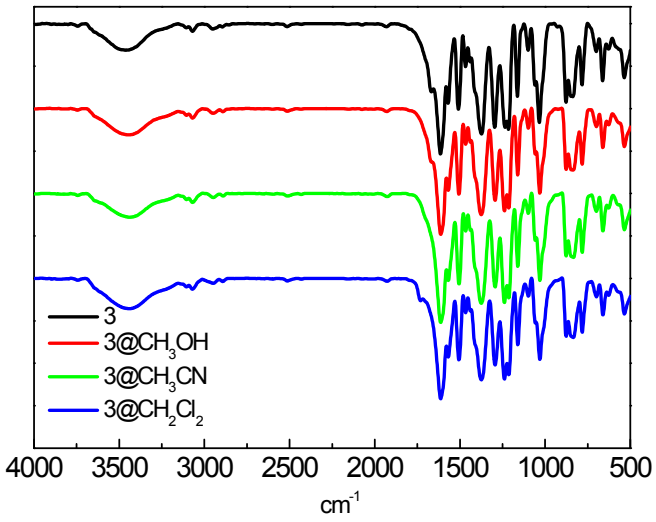


Figure S5. The luminescent property of free ligand TPOM



Figures S6 IR spectra of 2 and 2 contained different solvents.



Figures S7 IR spectra of 3 and 3 contained different solvents.