

# Divergent Kinetic and Thermodynamic Hydration of a Porous Cu(II) Coordination Polymer with Exclusive CO<sub>2</sub> Sorption Selectivity

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## Supporting Information

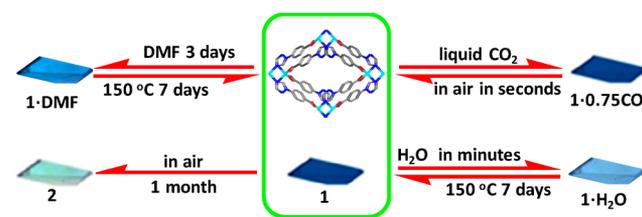
**ABSTRACT:** Selective adsorption and separation of CO<sub>2</sub> are of great importance for different target applications. Metal–organic frameworks (MOFs) represent a promising class of porous materials for this purpose. Here we present a unique MOF material, [Cu(tba)<sub>2</sub>]<sub>n</sub> (tba = 4-(1*H*-1,2,4-triazol-1-yl)benzoate), which shows high CO<sub>2</sub> adsorption selectivity over CH<sub>4</sub>/H<sub>2</sub>/O<sub>2</sub>/Ar/N<sub>2</sub> gases (with IAST selectivity of 41–68 at 273 K and 33–51 at 293 K). By using a critical point dryer, the CO<sub>2</sub> molecules can be well sealed in the 1D channels of [Cu(tba)<sub>2</sub>]<sub>n</sub> to allow a single-crystal X-ray analysis, which reveals the presence of not only C<sup>δ+</sup>–H...O<sup>δ-</sup> bonds between the host framework and CO<sub>2</sub> but also quadrupole–quadrupole (CO<sub>2</sub><sup>δ-</sup>...δ<sup>+</sup>CO<sub>2</sub>) interactions between the CO<sub>2</sub> molecules. Furthermore, [Cu(tba)<sub>2</sub>]<sub>n</sub> will suffer divergent kinetic and thermodynamic hydration processes to form its isostructural hydrate {[Cu(tba)<sub>2</sub>](H<sub>2</sub>O)}<sub>n</sub> and a mononuclear complex [Cu(tba)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>] via single-crystal to single-crystal transformations.

Carbon dioxide, the predominant greenhouse gas causing global warming, mainly originates from the combustion of carbon-based fossil fuels. Effective capture and separation of CO<sub>2</sub> are of great importance for relieving the environmental pressure and for some significant industrial applications, such as natural gas purification.<sup>1</sup> As a new class of porous materials, coordination polymers, or metal–organic frameworks (MOFs), have attracted intense interest due to their easily tunable pore structures and properties.<sup>2</sup> Thus far, the substantial potential of porous MOF materials for CO<sub>2</sub> storage and separation has been well corroborated.<sup>3</sup> Normally, introducing open metal sites,<sup>4</sup> Lewis basic sites,<sup>5</sup> and strongly polarizing functional groups<sup>6</sup> as well as their combinations<sup>7</sup> in MOFs can be anticipated to enhance the adsorption of CO<sub>2</sub> by forming interactions between the functional sites and the quadrupole of CO<sub>2</sub> molecules. Several methods have shown such interactions between the host framework and included CO<sub>2</sub> guest, including theoretical calculations,<sup>8</sup> spectroscopy,<sup>9</sup> and synchrotron powder X-ray diffraction (PXRD).<sup>10</sup> Single-crystal X-ray diffraction (XRD) analysis of the CO<sub>2</sub>-loaded composite structures will provide straightforward and convincing evidence that can reveal more details of such host–guest interactions,<sup>11</sup> despite the difficulty in practice for the gaseous nature of CO<sub>2</sub> at ambient conditions.

MOFs are usually prepared in solution through slow crystallization (e.g., diffusion or solvothermal synthesis).<sup>12</sup> Examples of solid-state reactivity of MOFs are uncommon, especially single-crystal to single-crystal (SCSC) transformations.<sup>13</sup> In this condition, molecular movement is restricted in the crystalline lattice, and it is difficult to retain crystallinity during structural transformation.<sup>13</sup> Nevertheless, solid-state SCSC reactions of MOFs can occur with destruction/formation of coordination bonds in response to external stimuli such as solvent, heating, and light.<sup>14</sup> Notably, significant modification of physicochemical properties such as magnetism, luminescence, and porosity is commonly observed in this course, which may be used to prepare new crystalline materials.<sup>15</sup>

We have reported a unique 3D MOF, {[Cu(iba)<sub>2</sub>](H<sub>2</sub>O)<sub>2</sub>]<sub>n</sub> (Hiba = 4-(1*H*-imidazol-1-yl)benzoic acid), with the 3-fold interpenetrating *lvt* framework, which shows distinct kinetic and thermodynamic SCSC transformations upon heating or spontaneous dehydration,<sup>14a</sup> demonstrating the duality—both rigid and flexible—of such porous framework materials upon dehydration. In the current work, by replacing the Hiba ligand with 4-(1*H*-1,2,4-triazol-1-yl)benzoic acid (Htba), another 3D MOF, {[Cu(tba)<sub>2</sub>](DMF)}<sub>n</sub> (**1**·DMF), with the 4-fold interpenetrating *dia* framework, can be obtained. It is very interesting that the desolvated MOF **1** has the dual nature of hydration, suffering distinct SCSC transformations via kinetic and thermodynamic control (Scheme 1). Remarkably, **1** shows exclusive capacity to adsorb CO<sub>2</sub> selectively over CH<sub>4</sub>/H<sub>2</sub>/O<sub>2</sub>/Ar/N<sub>2</sub>, which can be attributed to the thermodynamic equilibrium effect.<sup>3a</sup> Further, CO<sub>2</sub> molecules can be loaded in the 1D channels of **1**, and single-crystal XRD of **1**·0.75CO<sub>2</sub>

**Scheme 1. Schematic Representation of Single-Crystal to Single-Crystal Transformations for **1**, **1**·DMF, **2**, **1**·0.75CO<sub>2</sub>, and **1**·H<sub>2</sub>O**

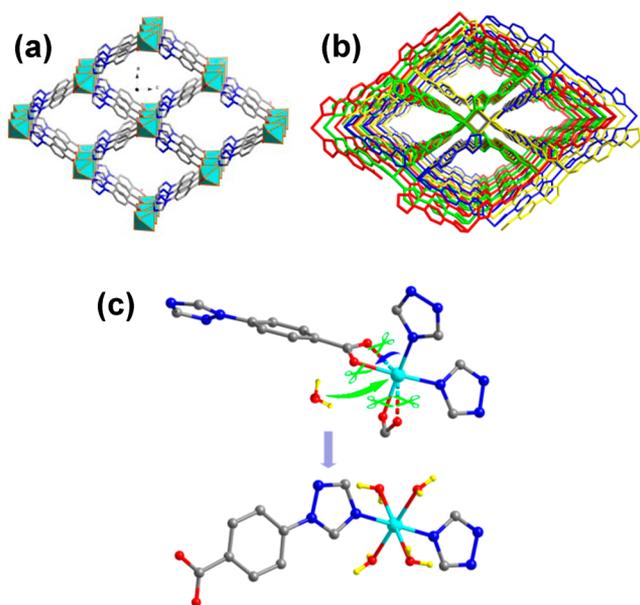


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clearly reveals both host–guest  $C^{\delta+}-H\cdots O^{\delta-}$  H-bonding and quadrupole–quadrupole interactions between the  $CO_2$  molecules.

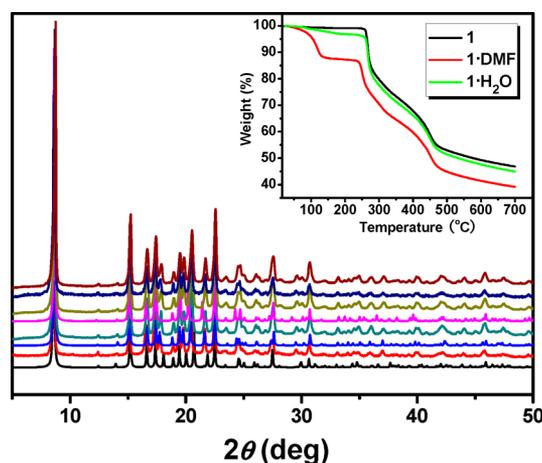
Solvothermal reaction of  $Cu(NO_3)_2$  with Htba in  $C_2H_5OH$ –DMF solution yields blue block crystals of  $\{[Cu(tba)_2](DMF)\}_n$  (**1**·DMF, Supporting Information (SI)). Single-crystal XRD analysis of **1**·DMF indicates that the asymmetric coordination unit consists of a half-occupied  $Cu^{II}$  center and one deprotonated tba ligand. Each  $Cu^{II}$  ion is four-coordinated by two carboxylate O's and two triazolyl N's from different tba ligands, with the presence of weaker  $Cu-O_{\text{carboxylate}}$  (2.515(4) Å) interactions (Figure S1a). The adjacent  $Cu^{II}$  centers are extended by the bridging tba ligands to construct a 3D coordination network with dia topology (Figure 1a).<sup>16</sup> In each diamondoid unit, the  $Cu\cdots$



**Figure 1.** (a) A single 3D coordination network (cyan polyhedra for  $Cu^{II}$ ) in **1**·DMF. (b) Representation of 4-fold [2+2] interpenetrating framework with four independent networks shown in different colors in **1**·DMF. (c) Destruction, reconstruction, and rearrangement of coordination interactions around  $Cu^{II}$  ion in SCSC transformation from **1** (top) to **2** (bottom) upon thermodynamic hydration.

$Cu\cdots Cu$  angles range from  $84.39(2)^\circ$  to  $131.58(2)^\circ$ , indicating considerable distortion from the ideal tetrahedral angle of  $109.8^\circ$ . Moreover, four such open networks are entangled in each other to form a 4-fold interpenetrating framework (Figure 1b), which represents a [2+2] roto-translational system comprising two sets of normal 2-fold interpenetrating patterns. According to Blatov's classification of interpenetrating networks, it can be ascribed to the rare type IIIa motif in RSCR notation, which accounts for only <5% of all reported examples.<sup>17</sup> Despite interpenetration, the intersecting 1D rhombus-shaped channels are still observed along the crystallographic  $b$  axis, with pore sizes of  $\sim 3.0 \times 6.0 \text{ \AA}^2$  (considering van der Waals radii of atoms). Calculation of the solvent-accessible area by the PLATON program<sup>18</sup> (1.8 Å probe radius) reveals a value of  $498.2 \text{ \AA}^3$  (22.5% per unit cell volume).

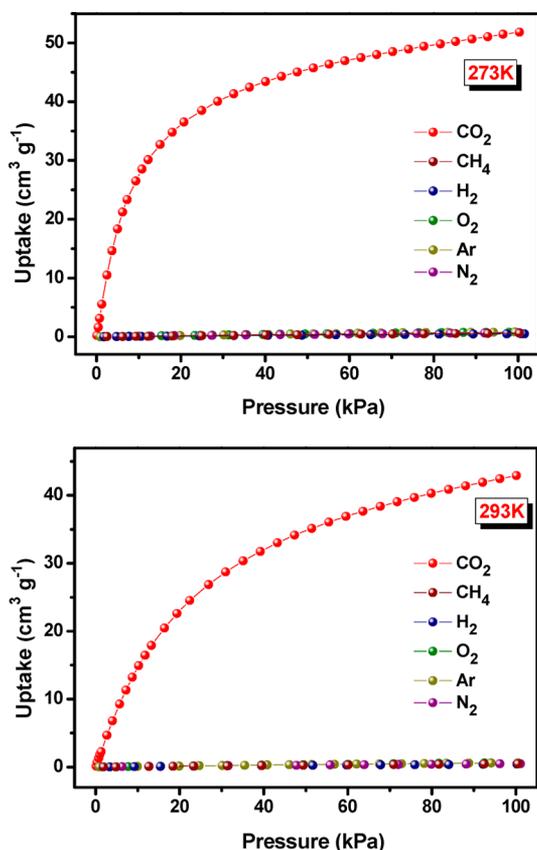
Thermogravimetric analysis (TGA) of **1**·DMF (Figure 2) reveals that the lattice DMF molecule will be removed upon heating and the coordination framework is thermally stable up to ca. 240 °C. Thus, desolvated **1** can be obtained by heating **1**·DMF at 150 °C under vacuum for 1 week, and TGA and IR (Figure S2) clearly indicate that the DMF guest was completely



**Figure 2.** PXRD patterns (from bottom to top) for **1**·DMF (calculated), **1**·DMF (experimental), **1** (calculated), **1** (**1**·DMF→**1**), **1**·H<sub>2</sub>O (calculated), **1**·H<sub>2</sub>O (experimental), **1** (**1**·H<sub>2</sub>O→**1**), and **1** (after gas adsorption). Inset: TGA curves for **1**, **1**·DMF, and **1**·H<sub>2</sub>O.

excluded. Single-crystal XRD of desolvated MOF **1** (Table S1) shows that the coordination framework is unchanged, and the PXRD pattern (Figure 2) also suggests phase purity of the bulk sample. As expected, inverse SCSC transformation from **1** to **1**·DMF will occur when the evacuated solid is immersed in DMF solution for 3 days. To confirm the water stability of **1**, which is very important for practical applications of MOF materials, the bulk sample of **1** was further placed in water solution, where a color change of the crystals from dark blue to light blue was observed in minutes. Single-crystal XRD analysis reveals the framework integrity of the resulting crystalline product **1**·H<sub>2</sub>O (Table S1). Dehydration of **1**·H<sub>2</sub>O by heating the sample at 150 °C for 1 week regenerates the evacuated crystal of **1** (Table S1). At this stage, it seems that the coordination framework of **1** is quite robust during the reversible solvation and desolvation processes and maintains excellent single crystallinity (Table S1 and Figure S3). However, when crystals of **1** are exposed to air for a long time (at least 1 month), a visible SCSC transformation of the sample is observed (Figure S4). Single-crystal XRD of the resulting cyan crystal reveals the formation of a distinct mononuclear coordination species,  $[Cu(tba)_2(H_2O)_4]$  (**2**). The asymmetric unit of **2** comprises one  $Cu^{II}$  center with half occupancy, one tba ligand, and a pair of water ligands (Figure S1b). Each octahedral  $Cu^{II}$  center is surrounded by two triazolyls from a pair of tba ligands and four water molecules. This observation can be regarded as a result of slow attack of water in air to MOF **1** crystals, which leads to complete destruction of all  $Cu$ –carboxylate interactions and, accordingly, the formation of four  $Cu$ –water coordination bonds. Meanwhile, the two cis-N donors of tba ligands around each  $Cu^{II}$  in **1** rearrange to their trans orientation in **2** (Figure 1c). The completely different water-induced SCSC transformations of **1**, which result in the kinetic and thermodynamic products **1**·H<sub>2</sub>O and **2**, respectively, first reveal the duality and sensitivity of such porous materials toward water.

The desolvated microporous MOF **1** shows no obvious sorption of  $N_2$  at 77 K (Figure S5), which can be attributed to the fact that its aperture is smaller than the kinetic diameter of  $N_2$  (3.64–3.80 Å).<sup>19</sup> For comparison, the adsorption isotherms of  $CO_2$ ,  $CH_4$ ,  $H_2$ ,  $O_2$ , Ar, and  $N_2$  gases were measured for **1** at 195, 273, and 293 K, respectively (Figures 3 and S6). Interestingly, a significant higher capacity for adsorption of  $CO_2$  compared to



**Figure 3.** Comparison of gas adsorption isotherms of **1** for CO<sub>2</sub>/CH<sub>4</sub>/H<sub>2</sub>/O<sub>2</sub>/Ar/N<sub>2</sub> at 273 K (top) and 293 K (bottom).

the other gases was observed in all these cases. At 195 K, the CO<sub>2</sub> adsorption of **1** displays a type I isotherm. The sorption amount of CO<sub>2</sub> at saturation is 77.6 cm<sup>3</sup>/g, which corresponds to 1.5 CO<sub>2</sub> molecules per formula unit of **1**. The adsorption isotherms of CO<sub>2</sub> show a gradual increase and reach the maximal amounts of 51.8 cm<sup>3</sup>/g (10.2 wt%) at 273 K and 43.9 cm<sup>3</sup>/g (8.6 wt%) at 293 K. The CO<sub>2</sub> uptake of **1** at 293 K is comparable to that reported for ZIF-96 (8.8 wt%) under similar conditions.<sup>5a</sup> In contrast, the capture capacities of **1** for CH<sub>4</sub>, H<sub>2</sub>, O<sub>2</sub>, Ar, and N<sub>2</sub> are extremely poorer (<2.2 cm<sup>3</sup>/g at all tested temperatures). In this context, the selectivity of CO<sub>2</sub> adsorption from binary gas mixture can be evaluated by the ideal adsorbed solution theory (IAST), which is well recognized and applied to predict gas mixture sorption behaviors in porous materials.<sup>20</sup> Based on the single gas adsorption isotherms and the IAST model, the sorption selectivity of CO<sub>2</sub> over other gases for **1** (Figure S7) is 33–51 at 293 K, which will be slightly higher at 273 K (Table 1). Remarkably, MOFs materials with selective sorption of CO<sub>2</sub> over one or two specific gases are familiar, while MOF **1** here represents a unique example for exclusively capturing CO<sub>2</sub> over a broad spectrum of gases with generally high selectivity, which

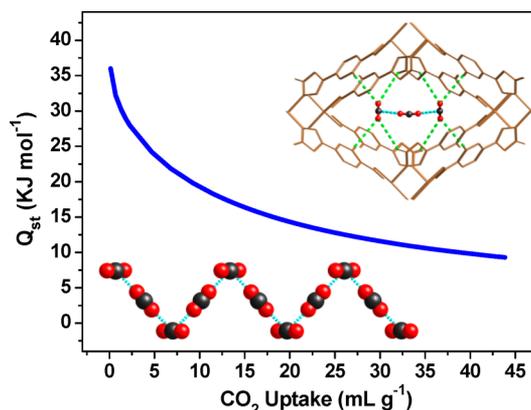
**Table 1.** Calculated IAST Selectivity (at 1 bar) for Binary Gas Mixtures<sup>a</sup>

	CO <sub>2</sub> /CH <sub>4</sub>	CO <sub>2</sub> /H <sub>2</sub>	CO <sub>2</sub> /O <sub>2</sub>	CO <sub>2</sub> /Ar	CO <sub>2</sub> /N <sub>2</sub>
273 K	55	68	43	41	51
293 K	45	51	34	33	45

<sup>a</sup>15% for CO<sub>2</sub> and 85% for the other gas in each case.

indicates its great potentials in applications of selective gas separation (normally with a selectivity >8).<sup>20b</sup>

The isosteric heats ( $Q_{st}$ ) of CO<sub>2</sub> were calculated with the Clausius–Clapeyron equation from the CO<sub>2</sub> isotherms measured at 273 and 293 K (see SI for details).<sup>21</sup> For CO<sub>2</sub> in **1**,  $Q_{st}$  = 36.0 kJ/mol at the onset of adsorption (Figure 4), comparable to



**Figure 4.** Adsorption enthalpies of CO<sub>2</sub> calculated by isotherms at 273 and 293 K. Inset: (upper right) a local view of **1**-0.75CO<sub>2</sub> showing the interactions between host framework and CO<sub>2</sub> molecules (green dashed lines), and (lower left) Z-shaped arrangement of CO<sub>2</sub> guests with quadrupole–quadrupole interactions.

some well-known MOFs examples such as MOF-5,<sup>22</sup> HKUST-1,<sup>4c</sup> bio-MOF-1,<sup>5c</sup> and MIL-53(Al)<sup>3f</sup> (34–36 kJ/mol). The high  $Q_{st}$  may indicate strong interactions between the coordination framework and CO<sub>2</sub> guest.<sup>11b</sup> To confirm this opinion and, further, find some clues to the CO<sub>2</sub> sorption sites and high sorption selectivity of MOF **1**, we successfully loaded the CO<sub>2</sub> molecules in the channels using a critical point dryer (SI). This method is very convenient to operate, and it may be applied for CO<sub>2</sub> encapsulation in other porous crystals. The resulting CO<sub>2</sub>-loaded single-crystal sample can be determined with a conventional X-ray diffractometer at 120 K. The single-crystal X-ray structure for **1**-0.75CO<sub>2</sub> undoubtedly reveals that the adsorbed CO<sub>2</sub> molecules can be accommodated in the 1D channels along the *b* axis (Figure 4 inset). As expected, one refined CO<sub>2</sub> molecule (with 1/4 occupancy) forms host–guest C–H···O interactions with phenyl and 1,2,4-triazolyl rings, respectively, with short H···O distances of 3.18 and 3.24 Å (Table S3). This suggests that the adsorbed CO<sub>2</sub> molecules prefer to be projected by H atoms and conjugated aromatic systems, which can be normally considered as the binding domains of CO<sub>2</sub> in MOFs. Notably, the rhombus-shaped cavities also allow another CO<sub>2</sub> to locate in the central site, and both types of adsorbed CO<sub>2</sub> molecules are distributed in the 1D channels in a Z-shaped manner (Figure 4 inset). Of further significance, intermolecular C<sup>δ+</sup>···O<sup>δ-</sup> interactions between adjacent CO<sub>2</sub> molecules are also observed with a C···O distance of 2.607 Å, which will also contribute to the high isosteric heats of CO<sub>2</sub> for **1**. Furthermore, when the sealed glass capillary tube holding the single crystal of **1**-0.75CO<sub>2</sub> was broken from one end, XRD analysis of the sample at the same conditions (Figure S8) indicates the regeneration of **1**. The maximum and minimum residual electron density peaks in this CO<sub>2</sub>-escaped crystal are only 0.434 and −0.266 e/Å<sup>3</sup> (Table S1), which can also definitely confirm the proper encapsulation of CO<sub>2</sub> molecules in the **1**-0.75CO<sub>2</sub> crystal.

In summary, the evacuated microporous framework **1** shows distinct hydration behaviors controlled by kinetic or thermody-

dynamic process, which provide new insights for the evaluation of water stability of MOF materials. Remarkably, top-rank CO<sub>2</sub> adsorption selectivity over a variety of gases is observed for **1**, which can be rationally attributed to synergistic C<sup>δ+</sup>—H<sup>δ-</sup>—O<sup>δ-</sup> (framework···O<sub>2</sub>C) H-bonding and CO<sub>2</sub><sup>δ-</sup>···δ<sup>+</sup>CO<sub>2</sub> quadrupole–quadrupole interactions, as confirmed by single-crystal XRD. These results will be helpful to understand the origin of CO<sub>2</sub> sorption in coordination frameworks and also to design new MOF materials for future applications.

## ■ ASSOCIATED CONTENT

### ■ Supporting Information

Experimental details, tables and structural figures, characterization for complex **2**, gas sorption isotherms of **1** at 77 and 195 K, IAST selectivity of **1** at 273 and 293 K, single-crystal photos of **1**, and crystallographic data (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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