Spin-Crossover Modification through Selective CO$_2$ Sorption

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⑤ *Supporting Information*

ABSTRACT: We present a spin-crossover Fe^{II} coordination polymer with no permanent channels that selectively sorbs CO$_2$ over N$_2$. The one-dimensional chains display internal voids of ~9 Å diameter, each being capable to accept one molecule of CO$_2$ at 1 bar and 273 K. X-ray diffraction provides direct structural evidence of the location of the gas molecules and reveals the formation of O=C=O(δ^-)···π interactions. This physisorption modifies the spin transition, producing a 9 K increase in $T_{1/2}$.

The design of stimuli-responsive materials is currently attracting considerable interest in view of their potential applications as chemical switches, memories, or molecular sensors upon application of an external stimulus.[1] A major source for these dynamic materials is provided by coordination polymers,[2,3] formed by metal ions or clusters which are connected by organic ligands into networks that are periodic and crystalline. Magnetic metal–organic frameworks (MOFs)[4] based on molecule-based magnets or spin-crossover (SCO) complexes have been used for this purpose.

The use of an external stimulus to affect the magnetic properties of a magnetic MOF has been recently explored,[5] especially the effects of chemical stimuli. Most commonly this involves the use of solvent guest molecules (H$_2$O, MeOH, aromatic molecules, etc.) that can penetrate the pores inducing changes in the crystal structures.[6,7] However, adsorbed gas molecules (H$_2$, N$_2$, CO$_2$, etc.) do not appreciably interact with the magnetic host network, thus causing no effects on the magnetic ordering or the spin transition temperature. In fact, modification of the magnetic ordering of a porous magnet through gas sorption has only been achieved in a Cu MOF in which the presence of CO$_2$ molecules in the pores causes an increase in T_N from 22 to 29 K,[8] whereas no effects have been reported in SCO MOFs. The latter materials are more interesting from an application point of view, since the SCO phenomenon can occur at higher temperatures, and even at room temperature, which may lead to an interplay of these properties.[9]

Our strategy to obtain a SCO coordination polymer whose properties can be affected by gas sorption consists in the use of flexible organic ligands to synthesize dynamic frameworks that can respond to an external stimulus. This contrasts with the most common strategy that involves the use of rigid ligands to bridge

Scheme 1. Chemical Structure of btzx Ligand (Arrows Indicate Possible Rotational Motion of the Phenyl Ring)
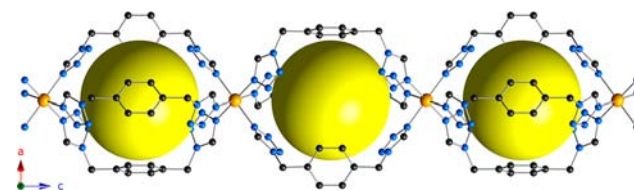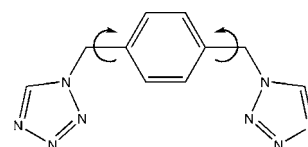

Figure 1. Crystal structure of compound **1** viewed along the *b*-axis. The ClO$_4^-$ anions and hydrogen atoms have been removed for clarity. Key: Fe, orange; C, gray; N, blue. The yellow spheres (diameter of 9 Å) are placed in the structure to represent the empty space of the internal voids.

between the metal nodes, which leads to robust and rigid frameworks with the formation of pores.[10] The main disadvantage of the use of flexible linkers arises from the difficulty in forming porous materials. However, we recently showed that the presence of pores is not a requirement to tune magnetic properties through gas sorption.[11]

Controlled reaction of Fe(ClO$_4$)$_2$·xH$_2$O and 1,4-bis(tetrazol-1-ylmethyl)benzene (btzx, Scheme 1) affords blocked-shaped crystals of [Fe(btzx)$_3$](ClO$_4$)$_2$ (**1**) after several hours. Structural analysis of **1** in the low-spin (LS) and the high-spin (HS) states were determined using the same single crystal at 120 and 240 K, respectively (see Supporting Information). In both states, **1** is composed of [Fe(btzx)$_3$]$^{2+}$ units that form linear chains that run parallel to the crystallographic *c*-axis (Figure 1). These chains are packed as would be expected for close packing of cylinders, separated by ClO$_4^-$ counterions (Figure S13), affording a framework with no permanent channels (space group $P6_3/m$). Interestingly, the cationic chains display internal voids with Fe···Fe distances of 11.5752(9) Å at 120 K and 11.7881(12) Å at 240 K. The void volumes were estimated using PLATON to be 11.8% (at 240 K) and 10.8% (at 120 K) of the unit cell (discrete voids of 132 and 117 Å^3, respectively). Remarkably, no solvent molecules
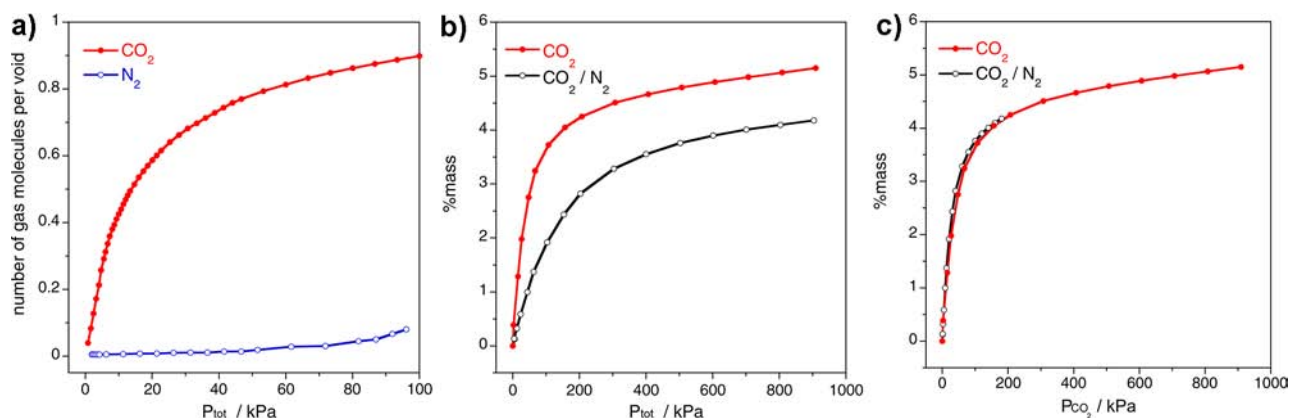
Figure 2. (a) CO_2 (filled red) and N_2 (empty blue) adsorption isotherms on **1** at 273 and 77 K, respectively. (b,c) Adsorption isotherms at 298 K of a 20/80 binary mixture of CO_2/N_2 (empty black) and pure CO_2 (filled red). Panel (b) is plotted versus total pressure (P_{tot}), while (c) is plotted versus CO_2 partial pressure (P_{CO_2}).

are present in these cavities,[12] as demonstrated by thermogravimetric (Figure S5) and SQUEEZE analyses.[13]

Each Fe^{II} center (which lies on the three-fold axis) is coordinated by six tetrazole nitrogen atoms from six *syn*-btzx ligands in an almost perfect octahedral environment (Table S2). At 120 K, all Fe−N distances are 1.996(4) Å, while these are 2.160(6) Å at 240 K, which are in the expected range for Fe−N distances at LS and HS, respectively, in Fe−tetrazolate systems.[14] This change in distance corresponds to a 8% decrease of the bond length upon the transition. In addition, the change in bond distances is accompanied by a color change of the crystal from pink (120 K) to colorless (240 K), further confirming the different spin states of the Fe^{II} centers.

Since the framework of **1** possesses flexibility in rotation through the $C_{aromatic}-C_{methylene}$ bonds of the btzx ligand, we have considered its relevance in terms of gas uptake and selectivity despite the lack of permanent channels connecting the internal voids. Gas adsorption studies on organic molecular solids[15] and metallocycles[16] containing internal voids showed that gas molecules can enter the solids through molecular motion of the host,[17] which is likely to occur in this case. A convenient way to study the solid−gas adsorption properties consists in evaluating the single-component gas adsorption isotherms. As shown in Figure 2a, single-component isotherms are applied to determine loading capacities of N_2 (77 K) and CO_2 (273 K) and significant differences can be observed between the gas sorption isotherms of these two gases. Importantly, **1** exhibits a preferential adsorption of CO_2 over N_2. In fact, N_2 molecules remain nearly unadsorbed even at low temperatures, whereas almost one CO_2 molecule is adsorbed per void at 273 K and 100 kPa. This is likely due to the larger kinetic diameter of N_2 compared to CO_2, and the large polarizability and quadrupolar moment of the CO_2 molecules, which result in a stronger interaction with the cationic framework.[18]

To further demonstrate the preferential adsorption of CO_2 over N_2 and dismiss the possible facilitated diffusion effect due to the different temperatures, single-component adsorptions of CO_2 and N_2 have been measured at the same temperature (298 K, see Figure S6). In these gravimetric adsorptions the same preferentiality is observed even at higher pressures. Unambiguous confirmation that **1** selectively sorbs CO_2 over N_2 was performed by evaluating the actual sorption capacity in a mixture of gases, which can provide experimental evidence of the sorption preference.[19] Figure 2b,c shows the binary gas-

adsorption isotherm for a 20/80 partial pressure mixture of CO_2/N_2 (black) compared to pure CO_2 isotherm (red) at 298 K up to 10 bar. The gas sorption in the mixture is in perfect agreement with CO_2 being the unique molecule sorbed, as the sorption isotherm in the mixture is equivalent to that of pure CO_2 when comparing the partial pressure of CO_2 (Figure 2c), indicating that CO_2 uptake is a function of P_{CO_2} rather than the total pressure (P_{tot}) for these mixtures. Hence, we unequivocally conclude that **1** preferentially absorbs CO_2 over N_2 with a selectivity close to 100%, and the presence of N_2 just acts as a diluting agent.

The isosteric heat of adsorption for CO_2 (Figure S8) was calculated from the Clausius−Clapeyron equation using adsorption data collected at 273, 283, 298, 313, and 333 K to quantify the adsorption affinity for CO_2. The isosteric heat of adsorption at zero coverage was estimated to be 21.2 kJ/mol and remains nearly constant upon increasing CO_2 uptake (20−25 kJ/mol). The calculated heat of adsorption on **1** is within the typical range for physisorption of CO_2 on a MOF.[20] Thus, as expected, the **1**−CO_2 interaction is mainly physisorptive in nature without significant chemical association. In addition, this low value might result from the compensation for the rearrangement of the framework for the CO_2 molecules to enter the crystal. Thus, although the energy of the system decreases when guest molecules are accommodated in the framework, the required deformation of the host implies an energetic penalty.

Magnetic susceptibility measurements were performed on a polycrystalline powder of **1** in the temperature range 2−300 K at 1 K·min^{-1} under an applied magnetic field of 0.1 T. Compound **1** displays a cooperative magnetic and chromatic thermal-induced spin transition centered at 200 K (Figure 3). At room temperature the $\chi_M T$ value is typical of Fe^{II} compounds in the HS state (3.7 emu·mol^{-1}·K), whereas at low temperatures a residual $\chi_M T$ value of 0.3 emu·mol^{-1}·K is observed, corresponding to a small fraction (∼8%) of HS Fe^{II}. The subsequent warming mode reveals the occurrence of a thermal hysteresis loop of 4 K wide (transition temperatures: $T_{1/2}\downarrow$ = 200 K and $T_{1/2}\uparrow$ = 204 K). Interestingly, it is surprising to observe a cooperativity in the SCO process, despite the fact that the distance between Fe centers is >10 Å.

We have studied the effect of the perturbation exerted by the CO_2 molecules on the magnetic properties of **1**. The response to gas molecules of SCO materials was previously studied in porous MOFs,[6] but they exert no influence on the magnetic properties.
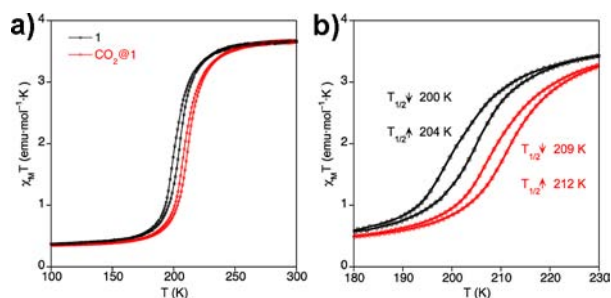
Figure 3. (a) Temperature dependence of $\chi_M T$ for $[Fe(btzx)_3](ClO_4)_2$ (**1**, black, as-synthesized) and loaded with CO_2 (**$CO_2@1$**, red). (b) Detailed view of the spin transition region.

Since **1** possesses more restricted accessible space than a typical porous material, we expect an interplay between the gas sorption and the SCO behavior.

As shown in Figure 3b, upon loading **1** with CO_2 an increase in the $T_{1/2}$ from 200 to 209 K is observed. Thus, physisorption of CO_2 molecules stabilizes the LS state. Additionally, the hysteresis is also maintained in the loaded sample, although with a slight decrease to 3 K. Interestingly, upon partial loading of **1** with ~0.3 molecule per void, a shift of $T_{1/2}$ toward higher temperatures is also observed, although this increase is only partial when compared to the fully loaded sample (Figure S9). Furthermore, upon removal of the CO_2 molecules, the $T_{1/2}$ is shifted back to lower temperatures, which perfectly matches with the spin transition of activated **1** (**1** after heating at 150 °C for 3 h), thus showing the reversibility of this process. In addition, we similarly measured the magnetic response of **1** under N_2 and under several CO_2/N_2 gas mixtures at 1 bar (Figures S11 and S12). As expected, the presence of N_2 does not influence the spin transition temperature, since N_2 is not adsorbed as demonstrated in the sorption experiments. Importantly, the possibility of the temperature shift being an effect of the gas pressure is thus also dismissed. Interestingly, in the gas mixtures the transition temperature increases as if only the same amount of CO_2 was present. This indicates the possibility of using SCO for sensing CO_2 in the presence of N_2.

To investigate the CO_2 sorption sites in **1**, we have determined *in situ* the structure of **1** with adsorbed CO_2 molecules (with a CO_2 pressure of 104 kPa) by Rietveld analysis[21] using synchrotron X-ray powder diffraction data (Figure 4a).[22] The gas molecules were refined as a rigid body and their occupancies were freely refined. The structure of **$CO_2@1$** (Figures 4b and S17) reveals that the framework remains unchanged with the CO_2 molecules located in the internal cavities. The gas molecules are disordered over six symmetry related positions, with a total refined occupancy of 0.93(1) CO_2 molecules per void, which agrees well with the calculated loading of 0.90 CO_2 molecules per void from the adsorption isotherms at 100 kPa and 273 K (which are comparable conditions to those of the powder diffraction experiments). Interestingly, in the structure of **$CO_2@1$** the CO_2 molecules interact with the cationic framework in an end-on mode through the nucleophilic oxygen atom, as previously established in other porous solids,[23] with a O=C=O-$(\delta^-)\cdots\pi_{N-N}$ distance of 2.514 Å, an interaction which is analogous in nature to the well established anion-π interactions.[24] No interaction between the framework and the electrophilic carbon atom is found.[16,23d,25] The end-on binding of the CO_2 molecules is in agreement with the increase in $T_{1/2}$, as donation of electron density stabilizes the LS state. Thus, the
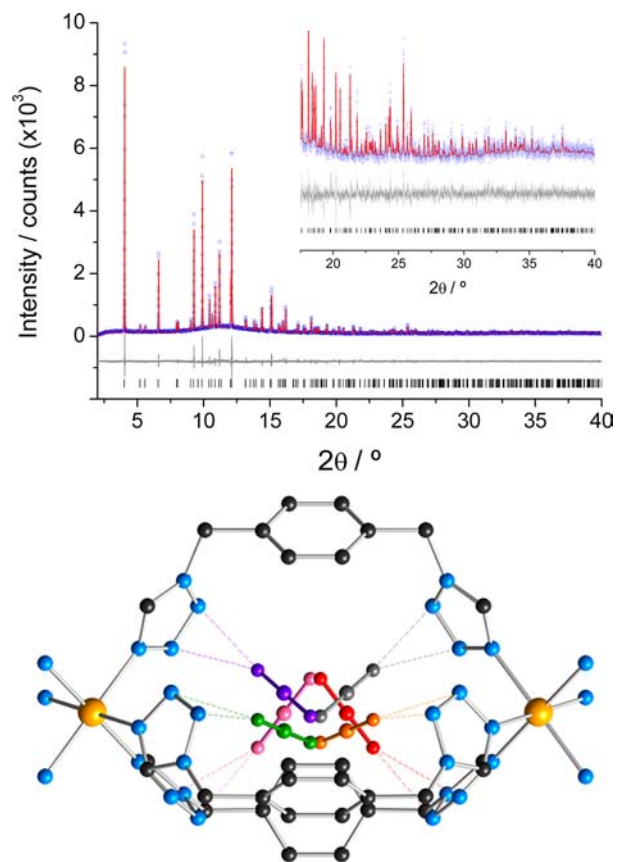

Figure 4. (a) Observed (blue) and calculated (red) profiles and difference plot $[(I_{obs} - I_{calc})]$ (gray) of the Rietveld refinement of compound **$CO_2@1$** (2θ range 2.0−40.0°, maximum resolution 1.21 Å). (b) Crystal structure of **$CO_2@1$** showing the end-on interactions between the gas molecules and the framework (O···N distances 2.591 and 2.608 Å). The symmetry-related CO_2 molecules are colored differently for clarity.

shift in the transition temperature seems to be caused by a change in the ligand field of the metal center due to the sorbed CO_2 molecules, which does not affect the cooperativity between the metal centers as the sharp transition is maintained. In addition, this stabilization of the LS state could also be due to an internal compressive effect arising from the O=C=O$(\delta^-)\cdots\pi_{N-N}$ interaction.[6b] In contrast, the effect of the internal pressure exerted by the CO_2 molecules is discarded because a decrease in $T_{1/2}$ (stabilization of the HS state) would be expected due to the larger cavity required for accommodating the gas molecules, acting as a negative pressure.

The most plausible mechanism for CO_2 sorption involves rotation of the phenyl rings of the btzx through the $C_{aromatic}$–$C_{methylene}$ bonds, as this would permit the connection between voids of different chains along the (100) and (010) directions (Figures S14 and S15). In addition, the extraframework ClO_4^- anions required to balance the framework charge are located at the planes formed by the Fe^{II} centers (Figure S16), without interfering with the sorption process. Thus, the aromatic rings can be viewed as flexible barriers to CO_2 transport within the crystals acting in a similar way to a rotary door.

In conclusion, we present a novel spin-crossover coordination polymer with multifaceted properties: (i) **1** possesses a sharp and hysteretic SCO transition at 200 K. (ii) Gas molecules can enter the crystal despite the lack of permanent pores due to the presence of a dynamic framework. (iii) Selective sorption of CO_2

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over N_2 is observed, with the CO_2 molecules located in the discrete voids of the framework through $O{=}C{=}O{\cdots}\pi$ interactions. (iv) Physisorption of CO_2 in the cavities produces a 9 K increase in the SCO temperature. The confined space of the voids seems to be essential for this unusual response to gas molecules.[26] In future work, the rotation of phenyl rings[27] and the insertion of other gas molecules in the voids will be studied for better understanding the response of this nonporous SCO coordination polymer toward gas sorption. This will permit the design of other multifunctional materials with larger response occurring near room temperature.

ASSOCIATED CONTENT

Supporting Information

Experimental details, X-ray data in CIF format, and additional figures. 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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