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## COMMUNICATION

## Single-crystal-to-single-crystal transformations and selective adsorption of porous copper(II) frameworks†

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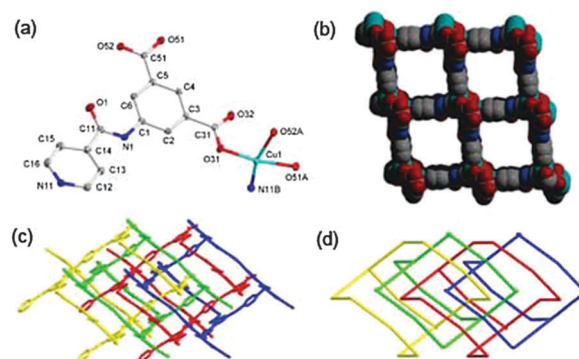
**A unique 4-fold interpenetrated (10,3)-b copper(II) framework exhibits reversible dehydration and rehydration in a single-crystal-to-single-crystal (SC–SC) process, and the dehydrated material can encapsulate CH<sub>3</sub>OH molecules, again in a SC–SC fashion, and shows selective adsorption of H<sub>2</sub> and CO<sub>2</sub> over N<sub>2</sub>.**

In recent years, metal–organic frameworks (MOFs) with well-defined channels have led to active investigation of their potential applications in gas storage, separation, ion exchange, catalysis and so on.<sup>1</sup> In the design and synthesis of such porous materials with new structures and permanent porosity, multi-carboxylate linkers are widely used as bridging ligands due to the high thermal and chemical stabilities of the carboxylate–metal fragment.<sup>2</sup> The available free volume in MOFs is normally occupied by solvent and/or guest molecules, which must be exchanged or removed in order to exploit the porous features. It has been well-documented that the primary frameworks were kept intact after the removal of guest molecules. But in most cases the single crystallinity of MOFs is not maintained after guest exchange, temperature change, or some other physical stimulus since the simultaneous shrinking or expansion of the overall framework may lead to its breakdown.

The single-crystal-to-single-crystal (SC–SC) transformation is highly desirable since it allows direct visualization of how the crystal structure is changing during the transformation process. Such a direct insight furthers understanding of the subtle interaction between the guest molecules and the hybrid backbone, and opens routes to study gas storage and

separation. So far the exploration *via* SC–SC transformations is uncommon.<sup>3</sup>

We report herein the synthesis† and reversible SC–SC transformations of a unique Cu(II) framework [Cu(INAIP)]·2H<sub>2</sub>O (**1**) [INAIP<sup>2−</sup> = 5-(isonicotinamido) isophthalate, Scheme S1, ESI†] with selective sorption property. Crystals of **1** were prepared by hydrothermal reaction and the results of X-ray diffraction analysis revealed that **1** is a 4-fold interpenetrated 3D (10,3)-b framework.<sup>4</sup> On the one hand, each Cu(II) shows a distorted square planar coordination geometry with one nitrogen (N11B) and three oxygen atoms (O31, O51A and O52A) from three different INAIP<sup>2−</sup> (Fig. 1a). On the other hand, each INAIP<sup>2−</sup> in **1** employs its one pyridyl and two carboxylate groups in turn to connect three metal atoms. Such coordination interactions between the four-coordinated Cu(II) and three-connecting INAIP<sup>2−</sup> make **1** a 3D framework (Fig. 1b). Firstly, 1D zigzag chain is formed by the connections between the carboxylate groups and Cu(II) when the coordination of the pyridyl group is neglected (Fig. S1, ESI†). Then the 1D chains are joined together by 5-isonicotinamido groups to result in the formation of the 3D framework. In order to minimize the hollow cavities and stabilize the framework, the potential voids formed *via* one 3D net combine with three other identical ones, leading to the formation of a 4-fold parallel interpenetrated structure (Fig. 1c). Although the



**Fig. 1** (a) The coordination environment of Cu(II) in **1**. Atoms with 'A' and 'B' in labels are symmetry-generated. Symmetry code: A:  $x, -y + 3/2, z + 1/2$ ; B:  $x + 1, -y + 1/2, z + 1/2$ . (b) The 3D structure of **1**. (c) The 4-fold interpenetrated structure of **1**. (d) Schematic representation of the 4-fold interpenetrated (10,3)-b topology.

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interpenetration occurs in **1**, after omitting the lattice water molecules, PLATON<sup>5</sup> analysis indicates that the porous structure is composed of voids of 340.5 Å<sup>3</sup> that represent 22.8% per unit cell volume [1491.2(12) Å<sup>3</sup>].

As discussed above, each INAIP<sup>2-</sup> in **1** is a three-connector and each Cu(II) acts as a three-connecting node. Thus **1** is a uniform 3-connected net with Point (Schläfli) symbol of (10<sup>2</sup>·10<sup>4</sup>·10<sup>4</sup>) calculated by TOPOS,<sup>6</sup> which represents a 4-fold interpenetrated (10,3)-*b* topology (Fig. 1d and Fig. S2, ESI†). There are known examples of (10,3)-*b* nets with 2-, 3-, 5- and higher-fold interpenetration, however, to the best of our knowledge, a 4-fold interpenetrated (10,3)-*b* net is rare.<sup>7</sup>

The TG curves (Fig. S3, ESI†) show that the first weight loss (9.33%) between 25–95 °C corresponds to the loss of water molecules (calcd 9.38%). The dehydrated phase remains stable up to 310 °C until the organic ligands start to be released. As shown in Fig. S4 (ESI†), it is clear that the diffraction profiles below 300 °C are essentially the same, indicating that the framework is stable up to this temperature and the crystal lattice remains intact after removal of the water molecules.

When a single crystal of **1** was heated at 180 °C, it was possible to collect single crystal diffraction data.<sup>8</sup> The result confirms that **1** was converted to the dehydrated species **1a** upon heating without significant change of the framework structure (Fig. 2). More interestingly, the dehydration process can be reversed by exposing the dehydrated crystal sample (**1a**) to the atmosphere for 48 h, giving the rehydrated phase **1'**, which was directly used for single-crystal X-ray diffraction measurements.<sup>8</sup>

To evaluate the porosity of **1a**, gas sorption studies were conducted. The bulk sample of **1a** was obtained by heating **1** at 200 °C for 10 h under vacuum. Interestingly, in the case of H<sub>2</sub> desorption a significant hysteresis loop was observed (Fig. 3a). **1a** showed 0.69 wt% H<sub>2</sub> uptake at 77 K and 1 atm. The most striking feature of **1a** is the steep slope in the H<sub>2</sub> sorption isotherm at initial pressure, indicating that the pores in **1a** strongly interact with H<sub>2</sub> molecules. This result prompted us to study the enthalpies of H<sub>2</sub> adsorption. The adsorption enthalpies, depending on the degree of H<sub>2</sub> loading, were estimated from the H<sub>2</sub> isotherms at 77 and 87 K by using a modified version of the Clausius–Clapeyron equation (Fig. S5 and S6, ESI†).<sup>9</sup> The overall enthalpies of the adsorption are larger than 10.5 kJ mol<sup>-1</sup> (Fig. S7, ESI†). The Cu(II) in **1a** is four-coordinated with open metal sites, the larger isosteric heat of H<sub>2</sub> adsorption clearly suggesting that the interaction between the host and H<sub>2</sub> is stronger for the

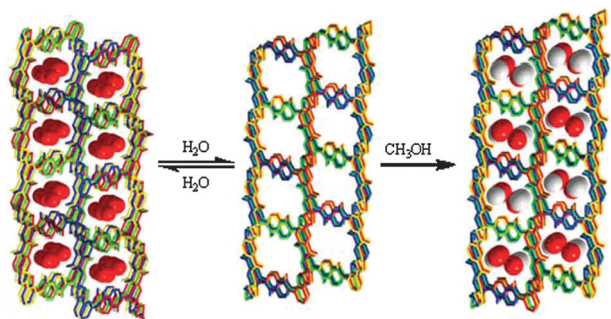


Fig. 2 SC-SC transformations of **1**(1'), **1a** and **1b**.

MOF with accessible metal sites (AMSs) than those without AMSs.

Further, gas sorptions were performed at near room temperature, to give more reliable results related to crystal structures determined at room temperature. It is interesting to find that the complex **1** (**1a**) shows selective gas adsorption for CO<sub>2</sub> over N<sub>2</sub> at near room temperatures. The sorption measurements of **1a** for CO<sub>2</sub> gave typical type I isotherms for microporous materials, and the uptakes around 1 atm are 57.64 and 47.34 cm<sup>3</sup> g<sup>-1</sup> at 273 and 298 K, respectively, while for N<sub>2</sub> only 4.68 and 2.71 cm<sup>3</sup> g<sup>-1</sup> were adsorbed at 273 and 298 K (Fig. 3b). The selective sorption of CO<sub>2</sub> over N<sub>2</sub> gases may be attributed to the smaller kinetic diameters of CO<sub>2</sub> than that of

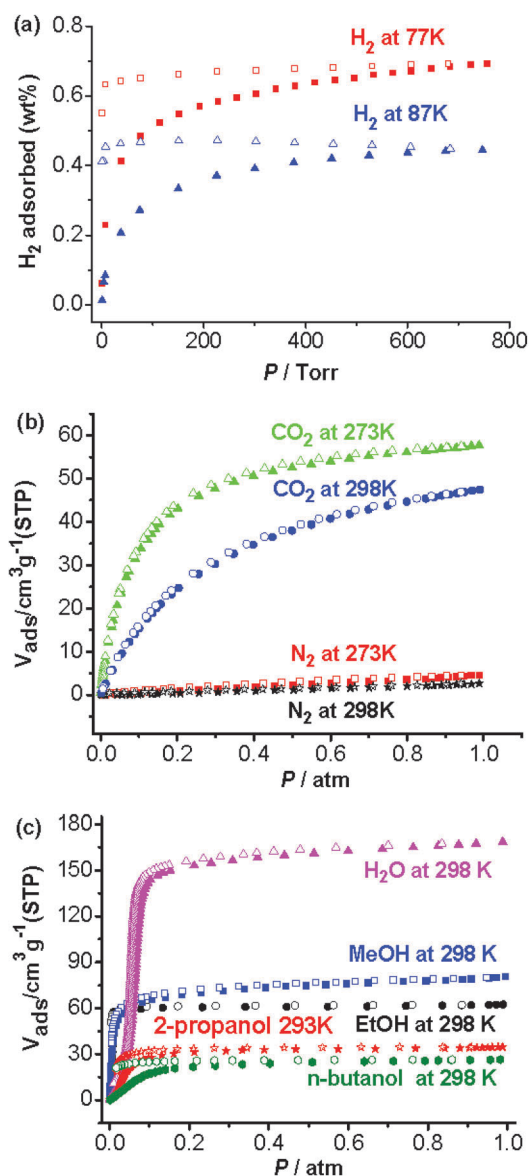


Fig. 3 (a) H<sub>2</sub> sorption isotherms of **1a** measured at 77 K and 87 K: triangles, 87 K; squares, 77 K. (b) Sorption isotherms of CO<sub>2</sub> and N<sub>2</sub> measured at 298 K and 273 K: triangles, 273 K CO<sub>2</sub>; circles, 298 K CO<sub>2</sub>; squares, 273 K N<sub>2</sub>; stars, 298 K N<sub>2</sub>. (c) Sorption isotherms of water, MeOH, EtOH and n-BuOH measured at 298 K: triangles, water; squares, MeOH; circles, EtOH; hexagons, n-butanol. Solid symbols: adsorption; open symbols: desorption.

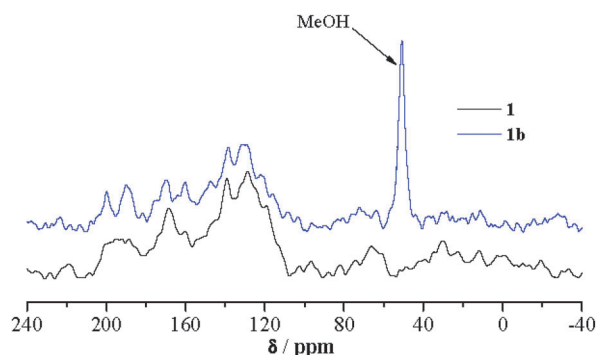


Fig. 4 Solid-state  $^{13}\text{C}$  NMR spectra of **1** and **1b**.

$\text{N}_2$  ( $\text{CO}_2$ , 3.3;  $\text{N}_2$ , 3.6 Å). The selective sorption of  $\text{CO}_2$  rather than  $\text{N}_2$  gas can also be attributed to the significant quadrupole moment of  $\text{CO}_2$  ( $-1.4 \times 10^{-39} \text{ cm}^2$ ), which generates specific interactions with the host framework.<sup>10</sup> The enthalpies of  $\text{CO}_2$  adsorption ( $Q_{\text{st}}$ ) were also calculated<sup>9</sup> from the adsorption isotherms measured at 273 and 298 K, and found to be around 33.76–35.36  $\text{kJ mol}^{-1}$  (Fig. S8–S10, ESI†), implying relatively strong interactions between the  $\text{CO}_2$  and the pore surfaces.<sup>11</sup>

In addition, **1a** was also subjected to vapor adsorption (Fig. 3c). It shows type-I isotherms for  $\text{H}_2\text{O}$  and alcohol. A rapid increase in the amount of adsorbed vapor under low pressure indicates the diffusion of adsorbates into the channels. Approximately 2.14  $\text{H}_2\text{O}$ , 1.02 MeOH, 0.79 EtOH and 0.33 n-BuOH molecules are adsorbed per formula unit at 1 atm, respectively. It is clear that the absorption of alcohol molecules is size dependent. Surprisingly, after the single crystals of **1** were used to adsorb methanol on volumetric adsorption apparatus at 298 K, a single crystal was selected and X-ray diffraction data collection was made.<sup>12</sup> The results show that **1** has been transformed into  $[\text{Cu}(\text{INAIP})]\cdot\text{MeOH}$  (**1b**). Both **1** and **1b** are isomorphous and **1b** contains one methanol molecule per formula unit (Fig. 2). The presence of methanol molecules in **1b** was further confirmed by the solid-state  $^{13}\text{C}$  NMR spectral measurements. As shown in Fig. 4, a peak at  $\delta = 50.9 \text{ ppm}$  was observed in the  $^{13}\text{C}$  NMR spectrum of **1b**, which is absent in **1** and can be assigned to the methanol molecule.

In conclusion, a unique 4-fold interpenetrating (10,3)-*b* copper(II) framework was synthesized and found to exhibit multiple functions: porosity, high stability, hydrogen-storage capacity and SC–SC transformation which may be due to the presence of 4-fold interpenetration and the amide functional group in the ligand of INAIP<sup>2–13</sup>.

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## Notes and references

† Synthesis: A mixture of  $\text{CuCl}_2\cdot 2\text{H}_2\text{O}$  (17.1 mg, 0.1 mmol),  $\text{H}_2\text{INAIP}$  (28.6 mg, 0.1 mmol), bpy (16.0 mg, 0.1 mmol) and NaOH (8.0 mg, 0.2 mmol) in 10 mL  $\text{H}_2\text{O}$  was sealed in a 16 mL Teflon lined stainless steel container and heated at 160 °C for 5 days. Green block crystals of **1** were collected with a yield of 42%. Anal. calcd for  $\text{C}_{14}\text{H}_{12}\text{CuN}_2\text{O}_7$ : C, 43.81; H, 3.15; N, 7.30%. Found: C, 43.78; H, 3.21; N, 7.33%.

- Recent reviews, for example: (a) L. Q. Ma, C. Abney and W. B. Lin, *Chem. Soc. Rev.*, 2009, **38**, 1248; (b) L. J. Murray, M. Dincă and J. R. Long, *Chem. Soc. Rev.*, 2009, **38**, 1294; (c) J. R. Li, R. J. Kuppler and H. C. Zhou, *Chem. Soc. Rev.*, 2009, **38**, 1248.
- For example: (a) C. N. R. Rao, S. Natarajan and R. Vaidyanathan, *Angew. Chem., Int. Ed.*, 2004, **43**, 1466; (b) X. L. Wang, C. Qin, S. X. Wu, K. Z. Shao, Y. Q. Lan, S. Wang, D. X. Zhu, Z. M. Su and E. B. Wang, *Angew. Chem., Int. Ed.*, 2009, **48**, 5291.
- (a) S. Takamizawa and R. Miyake, *Chem. Commun.*, 2009, 4076; (b) M. A. Garcia-Garibay, *Angew. Chem., Int. Ed.*, 2007, **46**, 8945; (c) B. W. Hu, J. P. Zhao, E. C. Sañudo, F. C. Liu, Y. F. Zeng and X. H. Bu, *Dalton Trans.*, 2008, 5556.
- Crystal data of **1**:  $\text{C}_{14}\text{H}_{12}\text{CuN}_2\text{O}_7$ ,  $M_w = 383.80$ , monoclinic,  $P2_1/c$ ,  $a = 8.405(5)$ ,  $b = 10.293(4)$ ,  $c = 17.812(8)$  Å,  $\beta = 104.582(19)^\circ$ ,  $V = 1491.2(12)$  Å<sup>3</sup>,  $Z = 4$ ,  $\rho_{\text{calcd}} = 1.709 \text{ g cm}^{-3}$ ,  $\mu = 1.506 \text{ mm}^{-1}$ ,  $T = 293(1)$  K, total data = 13 613, unique data = 3410 ( $R_{\text{int}} = 0.0365$ ),  $R_1 = 0.0477$  ( $I > 2\sigma(I)$ ),  $wR_2 = 0.1381$  (all data).
- A. L. Spek, *J. Appl. Crystallogr.*, 2003, **36**, 7.
- (a) V. A. Blatov, M. O'Keeffe and D. M. Proserpio, *CrystEngComm*, 2010, **12**, 44; (b) V. A. Blatov, Multipurpose crystallochemical analysis with the program package TOPOS, *IUCr CompComm Newsletter*, 2006, **7**, 4.
- (a) J. Zhang, Y. B. Chen, S. M. Chen, Z. J. Li, J. K. Cheng and Y. G. Yao, *Inorg. Chem.*, 2006, **45**, 3161; (b) Y. Qi, Y. X. Che, F. Luo, S. R. Batten, Y. Liu and J. M. Zheng, *Cryst. Growth Des.*, 2008, **8**, 1654; (c) M. S. Chen, Z. S. Bai, Z. Su, S. S. Chen and W. Y. Sun, *Inorg. Chem. Commun.*, 2009, **12**, 530.
- Crystal data of **1a**:  $\text{C}_{14}\text{H}_8\text{CuN}_2\text{O}_5$ ,  $M_w = 347.76$ , monoclinic,  $P2_1/c$ ,  $a = 8.497(5)$ ,  $b = 10.296(4)$ ,  $c = 17.749(7)$  Å,  $\beta = 104.624(18)^\circ$ ,  $V = 1502.4(12)$  Å<sup>3</sup>,  $Z = 4$ ,  $\rho_{\text{calcd}} = 1.537 \text{ g cm}^{-3}$ ,  $\mu = 1.477 \text{ mm}^{-1}$ ,  $T = 453(1)$  K, total data = 13 698, unique data = 3435 ( $R_{\text{int}} = 0.0387$ ),  $R_1 = 0.0424$  ( $I > 2\sigma(I)$ ),  $wR_2 = 0.1145$  (all data). Crystal data of **1'**:  $\text{C}_{14}\text{H}_{12}\text{CuN}_2\text{O}_7$ ,  $M_w = 383.81$ , monoclinic,  $P2_1/c$ ,  $a = 8.4048(12)$ ,  $b = 10.2379(15)$ ,  $c = 17.7707(18)$  Å,  $\beta = 104.405(5)^\circ$ ,  $V = 1481.1(3)$  Å<sup>3</sup>,  $Z = 4$ ,  $\rho_{\text{calcd}} = 1.721 \text{ g cm}^{-3}$ ,  $\mu = 1.517 \text{ mm}^{-1}$ ,  $T = 293(2)$  K, total data = 7435, unique data = 2752 ( $R_{\text{int}} = 0.0474$ ),  $R_1 = 0.0501$  ( $I > 2\sigma(I)$ ),  $wR_2 = 0.1335$  (all data).
- (a) F. Daniels, J. W. Williams, P. Bender, R. A. Alberty and C. D. Cornwell, *Experimental Physical Chemistry*, McGraw-Hill Book Co. Inc., New York, 1962; (b) D. C. Zhong, J. B. Lin, W. G. Lu, L. Jiang and T. B. Lu, *Inorg. Chem.*, 2009, **48**, 8656.
- S. Coriani, A. Halkier, A. Rizzo and K. Ruud, *Chem. Phys. Lett.*, 2000, **326**, 269.
- (a) K. D. Vogiatzis, A. Mavrandonakis, W. Kloppe and G. E. Froudakis, *ChemPhysChem*, 2009, **10**, 374; (b) J. An, S. J. Geib and N. L. Rosi, *J. Am. Chem. Soc.*, 2010, **132**, 38.
- Crystal data of **1b**:  $\text{C}_{15}\text{H}_{12}\text{CuN}_2\text{O}_6$ ,  $M_w = 379.82$ , monoclinic,  $P2_1/c$ ,  $a = 8.4283(11)$ ,  $b = 10.2553(13)$ ,  $c = 17.8159(18)$  Å,  $\beta = 104.408(5)^\circ$ ,  $V = 1491.5(3)$  Å<sup>3</sup>,  $Z = 4$ ,  $\rho_{\text{calcd}} = 1.691 \text{ g cm}^{-3}$ ,  $\mu = 1.500 \text{ mm}^{-1}$ ,  $T = 293(2)$  K, total data = 7172, unique data = 2694 ( $R_{\text{int}} = 0.0491$ ),  $R_1 = 0.1262$  ( $I > 2\sigma(I)$ ),  $wR_2 = 0.2841$  (all data).
- S. Hasegawa, S. Horike, R. Matsuda, S. Furukawa, K. Mochizuki, Y. Kinoshita and S. Kitagawa, *J. Am. Chem. Soc.*, 2007, **129**, 2607.