Electronic Supplementary Information (ESI)

Selective chemochromic and chemically-induced photochromic

response of a metal-organic framework

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Materials and Synthesis. All of the starting materials and solvents employed were commercially purchased and used without further purification.



Scheme S1. Synthesis of the [H₆L]Cl₃ ligand

Synthesis of [H₆L]Cl₃. The ligand was prepared according to Scheme S1. 2.0 mmol 2,4,6-tris(4-pyridyl)pyridine (0.62 g) and 7.0 mmol dimethyl 3-(bromomethyl)isopthalate (2.0 g) in 300 mL acetonitrile were refluxed for 48 h. After cooling, the yellow solid formed was collected by filtration, washed with CH₃CN, and then dried to give the ester precursor [Me₆L]Br₃. The ester was refluxed in concentrated HCl solution (50 mL) for 36 h. The pale yellow powder was filtrated, washed with water, and dried under vacuum. Yield: 54% base on 2,4,6-tris(4-pyridyl)pyridine. Main IR (KBr, cm⁻¹): 1702 (m), 1641 (s), 1612 (m), 1571 (s), 1520 (m), 1446 (w), 1410 (m), 1365 (w), 1210 (m), 1161(w), 1135 (w), 1052 (w), 762 (s), 720 (w), 686 (m), 640 (w), 577 (w), 520 (w). The final acid product is hardly soluble in common solvents. ¹H NMR is recorded with the ester precursor (400 MHz, DMSO-d₆, δ /ppm): 9.67 (d, 2H, J = 6.4 Hz, pyridinium), 9.57 (d, 4H, J = 6.5 Hz, pyridinium), 9.26 (s, 2H, pyridyl), 9.25 (d, 4H, J = 6.5 Hz, pyridinium), 9.26 (s, 2H, pyridyl), 9.25 (d, 4H, J = 6.5 Hz, pyridinium), 9.26 (s, 3H, benzene), 8.56 (s, 4H, benzene), 8.52(s, 3H, benzene), 6.12 (s, 6H, CH₂).

Synthesis of $Zn_3(L)_2 \cdot 18H_2O$ (1). A mixture of $Zn(NO_3)_2 \cdot 6H_2O$ (60 mg, 0.03 mmol) and $[H_6L]Cl_3$ (11 mg, 0.01 mmol) in H_2O (8 mL) and CH_3CN (4 mL) were sonicated for 10 min. Then, the reaction mixture was transferred to a 15 mL Pyrex glass tube, which was heated at 120 °C for 2 days. The yellow crystals were generated. The crystals were filtered off, washed with H_2O , and dried in air (43% yield based on ligand). Elemental analysis (%) calcd. for $C_{94}H_{94}N_8O_{42}Zn_3$: C 50.89, H 4.15, N 5.09; found: C 51.20, H 4.27, N 5.08. Main infrared spectral data (KBr, cm⁻¹): 3405br, 1639s, 1575s, 1513w, 1446w, 1398w, 1351s, 1236s, 1159m, 1135w, 1049w, 914w, 863w, 844m, 773s, 725s, 667w, 640m.

Physical Measurements. Powder X-ray diffraction (PXRD) was recorded on a Rigaku Smart D/Max-2500 diffractometer at 40 kV, 30 mA for a Cu-target tube and a graphite monochromator in a 20 range of 5-40° at room temperature. UV–vis spectra were obtained on a SHIMADZU UV-2700 spectrometer. BaSO₄ plates were used as references (100% reflection), on which the finely ground power of a sample was coated. FT-IR spectra were recorded in the range 500–4000 cm⁻¹ using KBr pellets on a Nicolet NEXUS 670 spectrophotometer. Electron spin resonance (ESR) spectra were recorded on a Bruker Elexsys 580 spectrometer with a 100 kHz magnetic field in the X band at 100 K. Thermogravimetric analysis was performed on a STA 449 F3 Simultaneous Thermal Analyzer in flowing air at 10°C/min. Cyclic voltammetry (CV) was conducted with a CHI 660E workstation (CH instruments, China) with a conventional three-electrode system, with a MOF-modified glassy carbon electrode (GCE) as the working electrode, a platinum wire as the counter electrode, and an Ag/AgCl electrode as the reference electrode. The supporting electrolyte was 0.1 M KCl aqueous solution, and the scan rate was set at 150 mV s⁻¹.

Electrode preparation for cyclic voltammetry. A ground sample of the MOF (2 mg) was dispersed in 100 μ L ethanol and Nafion mixed solution by sonication for 30 min. A precleaned GCE was drop-cast with a 2.5 μ L portion of the dispersion and then dried at 40°C.

Theoretical study. DFT calculations were performed using the DMol³ module in the Materials Studio software package.¹⁻³ The PWC local functional, the DNP 4.4 basis set and the fine quality were adopted in the calculations. All electrons were included with relativistic effects in the core. The orbital calculations for the MOFs were performed with the single-crystal structure. For the disordered atom in the ligand, only one set of coordinates was used.

Crystal structure determination. Data collection for **1** was performed at 299 K using a Bruker Apex (Cu-K α radiation, $\lambda = 1.54184$ Å) equipped with a graphite monochromator and a CCD area detector. Structure solution was carried out using the direct method, and full-matrix least-squares refinements were performed on F^2 with the SHELX-2014 program.⁴ Non-hydrogen atoms were all refined anisotropically. The H atoms attached to carbons were added geometrically and refined isotropically with the riding model. The free solvent molecules in the structure were highly disordered, and no satisfactory disorder model could be achieved. Thus, the PLATON/SQUEEZE routine⁵ was used to remove their diffraction contributions. Selected crystal data and structure refinement parameters are given in Table S1.

No v(C=N) absorption was observed in the IR spectrum of 1, so there are no acetonitrile molecules

in the structure and that the solvent should be water. The water content was determined according to the mutually corroborative results of elemental and thermogravimetric analysis (Fig. S5). The result (18 water molecules per formula, corresponding to 360 electrons per cell) is in fair agreement with the electron count of the SQUEEZE analysis, which indicates 340 electrons per cell in the solvent accessible voids. The difference is not unexpected because the solvent molecules are highly disordered.

	1
Empirical formula	$C_{94}H_{58}N_8O_{24}Zn_3$
Formula weight	1879.59
Crystal system	monoclinic
Space group	$P2_1$
<i>a</i> , Å	12.652(4)
b, Å	18.915(4)
<i>c</i> , Å	21.672(5)
a, deg	90
β , deg	105.25(2)
γ, deg	90
V, Å ³	5004(2)
ρ calcd, g cm $^{-3}$	1.25
μ , mm ⁻¹	1.44
θ range collected	3.150 to 68.453
S on F^2	0.993
$R_1 \left[I > 2\sigma(I) \right]$	0.0609
wR ₂ (all data)	0.1847

 Table S1. Crystal data and structure refinement for 1.



Fig. S1 Coordination environments of **1**. Symmetry code: A = -1+x, y, z; B = -1+x, 1+y, z; C = -1+x, 1+y, -1+z; D = -1+x, y, -1+z; E = 1+x, y, z; F = x, -1+y, z. H atoms are omitted for clarity.



Fig. S2 Topological analysis of the 2-fold interpenetrating frameworks of **1**. The point symbol for the 3,4-connected net is $\{6.8.10\}_4\{6^2.8^4\}_{6^2.8}_{$



Fig. S3 A view of the π - π stacking interactions between the interpenetrating frameworks in 1. The distances are given in Å.



Fig. S4 Cross section profiles of Connolly surfaces (radius 1 Å) down the a axis at the a = 0.5 (a), 0.9 (b), and the c axis at c = 0.5 level (c).



Fig. S5 Thermogravimetric curve of **1**. The weight loss before $160 \degree C$ (15.0 wt%) corresponds to the release of all water molecules (14.7 wt%) in $Zn_3(L)_2 \cdot 18H_2O$, and the constant weight above 500°C (11.0 wt%) is in good agreement with the value expected for the ZnO residue (11.1%).



Fig. S6 Pictures showing the color change of 1 when exposed to amine vapors. The estimated size of the amine molecules are also provided (in Å). MA = methylamine. EA = ethylamine. PA = *n*-propylamine. BA = *n*-butylamine. AA = amylamine. *i*-PA = isopropylamine. *t*-BA = *t*-butylamine. EA = ethylamine. DMA = dimethylamine. DEA = diethylamine. DPA = dipropylamine. TEA = triethylamine. AN = aniline.



Fig. S7 Top: two representative structural formulas of the radical (R represents the peripheral N-substituent). Bottom: the major single occupied molecular orbitals (SOMOs) calculated for the radical with R = methyl. The orbitals show that the unpaired electron is actually delocalized across the conjugating rings.



Fig. S8 Pictures showing the color change of **1** on exposure to alcohols under a UV light (365 nm). The estimated size of the alcohol molecules are also provided (in Å). n-PrOH = n-propanol. n-BuOH = n-butanol. n-PeOH = n-pentanol. i-PrOH = isopropanol. t-BuOH = t-butanol.



Fig. S9 UV-vis spectra (a) and pictures (b) showing the chemophotochromic response to aqueous ethanol. The ethanol concentration is given in volume percentage. Before each measurement, the MOF was soaked in aqueous ethanol for 2 h and then illuminated under a UV lamp (365 nm) for 5 min.



Fig. S10 (a) Solid-state UV-vis spectra of an ethanol-treated sample of **1** at different irradiation time under a UV lamp (365 nm). (b) Kinetic trace based on UV-vis absorption at 612 nm. A_t is the absorbance at time t, and A_0 and A are the initial and photostationary absorbance, respectively. The first-order rate constant is $k = 0.0081 \text{ s}^{-1}$, which corresponds to the slope obtained by linear regression ($R^2 = 0.991$).



Fig. S11 PXRD patterns of the original sample of **1**, those colored with propylamine (PA) or EtOH plus UV illumination, and those decolored by gentle heating. The simulated pattern is also included for comparison.



Fig. S12 IR profiles of the original sample of **1**, the sample successively treated with EtOH and UV, and the sample treated with propylamine (PA).



Fig. S13 Cyclic voltammograms of [H₆L]Cl₃ and 1 (0.1 M KCl solution, scan rate 150 mV·s⁻¹).



Fig. S14 Perspective view of a part of the void showing the exposure of the pyridinium N atoms (blue).

References

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