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Chemically blockable transformation and ultrasensitive low-pressure gas adsorption in a non-porous metal organic framework

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Metal organic frameworks (MOFs) are among the most exciting materials discovered recently, attracting particular attention for their gas-adsorption and -storage properties. Certain MOFs show considerable structural flexibility in response to various stimuli. Although there are several examples of 'breathing' MOFs, in which structural changes occur without any bond breaking, examples of transformations in which several bonds are broken and made are much rarer. In this paper we demonstrate how a flexible MOF, $\text{Cu}_2(\text{OH})(\text{C}_8\text{H}_3\text{O}_7\text{S})(\text{H}_2\text{O})\cdot 2\text{H}_2\text{O}$, can be synthesized by careful choice of the organic linker ligand. The flexibility can be controlled by addition of a supplementary coordinating molecule, which increases the thermal stability of the solid sufficiently for direct imaging with electron microscopy to be possible. We also demonstrate that the MOF shows unprecedented low-pressure selectivity towards nitric oxide through a coordination-driven gating mechanism. The chemical control over these behaviours offers new possibilities for the synthesis of MOFs with unusual and potentially exploitable properties.

Over the past decade advances in the science of MOF materials have led to many exciting discoveries^{1,2}. Although there is increasing recognition that non-porous frameworks have a range of potentially interesting and underutilized properties³, gas adsorption and storage in porous solids^{4,5} make up by far the most important potential applications of MOFs. Such uses span technologies associated with energy, environmental remediation and medicine, and the gases involved range from hydrogen^{6,7}, methane⁴, and carbon dioxide^{1,2} to nitric oxide⁸. One unique aspect of MOF materials involves those with highly flexible frameworks⁹ that undergo changes in structure and property on response to a specific stimulus. Flexible frameworks can be broadly subdivided into two categories: materials that are flexible without any bond breaking and materials that undergo responsive bond-breaking and -reforming reactions. Examples of the former type of transformation include the fascinating 'breathing' MOFs¹⁰ and others in which structural changes occur on application of an external stimulus¹¹, such as thermal dehydration^{12,13}. Transformations in which there is a significant change in network connectivity that involves the breaking and making of several bonds are rarer, with fewer examples in the literature^{14,15}. In solids, this is particularly true of changes of three-dimensional (3D) network connectivities, which are less coordinatively labile than their low-dimensional (1D and 2D) counterparts^{16,17}. Such solids make up an interesting and potentially useful class of 'soft porous crystals', and they offer the opportunity to develop new materials with vastly different properties to those currently available¹⁸. It is a significant challenge to design and control materials so they have such transformations, and to harness any interesting properties that arise.

In this paper we report the synthesis of a MOF material that incorporates an organic linker ligand deliberately chosen so that some bonds in the solid are weaker than others, which enables a structural change, stimulated by dehydration, to occur. The transformation involves a significant rearrangement of the bonds in the solid, but without loss of crystallinity. Also, we show that by altering the chemistry through the addition of a blocking ligand (pyridine) to the system we can stop the structural transition, which allows chemical control over the transformation. Addition of pyridine also increases the material's beam stability in an electron microscope to such a degree that direct imaging of the structure is possible using high-resolution transmission electron microscopy (HRTEM), which reveals defects that offer insight into the crystal-growth mechanism.

The dehydrated material shows extremely high selectivity at low pressures (subambient) towards one particular gas, NO, and does not adsorb any of the other common gases measured up to at least 10 bar. The NO-loaded material undergoes controlled NO release on addition of water, which reforms the original hydrated phase and so leads to potential applications as materials for NO storage and delivery in, for example, environmental and medical applications. The central theme of this paper is that the origin of these unusual features (blockable phase transformation, electron-beam stability and ultrasensitive gas adsorption) can be traced back to the choice of ligand in the parent material, and in particular to the possibility of breaking and reforming coordination bonds in the solid without forcing structural collapse. The combination of synthesis based on the ligand choice and the novel properties that result from this choice demonstrate a new way to think about the design of MOF materials.

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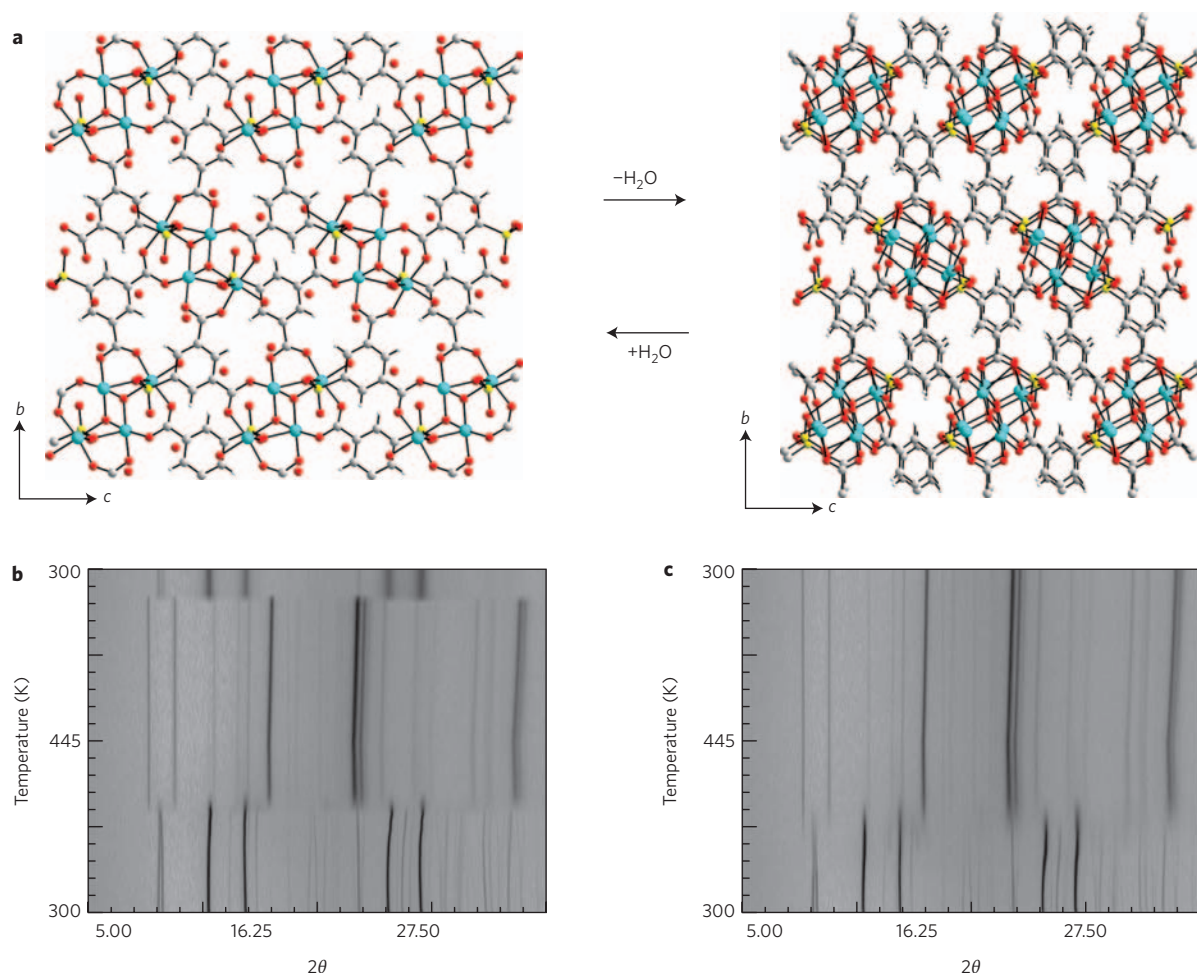


Figure 1 | The dehydration-rehydration transformations of Cu-SIP-3. **a**, Dehydration of Cu-SIP-3 causes a drastic transformation of the framework. Cyan circles = Cu, red circles = O, yellow circles = S, grey circles = C, white circles = H. **b,c**, Variable-temperature powder XRD under moist air (**b**) and under dry N₂ (**c**) clearly show the changes in structure on dehydration (388–409 K under air and 368–405 K under N₂) and also the line broadening associated with the transformation. Data were recorded in steps of 5 K and are displayed here as an artificial 2D ‘film’. On cooling under moist air the reverse rehydration transformation takes place between 329 and 320 K.

Results

One requirement for 3D solids to be capable of radical connectivity change is that the material must contain bonds of different strength (that is, some bonds must be more easily broken and reformed than others); if it does not, it simply falls apart, rather than transforms, as conditions are altered and so there is no topochemical control over the transformation. In the case of binary MOFs made from one metal and one organic linking group, this requires the use of a linker with more than one type of functionality. One such group is 5-sulfoisophthalate, which can build 3D structures via two strongly bonding carboxylate groups and one weaker sulfonate group^{19,20}. This gives potential for structural transformation to occur at the sulfonate group with the metal–carboxylate linkages kept intact.

With this in mind we hydrothermally synthesized a copper sulfoisophthalate MOF, Cu₂(OH)(C₈H₃O₇S)(H₂O)·2H₂O, which we name Cu-SIP-3·3H₂O. The structure was solved using single-crystal X-ray diffraction (XRD) and is shown in Fig. 1a. The material contains a tetramer of copper ions, linked by two three-coordinated hydroxide bridges to form the units shown in Fig. 2a,b, similar to others seen previously²⁰. Two of the four copper ions are five-coordinated by oxygen, and two are six-coordinated. These units are connected by the 5-sulfoisophthalate linkers to form a 3D structure.

Only two of the three oxygen atoms on the sulfonate group are used in framework bonding.

Cu-SIP-3·3H₂O contains three molecules of water per formula unit. Two lie in framework pores and are hydrogen-bonded to framework oxygen atoms. The third is directly coordinated to one of the copper ions in the framework. It has been shown that coordinated water molecules such as this can be removed to leave a coordinatively unsaturated metal ion, which can be used to conduct further chemistry to great effect^{21–23}. However, dehydration of Cu-SIP-3·3H₂O leads to a significant structural transformation with large changes in the connectivity and coordination of the metal ions (Figs 1 and 2). Variable-temperature powder X-ray diffraction patterns (Fig. 1) have been used to probe this and showed three main features. Firstly, a gradual change in peak positions to smaller *d*-spacings occurred on initial warming, caused by the loss of weakly bound pore-water molecules. An abrupt change in the crystal structure then happened at 388–409 K under static air (368–405 K under flowing N₂) through loss of the copper-bound water. As the material cooled down again under moist air the structure rehydrated at between 329 and 320 K, which indicates the reversibility of the transformation. Under dry N₂ no rehydration occurs. Variable-temperature, single-crystal X-ray diffraction experiments confirmed that the three water molecules were removed from

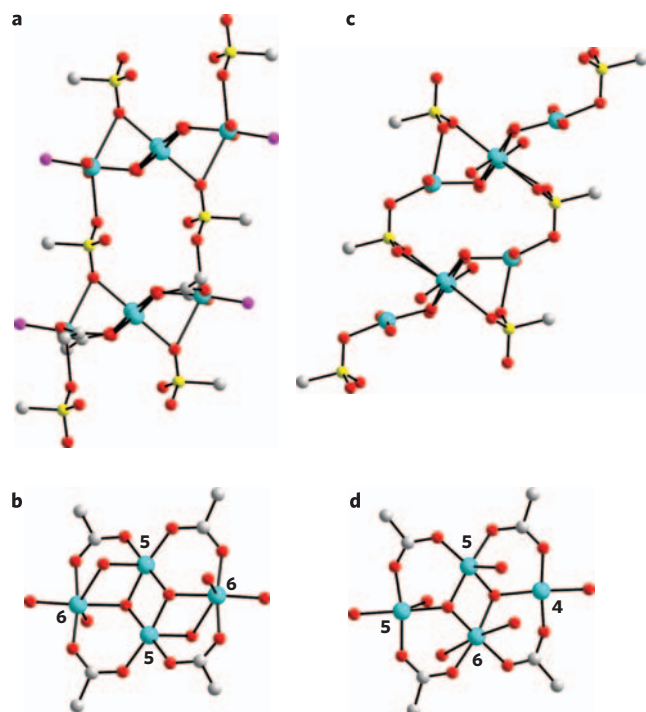


Figure 2 | Large changes in coordination and connectivity on removal of coordinated water (shown as pink spheres). a–d, Removal from the hydrated Cu-SIP-3·3H₂O structures (**a,b**) and the new framework formed (**c,d**). The connectivity of the sulfonate group changes markedly between **a** and **c** and the copper coordination changes from two five- and two six-coordinate for the hydrated structure (**b**) to one four-, two five- and one six-coordinate for the dehydrated structure (**d**). Cyan circles = Cu, red circles = O, yellow circles = S, grey circles = C.

the material at different temperatures. Thermogravimetric analysis supported these conclusions and showed a weight loss of approximately 11% below 500 K in at least two steps, consistent with the different types of water present in the material. The calculated weight loss for the removal of the three water molecules was 12.2%, but variable-temperature XRD during cycling indicated the possibility that the transformation trapped small amounts of water in the sample (see Supplementary Information).

Careful dehydration of single crystals at 500 K followed by single-crystal XRD revealed that the transformation is caused by severe changes in coordination and connectivity in the dehydrated structure (Fig. 2). Despite these changes, single crystals remained intact when heated carefully. On losing the water molecule coordinated to the copper, the previously unbonded oxygen of the sulfonate coordinates to the copper, but to do this other coordination changes have to take place, to leave one four-, two five- and one six-coordinate copper ions (Fig. 2d). Crucially, no changes occur in the carboxylate connectivity during this process. The strong binding of these groups is presumably why the crystallinity of the material remains intact.

Powder XRD indicates that the transition is associated with significant line broadening. This is unsurprising given the rather drastic nature of the reorganization of the material on dehydration. Assuming this arises from domain-size effects, the data suggest an initial reduction to around 40 nm on dehydration followed by a further reduction to about 15 nm on rehydration (see Supplementary Information). This effect is also seen in the single-crystal X-ray diffraction experiments in which the sharpness of the reflections decreases significantly on dehydration, although determination of single-crystal structure is still possible. On

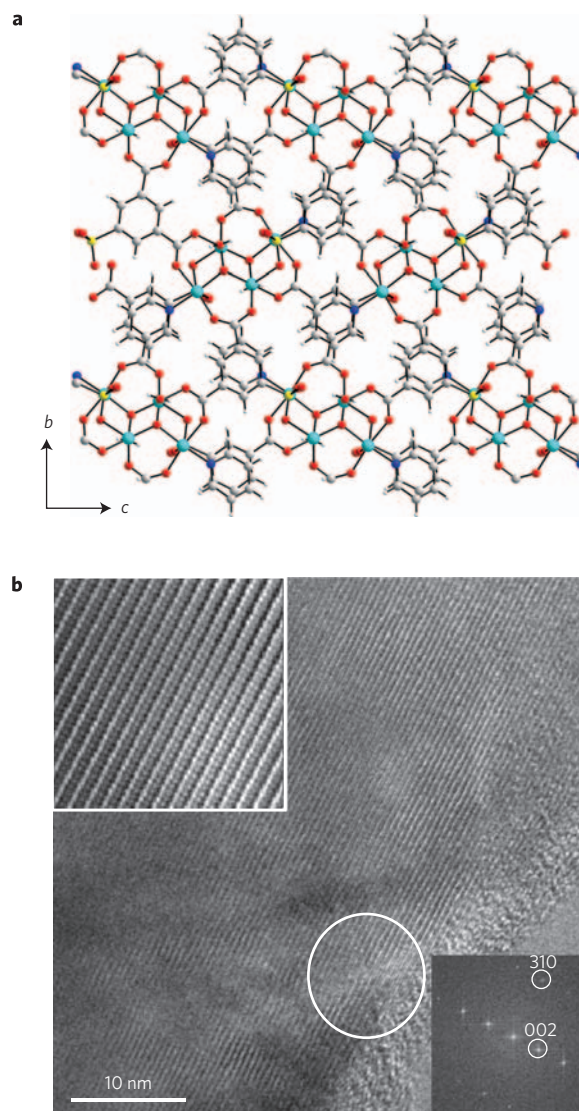


Figure 3 | The structure and electron microscopy of Cu-SIP-3-pyridine·H₂O. **a,** The structure of Cu-SIP-3-pyridine·H₂O is isorecticular with Cu-SIP-3·3H₂O (shown in Fig. 1). The pyridine replaces only the coordinated water molecule. Cyan circles = Cu, red circles = O, yellow circles = S, grey circles = C, white circles = H, blue circles = N. **b,** The HRTEM image of Cu-SIP-3-pyridine·H₂O viewed along the [130] zone axis. The bottom-right inset is a fast Fourier transform (FFT) diffraction pattern indexed to the unit cell determined by single-crystal XRD. The top-left inset shows a computer-created image (by removing the noise) from the FFT diffraction pattern. The area marked by the circle shows an antiphase-like defect.

further rehydration the deterioration of the diffraction pattern is such that the crystal can no longer be termed 'single'; instead, rehydration causes breakdown of the single crystals into multiple, small, but still crystalline, domains.

Diffraction data clearly show that the transformation of the Cu-SIP-3·3H₂O structure is initiated by loss of the water molecule coordinated to the copper ions. To control the transformation we attempted to replace this coordinated water molecule with a pyridine ligand that would be more difficult to remove. Indeed, when pyridine was added to the synthesis mixture a new compound formed in which the coordinated water molecule was replaced by a coordinated pyridine. The structure of Cu-SIP-3-pyridine·H₂O, Cu₂(OH)(C₈H₃O₇S)(C₅H₅N)·H₂O, is very similar to that of Cu-SIP-3·3H₂O (Fig. 3), except that the replacement of water by

pyridine leads to less space in the structure so that only one water molecule, rather than two, can be accommodated in the channels. The larger size of pyridine means that the volume of the unit cell of Cu-SIP-3-pyridine-H₂O is significantly expanded (by ~10%) compared with that of Cu-SIP-3, and to accommodate this large unit-cell expansion there is significant rotation and reorientation of the sulfonate group. However, the overall topology remains unchanged and the two structures can be regarded as isorecticular (that is, they have the same network topology)²⁴.

Thermal treatment of Cu-SIP-3-pyridine-H₂O resulted in full dehydration of the material at approximately 425 K (measured loss 3.7%, calculated 3.7%), but the pyridine was retained by the material so no structural phase transition was observed. Pyridine was not lost until the whole framework had been destroyed at 566 K, almost 100 K higher than that at which this destruction occurred for Cu-SIP-3 itself. Mass spectrometry indicated that oxides of carbon, sulfur and nitrogen were given off at this point, as the organic components of the framework broke down completely. The transformation seen for Cu-SIP-3-3H₂O is effectively prevented by the presence of the pyridine coordinated to the copper ions. This chemical blocking of framework changes is unprecedented.

An important consequence of the increase in thermal stability that results from pyridine inclusion in the structure is the possibility that HRTEM could be used to image the structure directly. The vast majority of MOFs are extremely beam-unstable²⁵ and Cu-SIP-3-3H₂O is no exception. Even with very low irradiation doses (<2 pA cm⁻²) and careful sample preparation, no HRTEM images could be obtained. In contrast, Cu-SIP-3-pyridine-H₂O is reasonably stable under beam irradiation and Fig. 3b shows the sample viewed down the [130] zone axis. On this projection, the structure shows copper-rich (dark) and pyridine (bright) alternating fringes along the [001] axis. Such images confirm the structure and show the presence of defects in the material, information that can lead to a better understanding of properties such as crystal-growth mechanisms (see Supplementary Information)²⁶.

Flexible frameworks display some of their most intriguing properties in the area of gas adsorption^{9,10}. So-called gated adsorption, in which adsorption only takes place above a certain threshold or gate-opening pressure, has received particular attention in recent years^{27–29}. We are especially interested in NO because of its environmental applications in gas separation and its use in NO_x traps for lean-burn engines. Also, NO is an extremely important molecule in biology, and we have used porous solids to store and deliver NO for potential applications, such as in antithrombotics^{30,31} and as NO-releasing materials for topical delivery to human skin³¹. The NO-storage and -delivery materials prepared so far are based on non-flexible porous solids, such as zeolites and ‘rigid’ MOF solids^{31–33}. These materials have no specific selectivity for NO and, in fact, the same materials are often good adsorbents for many of the common gases.

The transformation that takes place on dehydration means Cu-SIP-3 is essentially non-porous, and there is no significant uptake of N₂, H₂, CO₂, CO, N₂O or CH₄ by the material at any point below 10 bar. At very low pressures (<275 mbar), NO is also not adsorbed to any great extent (Fig. 4). However, above a gate-opening pressure of $p_{GO} = 275$ mbar there is a linear portion ($R^2 = 0.9941$) of the isotherm (276–428 mbar) equivalent to a Henry’s law region in a normal non-gated adsorption isotherm. Above this pressure, Cu-SIP-3 continues to adsorb NO until, at 1 bar, the storage capacity of the material is approximately 1.1 mmol NO per gram MOF, equivalent to approximately 0.88 NO molecules per formula unit. This capacity is comparable to that of zeolites and other MOFs that have been shown to store and deliver biologically active quantities of this medically important gas^{31,32}.

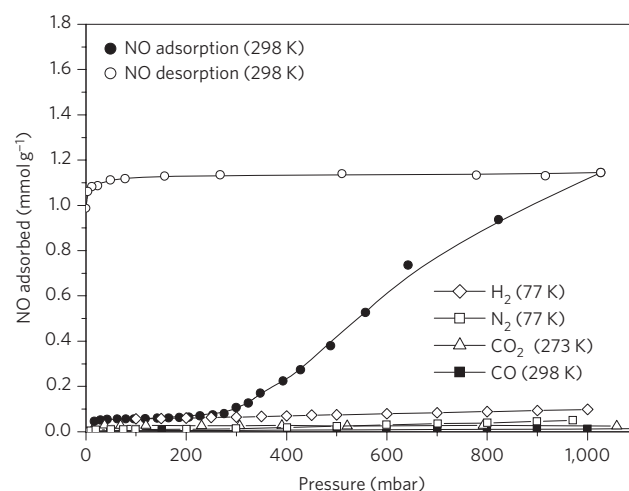


Figure 4 | Adsorption isotherms for the dehydrated Cu-SIP-3 structure for a variety of atmospheres. Only NO (298 K) is adsorbed below ambient pressure, and then only significantly above the gate-opening pressure of ~275 mbar. The desorption isotherm for NO shows the large hysteresis that indicates strong coordination of NO with metals in the framework. No adsorption is seen for CO₂ (273 K), CO (298 K), H₂ (77 K) and N₂ (77 K) up to 10 bar.

On reduction of the NO pressure, Cu-SIP-3 retains NO and shows a large hysteresis between the adsorption and desorption branches of the isotherm (Fig. 4). This feature results from the relatively strong coordination of the gas to metal sites in the structure^{8,33}. This ultraspecific adsorption of NO by Cu-SIP-3 is particularly noteworthy in that it takes place below ambient pressure and with no other gas adsorption, even of seemingly similar gases such as CO, below 10 bar.

As with rehydration, exposure of single crystals of Cu-SIP-3 to NO on the diffractometer leads to break-up of the single crystal into a polycrystalline sample, which precludes the use of single-crystal XRD to determine the structure of the NO-loaded material. The broadening of the powder-diffraction data also does not allow us to use Rietveld analysis to obtain an unambiguous structure of the NO-loaded material.

As NO is a relatively strongly coordinating gas, the large hysteresis in Fig. 4 is explained by its strong interaction with the metal ions present, similar to the expected process for NO binding to accessible metal sites, which has been confirmed by diffraction and infrared spectroscopy^{5,8,31,33}, with Cu–NO bond enthalpies of around 90 kJ mol⁻¹ (ref. 8). When NO is adsorbed by MOFs in which there is no possibility of binding to a metal site, little or no hysteresis is observed. The selectivity towards NO compared with that for the other gases is remarkable. It is evident that the ultraspecific low-pressure adsorption of NO arises directly from the interaction of the gas with the framework of the material. Above the gate-opening pressure, the NO coordinates to the copper sites in the material, which causes a transformation that opens up the framework to further adsorption. Once again, this process can be traced back to the coordinative flexibility of the material, and is likely to be a direct consequence of the presence of some coordination bonds that are more easily broken than others. Exposure of Cu-SIP-3-NO to water vapour leads to release of NO(g), and the original hydrated Cu-SIP-3-3H₂O structure is reformed. This facile release trigger makes Cu-SIP-3-NO a potential NO source for biological applications. The selective adsorption at subambient pressures also has potential applications in gas separation, removal of NO from gas streams and, possibly, in molecular sensing. We note that the dehydrated Cu-SIP-3-pyridine material

does not adsorb any NO (at room temperature, up to 1 bar) after dehydration under the same conditions.

Discussion

The unique properties of the Cu-SIP-3 MOF family (the controllable phase transformation, the increased thermal stability and imaging of the pyridine-containing material and the ultrasensitive low-pressure NO adsorption) can all be traced back to the coordination flexibility in the structure, created by using a ligand with the potential to form both stronger and weaker bonds. The stronger coordination bonds hold the material together and chemical transformation is enabled by the weaker bonds. The properties this feature imparts are novel, and the results we present will have impact on the fundamental design criteria chemists use to tailor and control framework solids. Phase transformations and the flexibility of so-called 'soft porous crystals' offer many opportunities for development, and the ability to control whether such transformations occur or not adds significantly to our design capabilities. Increasing the thermal stability of MOF materials to enable direct imaging using high-resolution electron microscopy by the approach we describe has the potential to revolutionize our understanding of the defects present and crystal-growth mechanisms in these solids. The hierarchical control of the phase transformation using pyridine is reminiscent of the use of non-covalent interactions to increase the stability of chiral frameworks³⁴. Finally, we have demonstrated that the flexibility in coordination chemistry shown by the Cu-SIP-3 MOF can also lead to step changes when it comes to the design of materials for specific applications. Our long-standing interest in NO-storage and -delivery applications in medicine has driven our research to engineer a material that has interesting and highly selective sorption properties for this one particular gas. The selective, low-pressure, reversible adsorption demonstrated in this work relies on the ability of the Cu-SIP-3 MOF material to change in response to the coordination of NO and H₂O. This illustrates how important the coordinative flexibility of a material is, and how it can be exploited to prepare materials for a specific function.

In summary, the work we present here highlights the possibilities available to chemists in the MOF field by virtue of the choice of a coordinatively flexible ligand. Bonding motifs of different coordinating strengths in the same linker offer many opportunities to design advanced materials that show new and interesting dynamic flexibility and properties.

Methods

Synthesis and crystal structure of Cu-SIP-3·3H₂O. In a typical synthesis, Cu(NO₃)₂·3H₂O (Alfa Aesar 98%, 2.42 g) and 5-sulfoisophthalic acid sodium salt (NaH₂SIP, Aldrich 95%, 2.68 g) were dissolved in a 12 ml EtOH–H₂O (50:50) solution. The mixture was heated in a 50 ml Teflon-lined autoclave at 383 K for five days. The crystals were cleaned by sonication in a 100 ml solution (EtOH–H₂O) for five minutes and then filtered. The aqua blue crystals were collected and dried in air. Cu₂(OH)(C₈H₃O₇S)(H₂O)·2H₂O, *M* = 440.3, monoclinic *P*2₁/*n*, *a* = 7.2806(5), *b* = 18.2421(11), *c* = 10.1075(6) Å, β = 94.886(1)°, *V* = 1,337.53(15) Å³, *Z* = 4, λ = 0.71030 Å, full-matrix least-squares refinement on *F*² converged to *R* = 0.0423 (3,140 observed data, θ_{max} = 30.94°), *wR*2 = 0.1126 (3,998 data), *S* = 1.037, *Npar* = 217 (Cambridge Crystallographic Data Centre (CCDC) number 733479).

Crystal structure of Cu-SIP-3 (dehydrated), Cu₄(OH)₂(C₈H₃O₇S)₂. *M* = 772.5, monoclinic *P*2₁/*n*, *a* = 13.833(7), *b* = 19.434(12), *c* = 12.102(7) Å, β = 139.16(3)°, *V* = 2,128(2) Å³, *Z* = 4, λ = 0.6911 Å, full-matrix least-squares refinement on *F*² converged to *R* = 0.0513 (2,423 observed data, θ_{max} = 26.01°), *wR*2 = 0.1551 (4,539 data), *S* = 1.038, *Npar* = 343 (CCDC number 733478).

Synthesis and crystal structure of Cu-SIP-3-pyridine. In a typical synthesis, Cu(NO₃)₂·3H₂O (Alfa Aesar 98%, 2.42 g), 5-sulfoisophthalic acid sodium salt (NaH₂SIP, Aldrich 95%, 2.68 g) and pyridine (Alfa Aesar 98%, 0.41 g) were mixed with a 12 ml EtOH–H₂O solution (50:50) in a 50 ml Teflon-lined autoclave. The mixture was heated at 383 K for five days and then cooled slowly to room temperature. The crystals were sonicated in a 100 ml EtOH–H₂O solution for five minutes, and then filtered. The blue crystals were collected and dried in air. *M* = 483.4, monoclinic *P*2₁/*n*, *a* = 7.492(4), *b* = 18.289(9), *c* = 10.942(6) Å,

β = 90.778(7)°, *V* = 1,499.2(13) Å³, *Z* = 4, λ = 0.6942 Å, full-matrix least-squares refinement on *F*² converged to *R* = 0.0734 (2,509 observed data, θ_{max} = 30.94°), *wR*2 = 0.2068 (4,236 data), *S* = 1.074, *Npar* = 243 (CCDC number 733480).

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Author contributions

B.X. and R.E.M. conceived and designed the experiments, B.X. completed the synthesis, P.S.W, P.J.B., D.S.W and J.E.W performed the single-crystal diffraction, L.P and J.S.O.E completed the powder-diffraction experiments, B.X., A.J.F., X.Z and K.M.T. completed the adsorption and W.Z. performed the electron microscopy.

Additional information

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