



Synthesis of an Exceptional Water Stable Two-fold Interpenetrated Zn(II)-Paddlewheel Metal-Organic Framework via Facile Conversion of Its Non-interpenetrated Isomer

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Synthesis of an Exceptional Water Stable Two-fold Interpenetrated Zn(II)-Paddlewheel Metal-Organic Framework via Facile Conversion of Its Non-interpenetrated Isomer†

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Based on the ligand tetrakis (4-carboxyphenyl) silane (TCS) and 4,4'-bipy, a novel 3D doubly interpenetrated Zn(II)-paddlewheel metal-organic framework Zn₂TCS(4,4'-bipy) (1) was synthesized via facile conversion of its non-interpenetrated isomer (2) upon solvent removal at ambient temperature. It exhibits high CO₂ and CH₄ adsorption capacity and exceptional water stability.

Metal-organic frameworks (MOFs) are a new class of porous materials that have received widespread attention owing to their potential applications in gas storage, separation, catalysis, chemical sensor, semiconductor, fuel cells, supercapacitors and more.¹ However, one drawback of MOFs is that most of them are unstable towards water and humid conditions. Generally, MOFs containing tri- or tetravalent metal cations, such as Cr³⁺, Al³⁺, Fe³⁺, Ti⁴⁺ or Zr⁴⁺ and ZIFs (Zeolitic imidazolate frameworks) display a high degree of stability toward water.²⁻⁵ We recently calculated the pKa and NBO (Natural Bond Orbital) charges of many ligands applied in MOF syntheses and indicated that these data can be used to predict water stabilities of MOFs.⁴ Ligands with higher NBO charges tend to form MOFs having better hydrothermal stability.

Binuclear metal clusters in which two metal ions are bridged by four carboxylic groups in syn-syn mode are called “paddlewheel” (PW) structures. Rieger et al. has reviewed the syntheses, structure and adsorption properties of MOFs based on Zn(II) paddlewheel structures.⁶ Except for ZIF materials, Zn-paddlewheel MOFs are much more stable than any other type of Zn-MOFs (e.g. MOFs based on Zn₄O units) in terms of stability towards humid air.⁷ The studies of Zn-paddlewheel MOFs mainly focused on their structures,

thermal stabilities, fluorescence, and gas absorption. However, their stabilities towards water were rarely studied. Two of them were reported to be stable in air for several minutes,⁸ two trimesic acid shared Zn-paddlewheel structures was found to be stable in air for 24 h,⁹ DUT-30 was found to be stable in air for two weeks, but unstable in water.¹⁰ Generally, Zn-paddlewheel MOFs are usually considered unstable in water.

Herein we reported the synthesis, characterization and properties of a water-stable two-fold interpenetrated Zn(II)-paddlewheel metal organic framework Zn₂TCS(4,4'-bipy) (1) which can be stable in water and air for 30 days, and in boiling water for 24 h. Based on theoretical calculations, we have predicted that some Zn-paddlewheel MOFs should also be water stable. The results we showed here do indicate that Zn-paddlewheel MOFs, like Al(III) MOFs and Zr(IV) MOFs can be water stable materials. 1 was also found to have high CO₂ and CH₄ storage capacities. 1 is also a material having fluorescence and semiconducting properties. Since d¹⁰ Zn(II) MOFs can be fluorescence and semiconducting materials, this discovery makes it possible to synthesize water-stable fluorescence and semiconducting MOF materials based on Zn-paddlewheel SBUs. In addition, we discovered the facile conversion between the non-interpenetrated 2 and the interpenetrated 1 even at ambient temperature due to solvent removal. Thus conversion is still rarely reported, but might be a common phenomenon.

A mixture of TCS, 4,4'-bipy and Zn(NO₃)₂·6H₂O in NMP (NMP = N-methyl-2-pyrrolidone) and DMA (DMA = dimethylacetamide) was heated at 80 °C in a 20 mL Teflon-liner reaction kettle for 2 days. The mixture was allowed to cool down to room temperature and resulted in colorless cuboid-shaped crystals of 2.[†] The wet product of 2 directly from the reaction vessel gives a PXRD spectrum, which is consistent with the simulated PXRD pattern of 2 based on its crystal structure. When 2 was dried in a 40 °C oven for 12 h, it converted to 1. After 2 was put into boiling water for 24 h, it turned to 1 (Fig. 2h). The conversion can even happen when the as-synthesized 2 was washed with CH₂Cl₂ three times and put in the air at room temperature for 3 d (Fig. S2c). Such facile conversion between non-interpenetrated and interpenetrated isomers at ambient temperature is rarely reported.¹¹⁻¹² Examples of changes of the degree of interpenetration due to solvent removal at temperature greater than 100 °C were only a couple.¹³⁻¹⁴ 1 cannot convert back to 2 by solvent exchange in NMP/DMA solvent at room temperature (Fig. S3i). If 2 was heated at 40 °C for 6-7 h, the

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† Electronic supplementary information (ESI) available: Experimental details, syntheses of 1-3, the crystal data for 2 and 3·H₂O, selected bond distances and angles for 2, PXRD patterns of 1-2, IR spectra of 1, fluorescence and diffuse reflectance UV-Vis spectra of 1 and the ligand TCS, the CO₂ sorption isotherms for 1 measured at 298 K.

intermediate phase from **2** to **1** was observed (Fig. 2c). We think the difference of the PXRD pattern between the intermediate and the simulated spectrum is due to the much less DMA and NMP solvents in the channels, which caused the intensity difference. However, interpenetration had not occur since the big molecules in the channel, although not many, prevent the interpenetration to occur.

1 has the 2-fold interpenetrated structure since the PXRD of **1** is very similar to that of the 2-fold interpenetrated $\text{Cu}_2\text{TCS}(4,4'\text{-bipy})\text{H}_2\text{O}$ (**3**) (Fig. 2). **3**, which was synthesized from a mixture of TCS, 4,4'-bipy and $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in water at 170 °C (SI) and its crystal structures were determined.[†] We also synthesized **1** in a mixture of TCS (6.40 mg, 0.0125 mmol), 4,4'-bipy (3.90 mg, 0.0250 mmol) and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (12.8 mg, 0.0400 mmol) in 4 mL H_2O at 170 °C for 3 d (SI). Its PXRD pattern (Fig. 2k) is again very similar to that of **3** and **1** converted from **2** as shown in Fig. 2.

Single-crystal X-ray diffraction analysis reveals that **2** crystallizes in the $P4_2/mmc$ space group. The asymmetric unit contains one crystallographically independent Zn(II) ion, a quarter TCS ligand, and a half 4,4'-bipy molecule (Fig. S1 in ESI[†]). As shown in Fig. 1, the Zn ion is 6-coordinated by four oxygen atoms from the ligand and two nitrogen atoms from the 4,4'-bipy molecules; the ligand, on the other hand, is fully deprotonated, coordinating to eight zinc centers, giving rise to a Zn-paddlewheel structure. It is a 3D binodal (4,6)-connected *sqc422* net with a point symbol of $(4^2 \cdot 5^{10} \cdot 7^2 \cdot 8)(4^2 \cdot 5^4)$. The structure includes two types of channels: the rhombic channels are about 9.5×8.1 (7.8×7.8) Å,²⁶ the pentagonal channels are about 8.1×9.8 (7.1×8.1) Å. **1** possesses a highly open framework and has a porosity of 61% (probing radius: 1.2 Å) as calculated by the PLATON program.¹⁵ The porosity is 59% if the probing radius is chosen to be that of van der Waals radii of N (1.55 Å).²⁷ The Materials Studio (MS) software¹⁶ predicts that the surface area of **1** to be $3358 \text{ m}^2 \text{ g}^{-1}$ using a spherical probe with a radius of 1.55 Å which is the van der Waals radius of N. To gain some insight of the structure of **1**, we present its isostructural MOF, the interpenetrated **3**[‡] in Figure 1c, clearly showing the 2-fold interpenetration pattern, while **2** is non interpenetrated structure as shown in Fig. 1b. Rhombic and triangle channels of **3** can be seen along b axis. Water molecules (kinetic diameter: 2.65 Å) were found in the rhombic channels (Fig. 1c). The size of rhombic channels is about 4.0×3.7 (2.3×1.9) Å, and the size of triangle pore is 4.5×2.0 (4.3×1.1) Å.²⁶ **3** has a porosity of 21% (probing radius: 1.2 Å) as calculated by the PLATON program.¹⁵ The porosity is 17.3% and 21.9%, respectively if the probing radius is chosen to be that of van der Waals radii of N (1.55 Å) and H (1.09).²⁷ The Materials Studio (MS) software¹⁶ predicts that the surface area of **3** is 0.

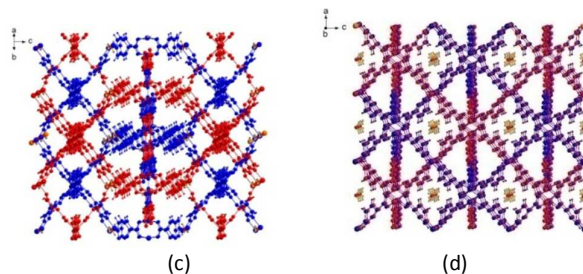
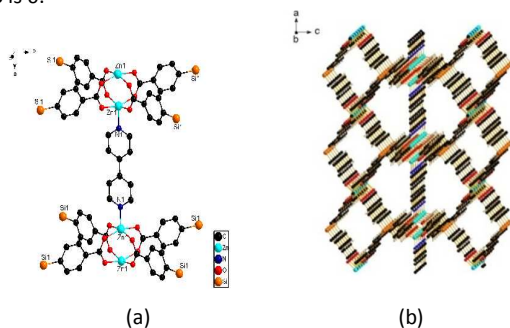


Fig. 1 The structures of **2** and **3**. (a) the coordination environment of the metals and ligands of **2**. (b) the 3D structure of **2**, showing the rhombic and pentagonal channels. (c) The 2-fold interpenetrated structure of **3**. (d) The triangle and square channels of **3**.

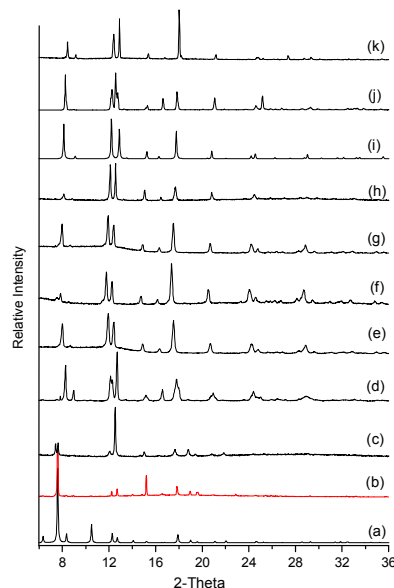


Fig. 2 The PXRD patterns. (a) Simulated **2**, (b) wet as-synthesized **2**, (c) as-synthesized **2** dried at 40 °C for 6-7 h, (d) as-synthesized **2** dried at 40 °C for 12 h and converted to **1**, (e) **1** exposed to air for 30 d, (f) **1** immersed in water for 30 d, (g) **1** in boiling water for 24 h, (h) **2** in boiling water for 24 h and converted to **1**, (i) simulated **3** based on its crystal structure, (j) synthesized **3** after dried at 40 °C for 6-7 h, (k) **1** synthesized in water.

1 is stable in air and water for 30 d and stable in boiling water for 24 h as shown in Fig. 2(e)-(g). To investigate the thermal stability of **1**, TG analysis was carried out (Fig. 3), showing that the framework starts to break down at 350 °C. The robustness and thermal stabilities of the framework of **1** were further checked by X-ray powder diffraction. After being heated at 200 °C for 12 h, it is still stable (Fig. 3).

6-coordinated Zn secondary building blocks (SBUs) are usually found more stable than the 4-coordinated Zn SBUs.⁷ However, Tan *et al.* found $\text{Zn}(\text{bdc})(\text{ted})_{0.5}$ (bdc = 1,4-benzenedicarboxylate; ted = triethylenediamine) are not stable towards water and the ted ligands can be replaced by water molecules. Kaskel *et al.* found $\text{Zn}_2(\text{adb})_2(\text{ted})_3 \cdot 4.5 \text{ DMF}$ (DUT-30(Zn), adb = 9,10-anthracene dibenzoate, DMF = N,N-dimethylformamide) are unstable towards water.¹⁰ The NBO charges of coordination atoms in a ligand may

play an important role in the water stability of MOFs: more charges a ligand contains, stronger the bond.⁴ Using a published method by us,⁴ we calculated the NBO charges of the coordination atoms of TCS and other ligands having been applied in synthesizing Zn-paddlewheel MOFs. The NBO charges of H₂adb (9,10-anthracene dibenzoate) is -0.778 which is less than -0.791, consisting with the fact that the Zn-paddlewheel framework based on H₂adb is unstable in water.¹⁰ However, the NBO charges of ted (-0.522) and bdc (-0.798) were found to be greater than those of 4,4'-bipy (-0.449) and TCS (-0.791), but Zn(bdc)(ted)_{0.5} was found unstable towards water.⁴ Thus, the water stability of **1** is most likely due to its much smaller pores compared to those of the above mentioned two compounds. The use of 4,4'-bipy (-0.449) could also be the possibility of resulting in a more water-stable phase. As water stability is also related to the polarity of the bond. Less charge on the N of 4,4'-bipy could result in a less polar Zn-N bond which will be more stable towards water.⁴ Results showed that the NBO charges of the coordination oxygen atoms of TCS is -0.791 which is less than those of ligands FMA (fumaric acid, -0.815),¹⁷ H₃BTC (trimesic acid, -0.813)⁹ and H₂BDC (terephthalic acid, -0.798).¹⁷ We predict that the Zn-paddlewheel structures based on FMA, H₃BTC and H₂BDC and 4,4'-bipy could likely to be stable in water.

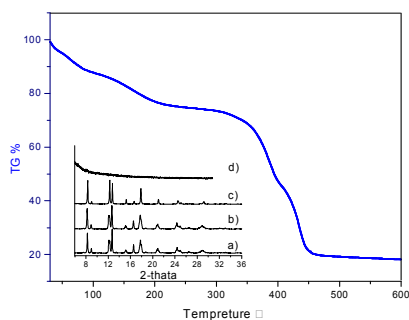


Fig. 3 The TG diagram of **2** made in NMP and NMA, and PXRD diagrams of **2** after desolvation. (a) as-synthesized dried at 40 °C for 12 h, converted to (b) 150 °C for 12 h (c) 200 °C for 12 h, (d) 350 °C for 4 h

The permanent porosity of **1** has been confirmed with the as-synthesized sample by nitrogen and hydrogen sorption experiments at 77 K (Fig. 4). The N₂ uptakes of **1** is 47 cm³ (STP)/g. The Brunauer–Emmett–Teller (BET) specific surface area is 156 m²g⁻¹ and the Langmuir surface area is 207 m²/g. The type I adsorption curve is consistent with the small pore nature of **1**. In the region of P/P₀ > 0.90, the isotherm began to increase sharply, indicating the presence of some textural mesopores.¹⁸ The H₂ uptake is 150 ml/g (1.34 wt%) under 1 bar and 77 K, which is moderate among MOF materials. For example, ZIF-8 (BET: 1630 m²/g) absorbs 1.27 wt%, MOF-5 (BET: 3362 m²/g) absorbs 1.32 wt% under 1 bar and 77 K.^{19–20} Thus, the H₂ (kinetic diameter: 2.89 Å) adsorption capacity indicates that **1** has a much higher surface areas than the 207 m²/g detected by N₂ gas. The small pores has make **1** selectively absorbs H₂ over N₂ at 77 K.

1 has high CO₂ and CH₄ uptake capacities as shown in Fig. 5. The CO₂ and CH₄ uptakes at 298 K and 1 bar are 47 cm³ (STP)/g (2.1 mmol/g, 9.2 wt%) and 19 cm³ (STP)/g (0.85 mmol/g, 1.4 wt%), respectively. The CO₂ uptakes increases to 85 cm³(STP)/g (3.8 mmol/g, 17 wt%) at 273 K and 1 bar. The second run obtained the same results, indicating the stability and easy desorption of CO₂

from **1**. The sample was only degassed at room temperature for less than 2 h between the two runs. These uptakes are higher than that of UiO-66 (Langmuir Surface area: 1066 m²/g, 65 cm³/g CO₂ at 273 K and 1 bar,²¹ 6.72 cm³/g CH₄ at 303 K and 1 bar.²² UiO(bpdc) was recently reported as a material has high CO₂ and CH₄ uptakes.²³ The CO₂ and CH₄ uptakes of **1** are similar to that of UiO(bpdc),²³ which has a much larger BET surface area (2646 m²/g) and absorbs 8.0 wt% CO₂ or 1.0 wt% CH₄ at 1 bar and 293 K; and 13.0 wt% CO₂ at 1 bar and 273 K.²³ To our knowledge, the adsorption of 1.4 wt% CH₄ is among the highest ones under the same condition with the maximum found to be 1.7 wt% by PCN-26.²⁴ For comparison, the PCN-14 only absorbs 1.0 wt% CH₄ at 1 bar and 290 K. These studies indicate that **1** could be a very good material for CO₂ and CH₄ storage. The adsorption selectivity of CO₂ and CH₄ over N₂ and H₂ at room temperature could be used for gas separations.

We observed hysteresis in those sorption experiments. Insufficient activation of the sample for sorption experiments could result in hysteresis phenomena because the solvent molecules may be released during the desorption process. We repeated the CO₂ adsorption/desorption measurement by heating the sample at 150 °C for 12 h under vacuum. This reduced the hysteresis of the isotherms compared with the previous experiment where the sample was evacuated only at room temperature for less than 2 h (Fig. S6 in SI). The different hysteretic sorption behaviours with respect to N₂ (3.64 Å), H₂ (2.89 Å), CO₂ (3.3 Å), and CH₄ (3.8 Å) could also be due to their different van der Waals interactions with the host framework. MOFs having pores of diameters less than 10 Å could also results in hysteresis phenomena due to their small pore nature as reported by Kim *et al.*²⁵

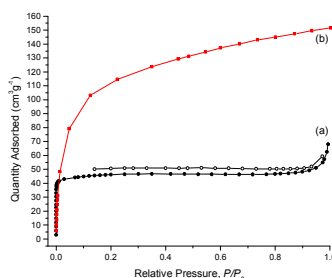


Fig. 4 Nitrogen (a) and hydrogen (b) gas sorption isotherm for **1** measured at 77 K (Filled and empty symbols represent adsorption and desorption data respectively).

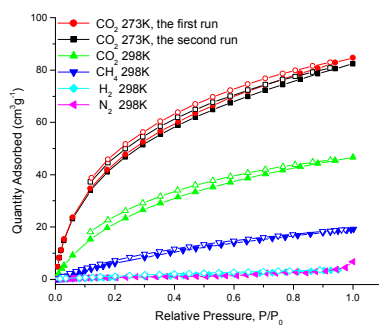


Fig. 5 The N₂, H₂, CH₄ and CO₂ sorption isotherm for **1** measured at 298/273 K (Filled and empty symbols represent adsorption and desorption data respectively)

The fluorescence emission of TCS ligand is at 435 nm ($\lambda = 260$ nm) (Fig. S4). The excitation of **1** at 260 nm also gives an emission peak at 435 nm but with much lower intensities. The same peak position and the similar shape of the spectrum of **1** to that of the ligand indicating the emission is ligand based. The weak intensities of the peaks are probably due to the solvent effect since **1** absorbs water from air as indicated by the IR spectra (Fig. S3). The UV-vis diffuse reflectance spectra of **1** and TCS were shown in Fig. S5. **1** absorbs ultraviolet light. The band gap (E_g) of **1** was found to be 3.87 eV, which is nearly identical to that of the ligand.

In conclusion, we demonstrated a Zn(II)-paddlewheel MOF, the 2-fold interpenetrated framework **1** can be stable in water, just like some of the Al(III) MOFs and Zr(IV) MOFs. The stability is probably due to its relative high NBO charges on the coordinating atoms. Based on theoretical calculations, we predicted that other water-stable Zn-paddlewheel MOFs might exist. **1** shows high CO₂ and CH₄ adsorption capacities and could be used as CO₂ and CH₄ storage material. **1** is also a fluorescent and semiconducting MOF material. Since d¹⁰ Zn(II) MOFs can be fluorescence and semiconducting materials, this discovery makes it possible to synthesize water-stable fluorescence and semiconducting MOF materials based on Zn-paddlewheel SBUs. In addition, we discovered the facile conversion between the non-interpenetrated **2** and the interpenetrated structure **1** even at ambient temperature due to solvent removal. Although only a couple similar examples have been reported,¹¹⁻¹² such conversions might be a common phenomenon which have not been widely aware.

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Notes and references

† Crystallographic data for **2**: C₃₈H₂₄O₈N₂Zn₂Si, $M = 795.7$, tetragonal, space group $P4_2/mmc$, $a = b = 13.9160(12)$ Å, $c = 21.142(4)$ Å, $V = 4094.2(9)$ Å³, $Z = 2$, $D_c = 0.645$ g cm⁻³, μ (MoK α) = 0.624 mm⁻¹, $F(000) = 808$, $T = 100(1)$ K, GoF = 1.054, final $R_1 = 0.0628$ and $wR_2 = 0.1899$ for $I > 2\sigma(I)$, $R_1 = 0.0695$ and $wR_2 = 0.1944$ for all data. CCDC 1034674. Crystallographic data for **3**·H₂O: C₃₈H₂₆O₉N₂Cu₂Si, $M = 809.8$, tetragonal, space group $P4_2/mmc$, $a = b = 9.7078(3)$ Å, $c = 21.7592(15)$ Å, $V = 2050.62(17)$ Å³, $Z = 2$, $D_c = 1.311$ g cm⁻³, μ (MoK α) = 1.117 mm⁻¹, $F(000) = 824$, $T = 291(2)$ K, GoF = 1.055, final $R_1 = 0.0471$ and $wR_2 = 0.1401$ for $I > 2\sigma(I)$, $R_1 = 0.0640$ and $wR_2 = 0.1503$ for all data. CCDC 1056672.

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Content

An exceptional water-stable two-fold interpenetrated Zn(II)-Paddlewheel Metal-Organic Framework was obtained via the facile conversion of its non-interpenetrated isomer at ambient temperature, showing high CO₂ and CH₄ uptake capacities.

