Supporting information

Construction of unprecedented pillared-layer metal organic frameworks *via* a dual-ligand strategy for dye degradation

Yu-Huan Tang,^{ab} Fei Wang*^a and Jian Zhang*^a

^aState Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, the Chinese Academy of Sciences, Fuzhou, Fujian 350002, P. R. China. E-mail:

wangfei04@fjirsm.ac.cn, zhj@fjirsm.ac.cn

^bUniversity of Chinese Academy of Sciences, 100049 Beijing, P. R. China

Experimental

Materials and measurements

All chemicals were obtained from commercial sources and used without further purification. Elemental analyses of C, H and N were measured on a Vario MICRO E III elemental analyzer. Powder X-ray diffraction (PXRD) analysis was performed on a MiniFlex2 X-ray diffractometer using Cu-K α radiation ($\lambda = 1.542$ Å) in the 2 θ range of 5–50° with a scanning rate of 5° min⁻¹. The thermogravimetric analyses (TGA) were carried out on a NETSCHZ STA-449C thermoanalyzer under N₂ (30-800°C range) at a heating rate of 10°C min⁻¹.

Single-Crystal Structure Determination

Crystallographic data of compound **1** and **2** were collected on a Rigaku Mercury70 CCD diffractometer equipped with graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å) at 298 K. Raw frame data (including data reduction, inter-frame scaling, unit cell refinement) for all structures were processed using CrysAlis Pro.¹ Structure was solved by direct method and refined by full-matrix methods against F2 using the SHELXTL-2014.² Non-hydrogen atoms were refined anisotropically, and all hydrogen atoms bond C were generated geometrically. The SQUEEZE option of PLATON was used in the case of compound **1** and **2** to eliminate the contribution of disordered guest molecules or counter ions.³ CCDC 1587007-1587008 contains the supplementary crystallographic data for this paper. This data are provided free of charge by The Cambridge Crystallographic Data Centre.

Preparation of compound 1-2

 $Zn_4(OH-bim)_2(D-Cam)_3$ (guest) (1): the mixture of OH-bim (0.1mmol, 0.0216g), D-H₂Cam (0.1mmol, 0.0166g), ammonium bromide (0.2mmol, 0.0194g), pyrazine (0.1mmol, 0.0080g), $Zn(NO_3)_2$ · 6H₂O (0.1mmol, 0.0297g), N,N-Dimethyl formamide (DMF, 4ml), water (2 ml) was

sealed in a 20 ml vial and heated to 120 °C for 6 days. After cooling to room-temperature, the colourless crystals were obtained in pure phase (Yield: 65%). Anal. Calcd for activated sample $C_{48}H_{58}N_4O_{14}Zn_4$ (1176.46): C, 48.99; H,4.97; N, 4.76. Found: C, 46.22; H, 4.04; N, 5.75.

Zn_{1.5}**Co**_{1.5}**(OH-bim) (D-Cam)**₂**(ethanol)**₂**·(guest) (2)**: the mixture of OH-bim (0.1mmol, 0.0216g), D-H₂Cam (0.1mmol, 0.0166g), ammonium bromide (0.2mmol, 0.0194g), pyrazine (0.1mmol, 0.0080g), Zn(NO₃)₂·6H₂O (0.05mmol, 0.0148g), Co(NO₃)₂·6H₂O (0.05mmol, 0.0145g) N,N-Dimethyl formamide (DMF, 4ml), ethanol(2ml), water (2 ml) was sealed in a 20 ml vial and heated to 120 °C for 6 days. After cooling to room-temperature, the colourless crystals were obtained in pure phase (Yield: 64%). **2** (Zn₁Co₂) was obtained by the similar method as described for **2** except for changing the molar ratio of Zn²⁺/Co²⁺, which Zn(NO₃)₂·6H₂O (0.01mmol, 0.0029g), Co(NO₃)₂·6H₂O (0.09mmol, 0.0261g), (Yield: 56%).

Zn(NO ₃) ₂ ·6H ₂ O (mmol)	Co(NO ₃) ₂ ·6H ₂ O (mmol)	Raw molar ratio of Zn/Co	Results	ICP of crystals (Zn/Co, %)
0.093	0.006	14/1	No crystal	—
0.087	0.013	13/2	Light purple crystals	11.39/2.53
0.05	0.05	1/1	Purple crystals	9.12/10.01
0.01	0.09	1/9	Dark purple crystals	6.00/11.67

Table S1 The molar ratio of Zn/Co in compoud 2

Photocatalytic Activity for Degradation of CV.

The photocatalytic activity of compound 2 ($Zn_{1.5}Co_{1.5}$) and 2 (Zn_1Co_2) was evaluated by the degradation of CV. The distance between the daylight lamp and the reaction solution was 15 cm. At room temperature, 20mg crystal was added into 10 mL of $1 \times 10^{-5}M$ 50 mg/L CV aqueous solution. Afterwards, the suspensions were exposed to the 500W daylight lamp. To monitor the extent of reaction, After each 10 min intervals, 1 mL of CV solution was removed from the system for analysis until the solution become colourless. Generally, 1 ml reaction solution was transferred and was diluted into 2 ml. Then the diluted reaction solutions were filtered and their absorbances were measured by a UV-Vis spectrophotometer (Lambda35). Furthermore, a blank experiment without the photocatalyst under was also performed, and the corresponding CV solution was deal with via the above-mentioned method.



Figure S1 The powder XRD patterns of (a) simulated 1; (b) as-synthesized 1; (c) 1 soaked in DMF; (d) 1 soaked in ethanol; (e) 1 soaked in water; (f) 1 soaked in methanol.

The chemical stability of **1** was examined by immersing the samples in common solvents, such as methanol, DMF, and so on. As-synthesized samples were immersed in each solvent for 7 days. During this process, samples were periodically observed under an optical microscope and found to be insoluble under each of these conditions. PXRD patterns showed that **1** maintained their full crystallinity and frameworks in such organic solvents for 7 days.



Figure S2 The powder XRD patterns of (a) simulated **2**; (b) as-synthesized **2** ($Zn_{1.5}Co_{1.5}$); (c) assynthesized **2** ($Zn_{4.5}Co_1$); (d) as-synthesized **2** (Zn_1Co_2); (e) **2** (Zn_1Co_2) after three times of photocatalysis and (f) **2** ($Zn_{1.5}Co_{1.5}$) after three times of photocatalysis.

PXRD patterns showed that 2 maintained their full crystallinity and framework after

photocatalysis.



Figure S3 The TG plots of compounds 1 and 2.

The TGA plots of the as-synthesized compounds **1** and **2** samples are shown in Figure s4. In particular, the initial gradual weight-loss step of 15% till 245 °C indicating the loss of guest molecule, then a plateau to ca. 450 °C and a sharp weight loss from that point onwards represents the decomposition of the material. For compound **2**, the frameworks begin to collapse under ca. 433 °C.



Figure S4 The UV-Vis absorption spectrum of spectrum of compounds 2 $(Zn_{1.5}Co_{1.5})$ and 2 (Zn_1Co_2) .



Figure S5 The crystal pictures of (a) compounds 1; (b) compounds 2 $(Zn_{1.5}Co_{1.5})$ and (c) compounds 2 (Zn_1Co_2) .

0min 10min 20min 30min 40min



Figure S6 The CV solution faded under Visible Light with the catalysis of compound **2** (Zn₁Co₂) (up), compound **2** (Zn_{1.5}Co_{1.5}) (middle) and CV solution without catalyst (down);



Figure S7 The temporal UV-Vis absorption spectrum changes of CV aqueous solutions with the photo-degradation catalyzed by (a) 2 (Zn₁Co₂) and (b) 2 (Zn_{1.5}Co_{1.5}).



Figure S8 The three times of photodegradation rates of (a) $2 (Zn_1Co_2)$ and (b) $2 (Zn_{1.5}Co_{1.5})$.



Figure S9 (a) The solid-state CD plot of **2** (Zn_1Co_2) and (b) the SHG plot of **2** ($Zn_{1.5}Co_{1.5}$). To verify its space group, nonlinear optical (NLO) property of the compound 2 ($Zn_{1.5}Co_{1.5}$) has been investigated (Fig. S9). The powder second-harmonic generation test was carried out on the sample by the Kurtz and Perry method. The result shows that compound **2** has weak SHG intensity of ca. 0.2 versus that of technologically useful potassium dihydrogen phosphate (KDP), which confirms its acentric symmetry.⁴ The solid-state CD plot of **2** (Zn_1Co_2) exhibits positive CD signals which verify the crystal is homochiral.



Figure S10 The FT-IR plot of 1 and 2 (Zn₁Co₂)

References

- 1 CrysAlisPro, Agilent Technologies.
- 2 G. M. Sheldrick, *SHELXL-2014*/7, University of Göttingen, Germany, 2014.
- 3 G. Sheldric, Acta Crystallogr., Sect. A: Found. Adv., 2015, 71, 3.
- 4 S. K. Kurtz, T. T.Perry, J. Appl. Phys., 1968, **39**, 3798.