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## Hysteretic carbon dioxide sorption in a novel copper(II)-indazole-carboxylate porous coordination polymer†

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**The synthesis, structural and gas sorption studies of a porous Cu(II) coordination polymer featuring 1*H*-indazole-5-carboxylic acid (**H<sub>2</sub>L**) are presented. [Cu(HL)<sub>2</sub>] is a thermally and hydrolytically robust 4-connected 3D coordination polymer of NbO topology and is replete with 1D channels that permit selective and hysteretic sorption of CO<sub>2</sub>.**

Remediation of the increasing levels of carbon dioxide in the atmosphere is probably the most serious environmental issue of our time.<sup>1</sup> Carbon capture and sequestration (CCS) is a potential means of reducing anthropogenic CO<sub>2</sub> contributions, although current pre- and post-combustion CCS technologies at CO<sub>2</sub> point sources involve energy intensive regeneration of the sorption media (amine based solutions) and are not yet cost effective for carbon emissions reduction.<sup>2</sup> In this respect, porous coordination polymers (PCPs, aka metal-organic frameworks, MOFs) offer promising alternatives for CCS because they can potentially display more favourable CO<sub>2</sub> sorption properties than other classes of porous materials.<sup>3</sup> The study of PCPs/MOFs is therefore an extremely topical area of current chemical research.<sup>4</sup> By virtue of their large internal surface areas PCPs may be used to purify hydrocarbon fuel gases, sequester CO<sub>2</sub> from natural gas streams, and to capture CO<sub>2</sub> post-combustion.<sup>5</sup> This variety of applications stems from the modular nature of PCPs, which allows their properties to be tuned by simply changing the constituent metal ions and/or ligand molecules from which they are made. Combining this modularity with various synthetic approaches augurs well for the preparation of innumerable PCPs with multiple potential applications. However, the hydrolytic sensitivity of some metal carboxylate-based PCPs/MOFs limits their potential industrial application and so

requires the generation of more robust PCPs.<sup>6</sup> The lack of resilience to water can be traced to the relatively weak metal-oxygen bond, and incorporating azolate-based ligands into a framework has been shown to be an effective means of increasing moisture stability.<sup>7</sup>

Herein we report the synthesis of a novel PCP derived from the 1*H*-indazole-5-carboxylic acid ligand **H<sub>2</sub>L**, representing the first example of an indazole-derived ligand acting as a link in a coordination polymer framework. **H<sub>2</sub>L** combines the utility of the carboxylate group with the versatile coordination ability of the azole functionality. The PCP [Cu(HL)<sub>2</sub>], **1**, is thermally and hydrolytically robust and shows selectivity toward CO<sub>2</sub> sorption.

The ligand **H<sub>2</sub>L**, prepared by a modified Jacobson procedure (ESI†),<sup>8</sup> was reacted solvothermally with Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O in aqueous MeOH in the presence of excess (NH<sub>4</sub>)<sub>2</sub>SiF<sub>6</sub> at 100 °C followed by slow cooling to RT, forming dichroic purple crystals of **1** in 59% yield. Single crystal X-ray diffraction data were solved and refined in the rhombohedral space group *R* $\bar{3}$ , (Table S1, ESI†). Interestingly, crystals of **1** only formed in the presence of either (NH<sub>4</sub>)<sub>2</sub>SiF<sub>6</sub> or, in comparable yields, (NH<sub>4</sub>)<sub>2</sub>ZrF<sub>6</sub>; no identifiable products were recovered when either Na<sub>2</sub>SiF<sub>6</sub> or NH<sub>4</sub>Cl were employed. Neither NH<sub>4</sub><sup>+</sup> nor SiF<sub>6</sub><sup>2-</sup> (or ZrF<sub>6</sub><sup>2-</sup>) appears in the structure of **1** suggesting possible templating roles for the ion pair, although their exact roles are currently unknown.

The asymmetric unit of **1** contains a mono-deprotonated ligand molecule coordinating to a Cu(II) ion *via* a carboxylate oxygen atom and an indazole nitrogen atom; four equivalent ligand molecules yield a square planar geometry about the Cu(II) ion, Fig. 1. Each Cu(II) ion in **1** is linked to four others *via* HL. Assigning the metal ions as nodes allows the network to be described as a 3-dimensional 4-connected (6<sup>4</sup>.8<sup>2</sup>) NbO-like framework. Close examination revealed **1** to be twofold interpenetrated, however due to the presence of hydrogen bonding interactions between the indazole N–H groups and carboxylate oxygen atoms on the adjacent frameworks, the two interpenetrated networks associate closely and align in register, allowing the unimpeded formation of 1D channels along the crystallographic *c*-axis, Fig. 1 and 2, while the interpenetration blocks any prospective channels parallel to the orthogonal *a* and *b* axes (Fig. S3, ESI†). The larger channels in **1** are hexagonal with cross channel Cu1...Cu1 separations of *ca.* 19.7 Å, corresponding to an accessible pore window of *ca.* 4.7 Å, and are surrounded by small trigonal channels, which are too small to allow significant guest access.

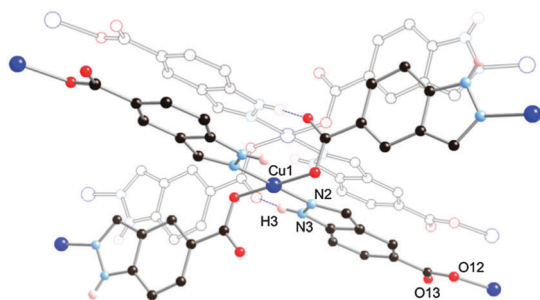
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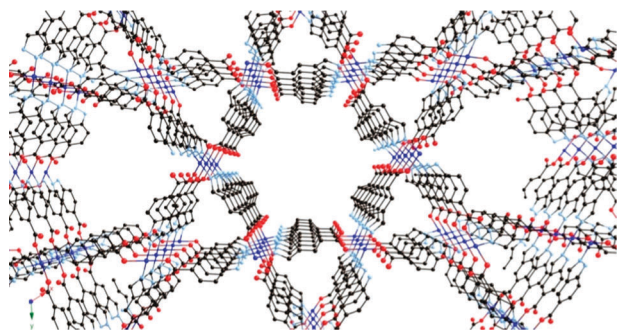
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† Electronic supplementary information (ESI) available: Synthesis and characterisation data for **H<sub>2</sub>L**, thermogravimetric analysis data for **1**, tables of crystallographic refinement data for **1** and **1A**, additional sorption data for **1**, powder diffraction patterns for **1** and **1A**, results of GCMC calculations of **1**. CCDC 894177 (**1**) and 894178 (**1A**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2cc37453f

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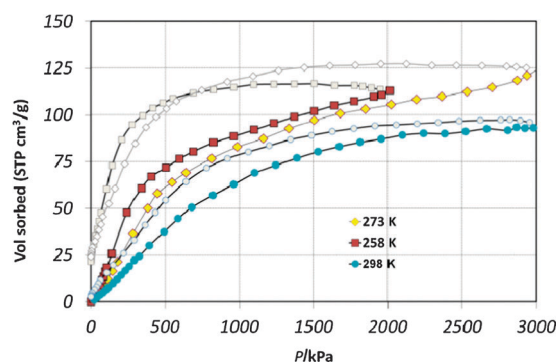
**Fig. 1** Molecular structure of  $[\text{Cu}(\text{HL})_2]$ , **1**, showing Cu1 as a 4-connected node and how adjacent interpenetrated frameworks hydrogen-bond to each other *via*  $\text{N3-H3}\cdots\text{O13}$ . Non-hydrogen bonding hydrogen atoms are omitted for clarity.



**Fig. 2** The interpenetrated 3D network of **1** showing 1D channels down the crystallographic *c*-axis. Hydrogen atoms omitted for clarity.

The large channels account for *ca.* 30% solvent accessible void volume within the unit cell as calculated by PLATON<sup>9</sup> and contain no crystallographically ordered guests. The calculated accessible surface area and pore volume of **1** are  $550 \text{ m}^2 \text{ g}^{-1}$  and  $0.30 \text{ cm}^3 \text{ g}^{-1}$ , respectively.<sup>10</sup> Analysis of the TGA data for **1** reveals an initial weight loss of *ca.* 9% between  $25 < T < 150 \text{ }^\circ\text{C}$  consistent with the loss of the channel constituents, after which a plateau region with no further weight loss is observed until decomposition begins at *ca.*  $310 \text{ }^\circ\text{C}$  (Fig. S4, ESI<sup>†</sup>). A crystalline sample of **1** displayed no visible loss of crystallinity on heating at  $150 \text{ }^\circ\text{C}$  for 2 hours, to give **1A** (the desolvated phase), and this was verified through the collection of a new single crystal dataset which returned near identical data for **1A** *cf.* **1** which were further corroborated by PXRD (Table S1 and Fig. S5, ESI<sup>†</sup>). Heating crystalline samples of **1** in  $\text{H}_2\text{O}$  for several days led to no apparent loss in crystallinity, attesting to its hydrolytic stability.

The presence of large channels in **1** coupled with its thermally and hydrolytically robust nature prompted an examination of gas sorption properties, in particular  $\text{CO}_2$  sorption, to evaluate this PCP's permanent porosity. Desolvation of **1** was achieved by maintaining it at a temperature of  $150 \text{ }^\circ\text{C}$  overnight whilst under dynamic vacuum.  $\text{CO}_2$  isotherms were measured at 258, 273 and 298 K. Inspection of Fig. 3 reveals that the 273 K isotherm has a sigmoidal shape with a point of inflection in the curve at a pressure of approximately 280 kPa; the sigmoidal shape is suggestive of a cooperative effect in the  $\text{CO}_2$  sorption. As the pressure is increased beyond this point the isotherm begins to flatten. At the maximum pressure measured,  $124 \text{ cm}^3$  of  $\text{CO}_2$  (at STP) is sorbed per gram of compound, corresponding to an uptake of 24%.<sup>11</sup> The desorption curve indicates significant hysteresis with over  $100 \text{ cm}^3$  of  $\text{CO}_2$



**Fig. 3** Isotherms for  $\text{CO}_2$  sorption for **1** at 258 K (red squares), 273 K (yellow diamonds) and 298 K (blue circles). The desorption isotherms are indicated by unfilled squares, diamonds and circles.

(at STP) retained per gram of the compound at 507 kPa. The sorption and desorption isotherms recorded at 258 K exhibit a similar shape and indicate slightly greater sorption at a given pressure compared with the 273 K measurement. Hysteresis is again evident within the desorption isotherm at the lower temperature. The 298 K isotherm shows a very gradual increase in  $\text{CO}_2$  sorption with pressure with  $93 \text{ cm}^3$  of  $\text{CO}_2$  (at STP) sorbed per gram of compound at the maximum pressure. The desorption trace indicates that the hysteresis is again apparent but it is far less pronounced at 298 K. Recent reviews have tabulated  $\text{CO}_2$  uptake for a range of PCPs and whilst the  $\text{CO}_2$  uptake here is well below the highest sorbent materials, the amount sorbed compares favourably with the values presented for a large number of PCPs listed, most of which fall in the range 15–50 wt%.<sup>12,13</sup> The isosteric heat of sorption calculated on the basis of the 258 K and 273 K isotherms is unexceptional with a value of  $-17.5 \text{ kJ mol}^{-1}$  at near zero loading (Fig. S6, ESI<sup>†</sup>), falling at the low end of the range of values recently tabulated by Long *et al.* of  $-12$  to  $-48 \text{ kJ mol}^{-1}$  for unfunctionalised pores.<sup>13</sup> From the crystal structure it can be observed that the pore walls are defined by the edges of aromatic rings, rather than the faces, which would be expected to give rise to only weak attractive forces with  $\text{CO}_2$  molecules. Although the Cu(II) ions adopt the square planar geometry, access to the axial positions is prohibited on steric grounds, and as such, no metal-sorbate interaction would be expected.

Following the collection of the high-pressure  $\text{CO}_2$  isotherms, a simulated adsorption isotherm for  $\text{CO}_2$  at 298 K in **1** was generated using Grand Canonical Monte Carlo (GCMC) simulation, details of which are provided in the ESI<sup>†</sup>. As shown in Fig. S12 (ESI<sup>†</sup>), the simulated results show good agreement with the experimental data over the entire pressure range examined. To better understand the location of adsorption sites, the radial distribution functions  $g(r)$  between  $\text{CO}_2$  and the framework atoms in **1** are also plotted (Fig. S13, ESI<sup>†</sup>). From  $g(r)$  it was observed that  $\text{CO}_2$  interacts with the phenyl ring atoms more strongly than the other framework atoms, most likely due to the edge-on arrangement of the rings with respect to the pore walls, allowing best access to indazole carbon atoms C6 and C5. In addition, the isosteric heat of adsorption predicted from simulation is *ca.*  $-15 \text{ kJ mol}^{-1}$  at zero loading, which is in approximate agreement with the experimentally observed zero loading value of  $-17.5 \text{ kJ mol}^{-1}$ .

The successful uptake of  $\text{CO}_2$  prompted an examination of the ability of the compound to sorb other gasses, specifically

methane, nitrogen and hydrogen. Somewhat surprisingly, compound **1** displayed negligible sorption of each of these gases, displaying a maximum uptake at 2500 kPa of less than 15 cm<sup>3</sup> (STP) g<sup>-1</sup> for H<sub>2</sub> across the temperature range 77–273 K (Fig. S8, ESI†), and similarly minimal uptake of N<sub>2</sub> (77 K) and CH<sub>4</sub> (273 K) (Fig. S9 and S7, ESI† respectively). In an attempt to quantify this apparent selectivity, a high-resolution sorption isotherm was measured for CO<sub>2</sub> at 273 K in the range 0.1–121 kPa (Fig. S10, ESI†), however, analysis of the sorption by the Ideal Adsorbed Solution Theory (IAST)<sup>14</sup> method was hampered by the extremely low uptake of methane and nitrogen under the same conditions, and as such, no quantification for selectivity under these industrially relevant conditions was able to be extracted. However, the high resolution CO<sub>2</sub> isotherm displayed a prominent step at ca. 66 kPa, further indicative of a cooperative sorption process.

Several factors have been identified to account for sorption discrimination between these gases in PCPs, including the limiting dimensions of the pores better matching the smaller kinetic diameter of the CO<sub>2</sub> molecules relative to the other gases, and differences in the gases electronic properties *i.e.* quadrupolar moments and polarizabilities, which lead to differing interactions with the host. However, we would not anticipate that the larger channels in **1** would permit such significant size discrimination (kinetic diameter of CH<sub>4</sub> = 3.8 Å, *cf.* pore window 4.7 Å), so the differentiation between CO<sub>2</sub> and CH<sub>4</sub>, N<sub>2</sub> and H<sub>2</sub> by **1** may be enthalpic in origin; the low enthalpy of sorption for CO<sub>2</sub> suggests a plausible mechanism for the sorption selectivity may exist simply in the unusually weakly interacting nature of the pore walls. However, it is evident from the hystereses observed for the sorption profiles of CO<sub>2</sub> in **1**, as well as the clearly defined step in the high-resolution sorption data, that some dynamic behaviour within the framework is induced by the presence of the CO<sub>2</sub> sorbate. Dynamic behaviour in PCP materials may conceivably take several forms<sup>15</sup> including reversible framework collapse; pore-size/shape change; ‘gate-opening’ or other structural rearrangement to allow (better) access to the pores. The verifiably robust nature of **1** would discount framework collapse and significant structural rearrangement, and would tend to suggest a more subtle rearrangement or breathing process is operative in **1**, possibly involving the hydrogen bonding interactions between the interpenetrated frameworks.

In conclusion, we have prepared a novel porous coordination polymer **1** from 1*H*-indazole-5-carboxylic acid, which, in addition to representing the first structurally characterised PCP containing an indazole moiety, is capable of adsorbing 24% CO<sub>2</sub> by weight, and displays substantial hysteresis behaviour. The unusual sorption properties of **1** are probably best explained by a cooperative sorption mechanism. The precise nature of this cooperativity, as well as the utility of related indazole-based ligands in similar systems, are currently under investigation in our group and will be reported in due course.

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