

Abstract: SIFSIX-14-Cu-i belongs to a family of metal-organic materials (MOMs) with exciting gas sorption properties and high technological impact. We report CO₂ adsorption isotherms for SIFSIX-14-Cu-i revealing very high uptake combined with CO₂ selectivity. Importantly, the isotherms show distinct inflection points that result from CO₂-induced structural transformations and that can be modulated by the CO₂ uptake quantity. The observed behaviour directly relates to the unique structure of this azopyridine-stabilised compound and gives rise to the highest known working capacity for CO₂ uptake between 0.1 and 1 bar. Further, we highlight synthetic procedures for the reversible transformation of SIFSIX-14-Cu-i to a non-porous hydrated form, and exploit the porous ⇔ non-porous phase transition for instantaneous, moisture-mediated CO₂ release.

The use of neutral, linear ditopic N-donor ligands, mononuclear metal centres, and charged inorganic anions, such as hexafluorosilicate ions (SiF₆²⁻), provides a simple, rational and cheap method for the synthesis of microporous metal-organic materials such as the SIFSIX family.[1-6] SIFSIX materials are landmark compounds in the storage of CH₄ and CO₂.[5,7] They reveal exceptionally high selectivity for CO₂ over N₂, and can be used for separations of small-molecule hydrocarbons[8,9] and other gaseous adsorbates.[10] SIFSIX MOMs are generally based on “pillared sheet” pcu-type networks whereby ligand-extensions can lead to isoreticular homologues and inter- or non-interpenetrated variants with tailored pore dimensions.[11]

CO₂ adsorption in such materials is particularly important in the context of pressing environmental concerns and critical future energy demands.[12] In microporous materials of this kind, ideal performance implies a strong selectivity for CO₂ over other gases, high volumetric uptake, and facile, low-energy recovery of the adsorbed CO₂. MOFs and other microporous materials with unsaturated metal centres (UMCs) or pendant amino functionalities often show high selectivities, but require elevated energies for CO₂ release and regeneration of the adsorbent.[13-14] SIFSIX MOMs do not have UMCs, but achieve exceptional selectivities through small, tailored pore diameters which optimise the degree of contact between the adsorbate and the adsorbent surface.[15] Some innovative approaches to tackle this problem have been reported, utilizing rational design to overcome these energetic difficulties.[16-18] With these considerations in mind, we identified the 4,4’-azopyridine (azpy) stabilised MOM [Cu(azpy)₂(SiF₆)] (SIFSIX-14-Cu-i), as an optimal material for CO₂ adsorption as it possesses the following structural and electronic attributes – (i) an electron-rich N=N backbone associated with the 4,4’-azopyridine ligand to enhance CO₂-surface interaction, (ii) a ligand sufficiently long enough to allow a high CO₂ uptake capacity, and (iii) an interpenetrated framework structure to restrict the effective pore diameter.[19,20] Here, we report the first study focusing on the CO₂ adsorption behavior in SIFSIX-14-Cu-i. The resulting isotherms, are characteristic for a structural bi-stability giving rise to a CO₂ uptake-structure relationship that is mediated by the CO₂ uptake quantity. This structural effect results in inflected isotherms and leads to the highest known working capacity for CO₂ sorption between 0.1 and 1 bar. Further, we find that SIFSIX-14-Cu-i shows a reversible porous-to-non-porous transition, which can
be harnessed to release loaded CO$_2$ on demand on exposure to water as a stimulus.

During attempts to synthesise SIFSIX-14-Cu-i from MeOH/H$_2$O solvent mixtures, we noticed that previously established synthetic methods for other Cu-SIFSIX materials, only led to the formation of the hydrated sq network in [Cu(H$_2$O)$_2$(azpy)$_2$]SiF$_3$·H$_2$O (H$_2$O-SIFSIX-14-Cu-i). However, phase-pure quantities of SIFSIX-14-Cu-i were synthesised by heating copper(II) hexafluorosilicate and 4,4′-azopyridine in dry methanol in a closed container, using a modified literature procedure (Sl).[19] Appropriately-sized crystals, suitable for single-crystal X-ray diffraction studies were grown by layering techniques using DMSO and MeOH solvents. The resulting crystal structure of SIFSIX-14-Cu-i contains constitutional MeOH guests, and the identified framework is consistent with previously reported SIFSIX-Cu homologues, and the reported network in SIFSIX-14-Cu.[15] We find the isolated MOM crystallises in the tetragonal crystal system in the space group $I4/m$ with unit cell axes lengths of 13.0690(3) and 8.3940(3) Å (SI). Our structural analysis confirms the doubly-interpenetrated nature of the compound (Figure 1). The square-grid motif in the structure is characterised by Cu(II)-N bond distances of 2.0201(25) Å involving the equatorially binding azpy ligands. The pillaring hexafluorosilicate anions that bind in the apical positions of the Cu(II) centres gives rise to a Cu-F bond distance of 2.4888(34) Å. Thus, the open-framework topology of SIFSIX-14-Cu-i differs significantly from the non-porous sq structure of H$_2$O-SIFSIX-14-Cu-i which to some extent may be regarded as an ionisation isomer of the former structure. In H$_2$O-SIFSIX-14-Cu-i two axially coordinated H$_2$O ligands occupy the Jahn-Teller elongated positions on each Cu(II) centre. Infinite, positively charged, square grid-like sheets with the composition [Cu(H$_2$O)$_2$(4,4′-azpy)$_2$]$_{2m}$ are charge-balanced by SiF$_6^{2-}$ ions, which locate in the spaces between interpenetrating sheets (Figure 1c,d). The hexafluorosilicate ions interact with the coordinated water molecules (F-O distance: 2.6826(17) Å) and constitutional pore water molecules (F-O distance: 2.7274(49) Å), forming an intricate H-bonded network and resulting in a stable, denser, non-porous structure.

Gas sorption experiments were carried out on SIFSIX-14-Cu-i and H$_2$O-SIFSIX-14-Cu-i after activation under high vacuum at 30 °C for 24 h (Figure 2 & SI). N$_2$ and CO$_2$ sorption experiments on H$_2$O-SIFSIX-14-Cu-i confirmed that it is a non-porous material with negligible gas uptake (BET surface area of ca. 3 m$^2$/g). In contrast, the N$_2$ adsorption isotherm for SIFSIX-14-Cu-i at 77 K shows steep micropore adsorption at low partial pressure. The compound is characterised by a BET surface area of 435 m$^2$/g and a micropore volume of 0.16 cc/g as calculated using the DFT method.[22] These values are lower but consistent with those reported for SIFSIX-2-Cu-i (735 m$^2$/g BET surface area and 0.26 cc/g micropore volume), a homologous MOM that is stabilised by bispyridylethylene linkers.[7] CO$_2$ sorption experiments on SIFSIX-14-Cu-i revealed high low-temperature uptake, with similar isotherms to the reported dipipyridylethene-based analogue, SIFSIX-Cu-2-i. Calculations on SIFSIX materials conclude that the adsorption mechanism is based on the relatively strong interactions between the partial positive charge on the CO$_2$ carbon atom and the partial negative charge on the electronegative equatorial fluorines of the SiF$_3^{2-}$ pillars.[7]

However, a number of remarkable features that distinguish this compound from homologous materials in the SIFSIX series as well as other benchmark MOFs for CO$_2$ adsorption were observed. On measuring CO$_2$ isotherms across a range of temperatures, a distinct step in the isotherms was observed, becoming more pronounced at higher P(CO$_2$) at higher temperatures. In terms of adsorption capacity, 1 cc of SIFSIX-14-Cu-i adsorbs 131.7 cc of CO$_2$ at 1 bar at 298 K. This value compares very well with other benchmark adsorbents for CO$_2$ capture, such as Zeolite 13X,[23] SIFSIX-2-Cu-i,[24] MIL-101,[21,24] and MIL-68.[16] On the other hand, due to the inflection in the isotherm, the CO$_2$ quantity adsorbed at 0.1 bar is very low. In fact, of the listed benchmark materials only MOF-177[27] and MIL-101(Cr)[28] (SI), which are both mesoporous MOFs, absorb less CO$_2$ in this pressure range. Thus, the observed change in the sign of the isotherm curvature results in an exceptionally high working capacity of 114.3 cc/cc between 0.1 and 1 bar. This is to the best of our knowledge the highest reported CO$_2$ working capacity in this pressure range and thus, renders SIFSIX-14-Cu-i an interesting material for use in pressure swing adsorption (PSA) technologies. SIFSIX-14-Cu-i shows no significant adsorption of N$_2$ at 293 K (SI). Using the Henry coefficients of the corresponding CO$_2$ isotherm, we calculate very high experimental CO$_2$/N$_2$ selectivities of 108 and 335 corresponding to fitted curves of the pre-infection and post-infection parts of the CO$_2$ isotherm (at 293 K), respectively.[29]

The inflection in the CO$_2$ isotherms implies a structural framework transition upon which a ‘closed framework’ with low CO$_2$ uptake capacity opens up to form an ‘open framework’ structure with a high CO$_2$ storage capacity. The transition occurs...
over a very small pressure range and is triggered by the adsorption of a specific amount of CO\(_2\). The onset of the inflection is temperature-dependent and occurs at higher pressures for isotherms that were recorded at higher temperatures. The reversibility of the uptake mechanism is assumed as the adsorption and desorption curves are superimposed and no differences are observed after 15 measurements without activation (SI). The reversibility is further consistent with the calculated isosteric heats of adsorption. Calculations using a Clausius-Clapeyron treatment based on the 278, 293, and 308 K isotherms, give moderate values that vary between 35-37 kJ/mol and which are expected to translate to reversible physisorption phenomena.\(^{[29]}\) Through computation of the derivative of the experimental isotherms and expressing these as a function of the number of CO\(_2\) molecules per the unit cell, we determine that at the inflection point, 1.5 CO\(_2\) molecules are accommodated per unit cell in the structure of SIFSIX-14-Cu-i (Figure 2b). From this we infer that initial adsorption of CO\(_2\) stabilises a framework modification that is more amenable to CO\(_2\) uptake than the empty framework. Gating,\(^{[30]}\) breathing,\(^{[31]}\) and swelling phenomena\(^{[32]}\) can be ruled out on the basis of the absence of hysteretic desorption. The azpy ligand is a single aromatic system, and therefore the effect of rotation about the Cu-N bonds is reflected across the entire ligand. This, together with the characteristics of the desorption isotherms, and the similarity of powder X-ray diffraction (PXRD) patterns for the activated (‘closed’) and MeOH-included (‘open’) samples of SIFSIX-14-Cu-i (SI), lead to the conclusion that the relevant structural change is associated with a particular ordering of the azpy ligands defining the channel axis after guest adsorption and leading to more accessible voids. A crystallographic determination of the channel diameter (SI) indicates an effective pore diameter of ca. 3.6 Å in the structure, a value sufficiently close to the kinetic diameter of CO\(_2\) (3.3 - 3.9 Å) for minor changes in ligand orientation to have marked effects.\(^{[23]}\) On the basis of the evidence presented, we suggest a simple parallel ordering of ligands to the channel axis, or a stabilisation of suitable non-parallel ligand conformations (subject to the complication that there are no distinct ‘cages’ in SIFSIX-14-Cu-i, because of the emergence of the channels from framework interpenetration).\(^{[24]}\) We determined the difference in the free energies between frameworks before and after the inflection using the method developed by Coudert \textit{et al.} (SI).\(^{[35]}\) The resulting Δ\(F_{\text{host}}\) value is equal to 2.7 kJ/mol and agrees well with the predicted energies of the encountered structural transition.

As with all Cu-SIFSIX structures, the title compound SIFSIX-14-Cu-i is susceptible to hydrolytic degradation in the presence of H\(_2\)O. However here, this hydrolytic instability can be utilized to trigger a well-defined phase transition - a structural re-arrangement that is more severe than the formerly outlined CO\(_2\)-mediated re-ordering. The H\(_2\)O-initiated transformation produces H\(_2\)O-SIFSIX-14-Cu-i upon which the entire quantity of the captured CO\(_2\) is instantaneously released on demand. Importantly, the rearrangement is reversible, thus rendering SIFSIX-14-Cu-i as a stimulus-responsive material that can be recycled.

On exposure to air under ambient humidity, one notices a green-colourisation of the original red/brown crystalline material, whereby SIFSIX-14-Cu-i converts quantitatively to H\(_2\)O-SIFSIX-14-Cu-i over a time period of few hours (SI). A more rapid structural transition forming the corresponding non-porous structure can be triggered through the addition of liquid H\(_2\)O and is associated with an instant release of the captured CO\(_2\). The conversion can be monitored by PXRD measurements. The phase transition entails a large-scale structural re-ordering, involving a substitution of Cu-F bonds with Cu-O bonds, migration of SiF\(_4^2-\) ions into voids, and an overall change in the mode of interpenetration, and a total reorganisation of networks involving the breaking and re-forming of Cu-N bonds. This observation agrees very well with previous conducted water vapour sorption studies.\(^{[19]}\)

The important regenerative, reversible transformation from the non-porous H\(_2\)O-SIFSIX-14-Cu-i phase to SIFSIX-14-Cu-i was achieved by heating H\(_2\)O-SIFSIX-14-Cu-i in MeOH. Methanol effects a transformation by removing the kinetically labile, Jahn-Teller elongated, axial H\(_2\)O ligands from the Cu(II) centres. This destabilises the H-bonding network that holds the SiF\(_4^2-\) ions in place in the square pore windows by removing the axially coordinated H\(_2\)O groups that participate in H···F interactions. As a consequence, the SiF\(_4^2-\) ions migrate to bridge adjacent Cu(II) centres, and force a reconfiguration of the network into a porous 3D structure. The reverse conversion occurs when H\(_2\)O molecules bind to axial positions on the Cu(II) centres in the dry 3D network: SiF\(_4^2-\) ions are displaced, occupy H-bonded positions in the pore windows, and the non-porous 2D framework is formed – this is the most stable arrangement in wet conditions. Hence the 2D ⇌ 3D transformation occurs reversibly with the introduction or removal of H\(_2\)O acting as a stimulus.

![Figure 3: Pressure versus time for the release of loaded CO\(_2\) from SIFSIX-14-Cu-i. Excess liquid water was allowed to make contact with the sample at \(t = 210\) s.](image-url)
Unlike many of the paradigm-defining recyclable MOFs, the SIFSIX-14-Cu-i – H₂O-SIFSIX-14-Cu-i pair represents a system of two distinct structures both of which contain identical (non-solvent) components; in the process of converting one to the other, no building blocks need to be re-added. In preceding literature, MeOH has been shown to effect the removal of coordinated H₂O moieties from Cu(II) – N-donor coordination polymers. Coordination polymers of this kind are also known to undergo changes in structure and porosity on dehydration. In agreement with the translational scale of the molecular re-arrangements that facilitate the SIFSIX-14-Cu-i ⇄ H₂O-SIFSIX-14-Cu-i transition, we were unable to observe any evidence of the transformation proceeding in a single crystal – single crystal fashion under the applied conditions. The samples obtained after one conversion-reconversion cycle are phase pure as characterized by PXRD, but the system is limited by some loss of yield due to leaching of ligand into MeOH (SI).

The very high CO₂ uptake capacity of SIFSIX-14-Cu-i and the contrasting non-porous nature of H₂O-SIFSIX-14-Cu-i, in combination with the facile reversible transition between the compounds, are properties that we combined to develop a stimulus–responsive system for the instantaneous release of large volumes of CO₂. Thus, samples of SIFSIX-14-Cu-i were evacuated, saturated with CO₂, exposed to ambient air for a few seconds, and sealed in a flask. On contact with liquid H₂O, a large increase in CO₂ pressure was observed (Figure 3). Upon addition of a small quantity of MeOH and heating, H₂O-SIFSIX-14-Cu-i could be reverted to SIFSIX-14-Cu-i and reused (SI). We note that moisture has been used as a stimulus for mechanical and displacement-based release of adsorbates from MOFs. However, moisture-triggered release from H₂O-SIFSIX-14-Cu-i represents a landmark in that CO₂ is forcibly excluded from the framework, leading to significantly faster release than would be seen by simple diffusion or displacement processes. Further, the large differences between the CO₂ sorption capacities of the porous and non-porous forms, lead to significantly larger gas uptake/release volumes in comparison to those of previously described materials.

The key characteristics of the presented reaction system are summarized in Scheme 1. In conclusion, we report excellent CO₂ adsorption and desorption characteristics for SIFSIX-14-Cu-i. Uptakes at 1 bar and at room temperature are high, and a high selectivity for CO₂ over N₂ is observed. Importantly, we note that the adsorption isotherms are inflected, providing evidence for framework ordering mediated by the adsorbed CO₂ molecules. This effect results in the highest reported CO₂ sorption capacity between 0.1 and 1 bar. SIFSIX-14-Cu-i and the nonporous coordination polymer H₂O-SIFSIX-14-Cu-i are easily interconvertible. This reversible conversion can be used for the fast, moisture-triggered mechanical release of adsorbed CO₂.

Acknowledgements

The authors thank the Science Foundation Ireland (13/IA/1896) and the European Research Council (CoG 2014–647719).

Keywords: CO₂ capture • metal-organic frameworks • porous materials • coordination chemistry • copper
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High and stimuli-responsive CO₂ sorption characteristics of the metal-organic material SIFSIX-14-Cu-i are modulated through structural re-organisations leading to an exceptional high working capacity between 0.1 and 1 bar. A reversible H₂O-triggered transition to a non-porous phase allows the CO₂ release on demand and facilitates the recyclability.