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Tuning the switching pressure in square lattice coordination networks by metal cation substitution†

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Coordination networks that undergo guest-induced switching between “closed” nonporous and “open” porous phases are of increasing interest as the resulting stepped sorption isotherms can offer exceptional working capacities for gas storage applications. For practical utility, the gate ad/desorption pressures (P_{ga}/P_{gd}) must lie between the storage (P_{st}) and delivery (P_{de}) pressures and there must be fast switching kinetics. Herein we study the effect of metal cation substitution on the switching pressure of a family of square lattice coordination networks $[M(4,4'\text{-bipyridine})_2(\text{NCS})]_n$ (**sql-1-M-NCS**, $M = \text{Fe}$, Co and Ni) with respect to CO_2 sorption. The Clausius–Clapeyron equation was used to correlate P_{ga}/P_{gd} and temperature. At 298 K, P_{ga}/P_{gd} values were found to vary from 31.6/26.7 bar ($M = \text{Fe}$) to 26.7/20.9 bar ($M = \text{Co}$) and 18.5/14.6 bar ($M = \text{Ni}$). The switching event occurs within 10 minutes as verified by dynamic CO_2 sorption tests. In addition, *in situ* synchrotron PXRD and molecular simulations provided structural insight into the observed switching event, which we attribute to layer expansion of **sql-1-M-NCS** via intercalation and inclusion of CO_2 molecules. This study could pave the way for rational control over P_{ga}/P_{gd} in switching adsorbent layered materials and enhance their potential utility in gas storage applications.

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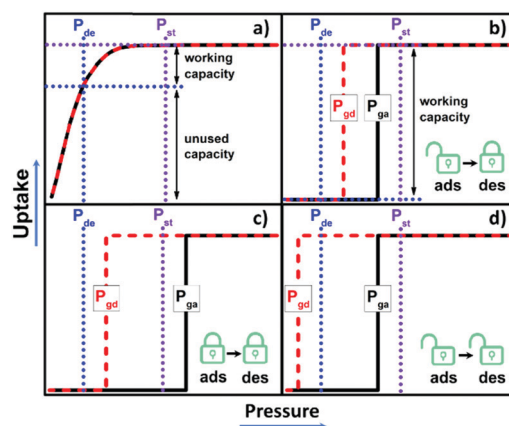
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Introduction

New approaches to gas storage/delivery are needed in the “age of gas” to address the large energy footprint associated with existing technologies such as compressed or liquefied gas storage.¹ Whereas physisorption holds promise for greatly improving the energy efficiency of industrial gas storage, it does not yet meet the prerequisites for practical deployment such as adsorbed natural gas (ANG) storage.² This is at least partly because rigid physisorbents such as zeolites tend to suffer from inappropriate sorption isotherms (Langmuir or type I³), resulting in lower working capacity than the saturation uptake (Scheme 1a).⁴

Metal–organic materials (MOMs),^{5,6} such as metal–organic frameworks (MOFs),^{7,8} or porous coordination polymers/networks (PCPs/PCNs),^{9–12} have attracted attention from academic and industrial researchers thanks to their potential utility in the areas as broad as storage, separation and catalysis.^{13,14} A prominent feature of MOMs is their inherent modularity which



Scheme 1 Comparison of different types of gas sorption isotherms. (a) type I; (b) type F-IV ($P_{de} < P_{gd} < P_{ga} < P_{st}$); (c) type F-IV ($P_{de} < P_{st} < P_{ga}$) and (d) type F-IV ($P_{gd} < P_{de} < P_{ga} < P_{st}$). Black solid line: adsorption; red dash line: desorption; P_{ga} : gate adsorption pressure; P_{gd} : gate desorption pressure; P_{de} : delivery pressure; P_{st} : storage pressure; ads: adsorption; des: desorption.

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enables fine tuning of structures through crystal engineering or reticular chemistry.^{15,16} However, although *ca.* 1 00 000 MOMs have been deposited in the MOF subset of the Cambridge Structural Database (CSD),¹⁷ most are rigid physisorbents that

exhibit the aforementioned type I sorption isotherms. In contrast, flexible MOMs (FMOMs) or soft porous crystals (SPCs) can undergo guest-induced switching between nonporous and porous phases and exhibit perhaps the most desirable isotherm type, a stepped or type F-IV isotherm.^{18–20} The optimal type F-IV isotherm would offer gate adsorption (P_{ga}) and desorption (P_{gd}) pressures that lie between the storage (P_{st}) and delivery (P_{de}) pressures to enable high working capacity (Scheme 1b). There is little margin for error, however, as FMOMs that remain closed during adsorption ($P_{\text{ga}} > P_{\text{st}}$, Scheme 1c) or open during desorption ($P_{\text{gd}} < P_{\text{de}}$, Scheme 1d) will offer negligible working capacity. Furthermore, gas storage criteria for P_{st} and P_{de} could vary significantly in different circumstances. The ability to fine-tune the switching pressures in FMOMs is thus important to enable the development of bespoke adsorbent materials for gas storage/delivery. Thus far, to our knowledge, only a relatively small subset of FMOMs feature type F-IV isotherms and even fewer have been subjected to systematic studies that address how to control their switching pressures.²¹

Crystal-engineering approaches can be exploited to tailor structures, compositions and, therefore, properties of MOMs.²² In the context of FMOMs, ligand “linker” or metal “node” substitution can be used to modulate flexibility.^{23–26} Ligand functionalization was used to adjust the switching of parent sorbents such as MIL-53(Fe) and [Co(bdp)].^{27–29} Regarding ligand substitution, we recently reported a family of two-fold interpenetrated FMOMs, X-pcu-*n*-Zn (*n* = 5–8), which exhibited pronounced switching behavior with comparable uptakes but different switching pressures.^{30,31} Considerable attention has been paid to exploiting metal cation substitution to modulate FMOM platforms, however, it can be a challenge to retain the type F-IV sorption profile.^{32–37} For example, MIL-53(Cr or Al) were found to exhibit type F-I isotherms for CO₂ sorption,³² while MIL-53(Fe or Sc) featured type F-IV isotherms.^{33,34} In addition, the Co and Fe variants of [M(bdp)] exhibited type F-IV isotherms,⁴ but their Zn and Ni analogues showed type I isotherms.³⁵ The pillared-layer coordination networks, DUT-8(M), exhibited type F-IV (DUT-8(Ni)), type F-I (DUT-8(Co)) or type I (DUT-8(Cu)) isotherms upon CO₂ sorption.³⁶ Even though the zeolitic imidazolate frameworks [M(bim)₂] (M = Co, Zn and Cd) retained their switching nature, there a significant pre-step was observed in the Co and Zn variants.³⁷ Herein we address the use of metal cation substitution to tune the switching pressure in a family of three square lattice (sql) coordination networks [M(bpy)₂(NCS)₂]_{*n*}, **sql-1-M-NCS** (1 = bpy = 4,4'-bipyridine, M = Fe, Co and Ni).

Square lattice (sql) coordination networks account for nearly half of reported 2D coordination networks (CNs).³⁸ sql CNs with general formula [M(L)₂(A)₂] can be readily formed by self-assembly of octahedral metal ions (M), axial counter anions (A) and linear linker ligands (L).³⁹ The prototypal non-interpenetrated sql CN, [Cd(bpy)₂(NO₃)₂]_{*n*}, was reported by Fujita's group in 1994.⁴⁰ This seminal work was followed by a series of studies that focused more upon the structural features of such networks rather than sorption properties until [Cu(bpy)₂(BF₄)₂] (ELM-11) was investigated.^{41,42} ELM-11 was found to exhibit

switching when exposed to gases such as CO₂, C₂H₂ and *n*-butane.^{43–47} Its metal cation substituted analogue, [Ni(bpy)₂(BF₄)₂] (ELM-31), also exhibits a type F-IV isotherm upon CO₂ sorption but with different uptake and switching pressure.⁴⁸ Nevertheless, the metal substitution strategy has not yet been fully exploited in the ELM-11 family.

Recently, our group reported the sorption properties of a previously known sql CN [Co(bpy)₂(NCS)₂],⁴⁹ **sql-1-Co-NCS**,^{50,51} which is closely related to the ELM family.^{43,44} The 195 K CO₂ sorption isotherm of **sql-1-Co-NCS** was observed to be type F-IV.⁵⁰ High-pressure CO₂ sorption at different temperatures exhibited type F-IV sorption profiles and the temperature *vs* switching pressure obeyed the Clausius–Clapeyron equation. Crystallographic studies revealed that the interlayer distance in the closed phase (4.5 Å) increased in the CO₂ loaded phase (5.4 Å), although the location of CO₂ molecules was not determined.⁵⁰ In this contribution, we report the Fe and Ni analogues of **sql-1-Co-NCS** and their CO₂ sorption profiles and switching kinetics.

Results and discussion

sql-1-M-NCS (M = Fe and Ni) were synthesized in powder form (rod shape, 0.5–2 μm, Fig. S14, ESI†) by heating their precursors {[M(bpy)(NCS)₂(H₂O)₂]-bpy}_{*n*} at 50 °C *in vacuo*. These precursors were prepared by a water slurry method. The crystal structures of **sql-1-Co-NCS** and **sql-1-Ni-NCS** were previously determined by single-crystal X-ray diffraction^{50,52} and we determined the crystal structure of **sql-1-Fe-NCS** herein by refinement of synchrotron PXRD data (Fig. S1 and S3a, ESI†). The three **sql-1-M-NCS** CNs are comprised of M(II) cations coordinated to four equatorial bpy ligands and two axial NCS[−] ligands and they are isostructural. Their synchrotron PXRD patterns match well (Fig. S1, ESI†). The effective cavity sizes (7.5 Å × 7.5 Å) and interlayer distances (4.5 Å) are also equivalent, although there are minor differences in the torsion angle of the bpy linker ligands (54.3°–54.7°) and the M–M–M (75.3°–76.4°) and M–N–CS (169.5°–170.9°) angles (Fig. 1). Terminal NCS ligands interdigitate adjacent layers (Fig. 1d–f) and block the cavities.

Although the cavity size and interlayer distance of **sql-1-M-NCS** are comparable to those of ELM-11, the hydrophilicity of **sql-1-M-NCS** towards humidity is mitigated thanks to utilisation of the relatively hydrophobic NCS[−] anion (Fig. S4, ESI†). Thermogravimetric analysis (TGA) revealed that **sql-1-Ni-NCS** exhibits better thermal stability (*ca.* 180 °C) than its Fe and Co analogues (*ca.* 150 °C) (Fig. S5, ESI†), which follows the empirical Irving–Williams series.⁵³ 195 K CO₂ sorption studies revealed that **sql-1-M-NCS** CNs exhibit the same saturation uptake (*ca.* 138 cm^{−3} g^{−1}), equivalent to three CO₂ molecules per formula unit (denoted as **sql-1-M-NCS-3CO₂**), but with distinct $P_{\text{ga}}/P_{\text{gd}}$ values: Fe (15/12 kPa) > Co (10/8 kPa) > Ni (4/3.5 kPa) (Fig. 2). Unlike ELM-11 which exhibits multi-step CO₂ sorption isotherms at 195 K,^{54,55} **sql-1-M-NCS** registered single-step sorption isotherms although **sql-1-Fe-NCS** had a small sub-step with 17 cm^{−3} g^{−1} uptake between 11 and 15 kPa.



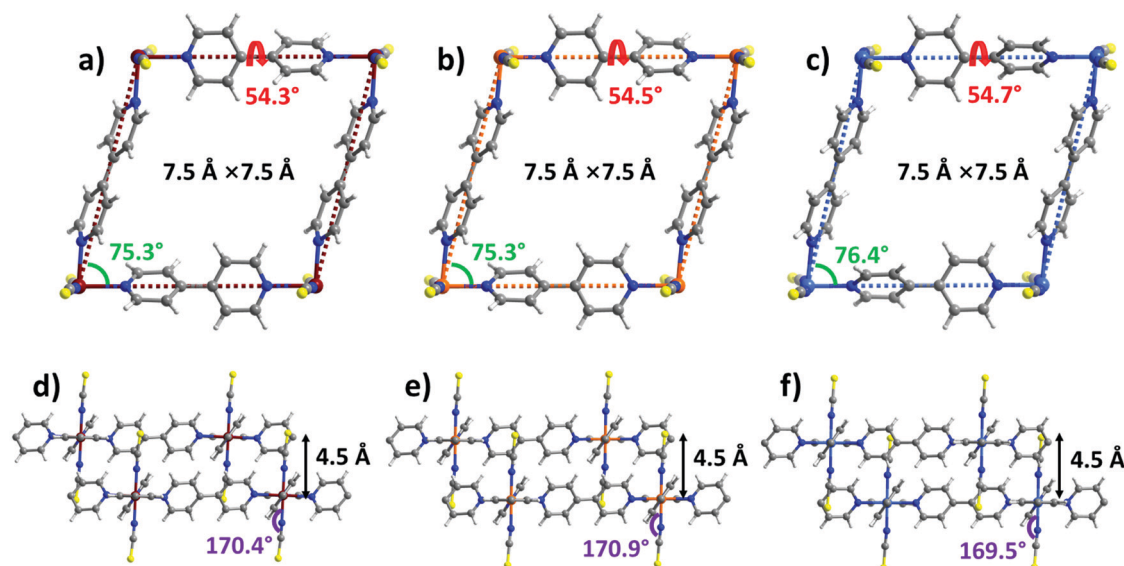


Fig. 1 Comparison of the crystal structures of **sql-1-M-NCS**. (a and d) M = Fe; (b and e) M = Co; (c and f) M = Ni.

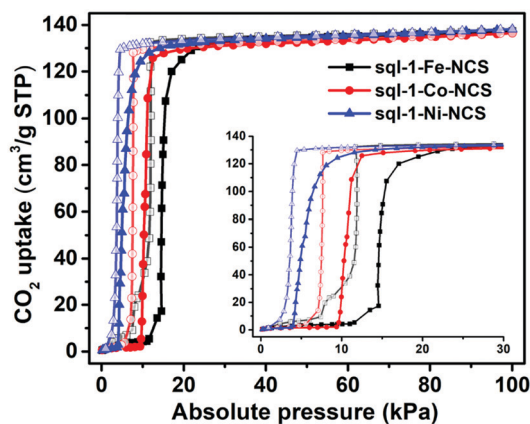


Fig. 2 CO_2 sorption isotherms for **sql-1-M-NCS** (M = Fe, Co, and Ni) at 195 K. The solid and open symbols represent adsorption and desorption branches, respectively.

We next collected high-pressure (up to 38 bar) CO_2 sorption isotherms on **sql-1-M-NCS** (M = Fe and Ni) between 273 and 298 K (5 K intervals) as previously conducted for **sql-1-Co-NCS** (Fig. 3a, b and Fig. S6, ESI†). The $P_{\text{ga}}/P_{\text{gd}}$ values for **sql-1-Fe-NCS** were 12.5/10.5, 15.2/12.8, 18.5/15.5, 22.3/18.7, 26.6/22.6 and 31.6/26.7 bar from 273 to 298 K, respectively. In contrast, **sql-1-Ni-NCS** was found to offer lower $P_{\text{ga}}/P_{\text{gd}}$ values: 6.5/5.1, 8.1/6.4, 10.1/7.9, 12.5/9.8, 15.2/11.9 and 18.5/14.5 bar from 273 to 298 K, respectively. The CO_2 sorption isotherms of **sql-1-M-NCS** (M = Fe and Ni) revealed a relationship between the $P_{\text{ga}}/P_{\text{gd}}$ and temperature which obeys the Clausius–Clapeyron equation $d \ln P / (d(1/T)) = (\pm)\Delta H/R$ (Fig. 3c, d and Fig. S7, ESI†). The phase transition enthalpies ΔH (the signs of ΔH are negative/positive for adsorption/desorption, respectively, absolute values are used hereafter) were calculated to be *ca.* 25.2 and 28.4 kJ mol^{-1} for **sql-1-Fe-NCS** and **sql-1-Ni-NCS**, respectively, 1.0 kJ mol^{-1} lower and 2.2 kJ mol^{-1} higher than that of **sql-1-Co-NCS** (26.2 kJ mol^{-1}).⁵⁰

One advantage of switching CNs is the switching pressure can be calculated at a given temperature once ΔH in the Clausius–Clapeyron equation has been determined.^{47,50} We thus plotted calculated switching pressure *vs* temperature from 195 to 298 K for **sql-1-M-NCS** (M = Fe, Co and Ni) (Fig. 3e, f and Fig. S8, Table S1, ESI†). The P_{ga} and P_{gd} were thereby tuned by the metal centers: $P_{\text{ga}}/P_{\text{gd}}$ (Fe) > $P_{\text{ga}}/P_{\text{gd}}$ (Co) > $P_{\text{ga}}/P_{\text{gd}}$ (Ni). Since the switching pressure is exponentially correlated to the temperature, it increases substantially at elevated temperature. For example, at 298 K, the $P_{\text{ga}}/P_{\text{gd}}$ were calculated to be 31.6/26.7, 26.7/20.9, and 18.5/14.6 bar when M = Fe, Co and Ni, respectively, two orders of magnitude higher than at 195 K. The magnitude of the hysteresis between P_{ga} and P_{gd} was also affected by temperature (Fig. S8, ESI†). The hysteresis gaps were found to be 4.9 (Fe), 5.8 (Co) and 3.9 (Ni) bar at 298 K, 163, 290, and 780 times their values (3.0, 2.0, and 0.5 kPa) at 195 K. The hysteresis in **sql-1-M-NCS** suggests that CO_2 can be stored at lower pressure (between P_{gd} and P_{ga}) than the charging pressure (P_{ga} or above).

When compared to other switching CNs which exhibit wide ranges of CO_2 uptakes (40–590 $\text{cm}^3 \text{g}^{-1}$) and switching pressures (1.3–75 kPa) at 195 K (Table S2 and Fig. S9a, ESI†),²¹ **sql-1-M-NCS** exhibit moderate uptakes and relatively low switching pressures. At elevated temperature (*e.g.* 298 K), **sql-1-M-NCS** retained almost the same uptake, whereas some benchmark switching CNs like DUT-8(Ni) and X-pcu-*n*-Zn tend to exhibit lower or even negligible CO_2 uptakes (Table S2 and Fig. S9b, ESI†),^{31,36} due to P_{ga} values (*e.g.* > 35 bar) that are beyond the maximum testing pressures. The prototypical switching **sql** CN, ELM-11, was observed to exhibit 80 and 173 $\text{cm}^3 \text{g}^{-1}$ of CO_2 uptake at the first ($P_{\text{ga}1} = 0.65$ bar) and second steps ($P_{\text{ga}2} = 19$ bar) at 298 K.⁵⁴ The distinct differences between ELM-11 and **sql-1-M-NCS** demonstrate the feasibility of tuning the switching pressure and even the uptake in families of **sql-1** CNs.

The sorption kinetics of sorbents is also relevant to their storage and separation performance,^{56–58} especially for FMOMs



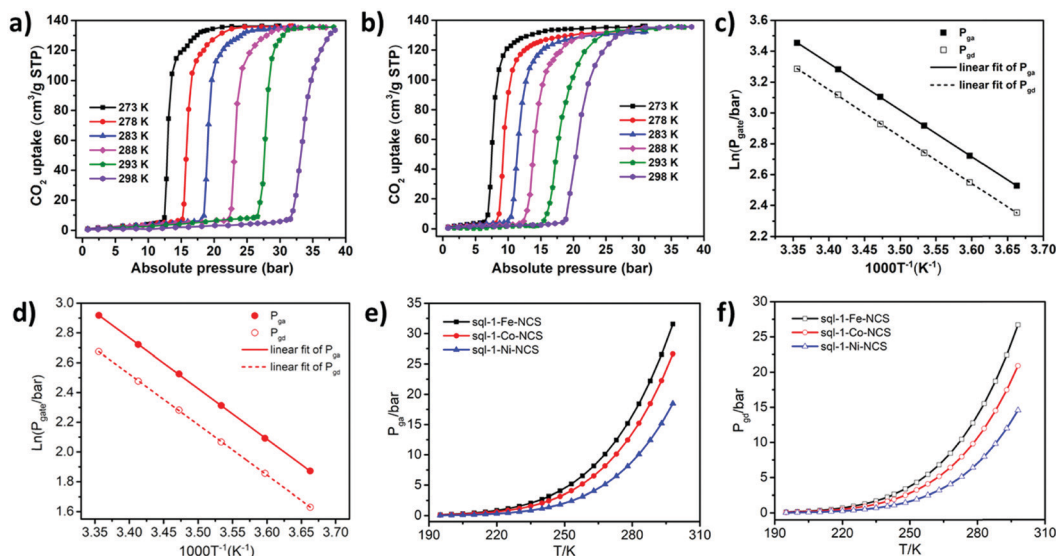


Fig. 3 High-pressure CO₂ sorption isotherms of (a) **sql-1-Fe-NCS** and (b) **sql-1-Ni-NCS**. The linear fit of gate sorption pressure (LnP) and temperature ($1000\ T^{-1}$) using the Clausius–Clapeyron equation for (c) **sql-1-Fe-NCS** and (d) **sql-1-Ni-NCS**. (e) Calculated P_{ga} and (f) P_{gd} for **sql-1-M-NCS** (M = Fe, Co, and Ni).

featuring structural transitions that might control the kinetics.^{51,59–61} We conducted dynamic CO₂ sorption studies on **sql-1-M-NCS** gravimetrically at 288 K and 1–36 bar. The CO₂ pressure was elevated/reduced constantly with a maximum rate of 2.5 bar min⁻¹ for adsorption/desorption process. It was observed that **sql-1-M-NCS** started adsorbing/desorbing CO₂ at 11.5/7.8, 10.0/9.5 and 7.5/10.8 min (equivalent to 23.9/18.0, 20.0/13.9 and 13.5/10.7 bar) for M = Fe, Co and Ni, respectively (Fig. 4). It is consistent with the P_{ga}/P_{gd} values (22.2/18.7, 18.5/14.5 and 12.4/9.8 bar) calculated from the Clausius–Clapeyron equation at 288 K. We determined that it took 7.5/5, 6/6 and 5/7.5 min to reach full loading/unloading for **sql-1-M-NCS** (M = Fe, Co, and Ni, respectively), indicating *ca.* 12.5 min for a sorption cycle and 22 cm³ g⁻¹ min⁻¹ for the average sorption rate. It was reported that ELM-11 reaches full loading of CH₄ (*ca.* 80 cm³ g⁻¹) in 10 min at 303 K.⁴³ Such sorption kinetics of **sql** CNs is comparable or even superior to some rigid sorbents.^{56,62}

To better understand the switching mechanism of **sql-1-M-NCS**, *in situ* CO₂ loaded synchrotron PXRD experiments (Fig. S2, ESI†) and molecular simulations were conducted. As revealed by Fig. 5, the cavity size of **sql-1-M-NCS·3CO₂** remains unchanged compared to that of **sql-1-M-NCS**, however, the cavity geometry deforms from a rhombus in the closed phase to a square in the open phase accompanied by an interlayer distance increase from 4.5 to 5.4 Å. Such intra-network and inter-network deformations induced by guest molecules are quite common amongst switching and flexible CNs.^{21,63,64} In addition, the bpy ligand twists by 10.3° (Fe), 9.6° (Co), and 8.9° (Ni) to accommodate the CO₂ molecules which occupy the interlayer and cavity voids as visualised by molecular simulations. It also reveals that [CO₂]₃ cluster units are formed (C··O distance: 2.755–3.265 Å) in the cavities of **sql-1-M-NCS·3CO₂**

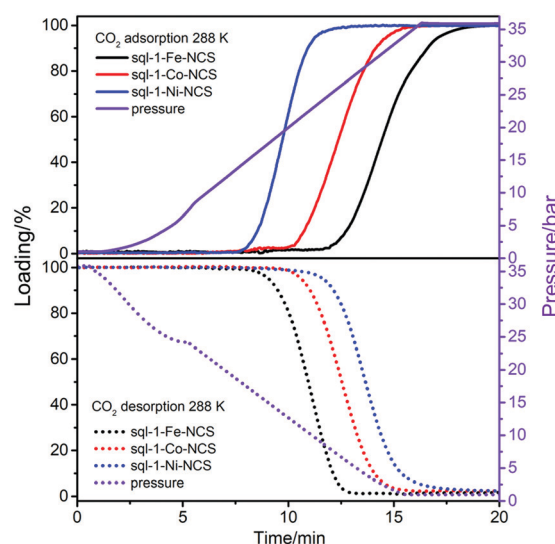
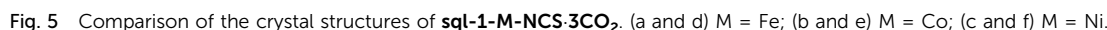


Fig. 4 Kinetics of CO₂ adsorption (top) and desorption (bottom) for **sql-1-M-NCS** (M = Fe, Co and Ni) at 288 K.

and propagate along *a* axis (Fig. S10–S12, ESI†). Each strand of {[CO₂]₃}_n is constrained in half of the cavity thanks to the ABAB stack mode of layers. Notably, the M–N–CS angles are compressed to 144.9° (Fe), 156.1° (Co) and 162.1° (Ni) in the open phases, corresponding to a change of 25.5°, 14.8°, and 7.4° from those in the closed phases, respectively. Overall, transformations between **sql-1-M-NCS** and **sql-1-M-NCS·3CO₂** followed the trend $P_{ga}(\text{Fe}) > P_{ga}(\text{Co}) > P_{ga}(\text{Ni})$, corresponding enthalpy changes being 25.2 (Fe) < 26.2 (Ni) < 28.4 (Ni) kJ mol⁻¹ (exothermic or endothermic for adsorption or desorption, respectively). Such trends could be attributable ligand twisting, metal coordination sphere distortion, layered net expansion



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Density functional theory (DFT) calculations

All periodic DFT calculations were carried out using the Castep as implemented in the Materials Studio package. Vanderbilt-type ultrasoft pseudopotentials and the generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE) exchange correlation were used for all structure calculations. A semi-empirical dispersion correction was included in the calculation to take the van der Waals interactions into account. A cutoff energy of 544 eV and a $2 \times 3 \times 2$ *k*-point mesh (generated using the Monkhorst–Pack scheme) were found to be sufficient for total energy to converge within 0.01 meV atom^{−1}. The starting structures (**sql-1-M-NCS-3CO₂**) were obtained from the synchrotron PXRD refinement as described above. Three CO₂ molecules per formula unit were added into each structure based on CO₂ sorption studies and were set flexible to allow the optimization of their binding sites. All the simulations on the structures were conducted in *P1* space group.

Thermogravimetric analysis (TGA)

TGA for all the compounds were carried out under N₂ atmosphere in a TA instruments Q50 thermal analyzer between room temperature and 300 °C with a constant heating rate of 10 °C min^{−1}.

Scanning electron microscopy (SEM)

SEM analysis was performed using an SU 70 Hitachi instrument. The samples were sputter-coated with gold (20 mA, 90 s) prior to imaging.

Low pressure CO₂ adsorption

Low pressure CO₂ adsorption experiments (up to 1 bar) of **sql-1-M-NCS** (M = Fe and Ni) were conducted on the Micromeritics TriStar II PLUS 3030 instrument at 195 K which was maintained by a 4 L Dewar flask filled with the mixture of acetone and dry ice. High-purity CO₂ was used as received from BOC Gases Ireland, CP grade (99.995%).

High pressure CO₂ adsorption

High pressure CO₂ isotherms of **sql-1-M-NCS** (M = Fe and Ni) were collected on a Micromeritics HPVA II-100 instrument at different temperatures (273–298 K). The activated sample (*ca.* 300 mg) was further degassed *in situ* for 1 hour before the measurements. Free spaces were determined at 0.7 bar Helium (He) and 25 °C. A background correction was performed by subtracting the adsorption of the empty sample cell from the obtained isotherms.

Water vapor sorption

Water vapor sorption measurements were conducted using a Surface Measurement Systems DVS Vacuum at 298 K. Samples of ELM-11 (purchased from TCI) and **sql-1-M-NCS** (M = Fe and Ni) were further degassed under vacuum (1×10^{-4} Torr) *in situ* and stepwise increase in relative pressure from 0 to 90% were controlled by equilibrated weight changes of the sample ($dM/dT = 0.01\% \text{ min}^{-1}$). Vacuum pressure transducers were

used with ability to measure from 1×10^{-6} to 760 Torr with a resolution of 0.01%. Approximately 10 mg of sample was used for each experiment. The mass of the sample was determined by comparison to an empty reference pan and recorded by a high-resolution microbalance with a precision of 0.1 µg.

Dynamic CO₂ sorption study

Dynamic CO₂ sorption experiments were carried out using a Hidden Isochema XEMIS microbalance at 288 K. In each experiment, around 20 mg of sample (**sql-1-M-NCS**) was used and further evacuated *in situ* at 323 K for 5 h. Pressure was then maintained at 1 bar without pumping out until mass equilibrium was reached. The pressure was first elevated from 1 to 36 bar, held until mass equilibrium was reached, and then reduced from 36 to 1 bar with a maximum constant rate of 2.5 bar per min. Background calibration was applied by repeating the same procedure except that the **sql-1-M-NCS** sample was replaced by a 20 mg counterweight in the sample cell.

Author contributions

Shi-Qiang Wang: conceptualization, methodology, investigation, formal analysis, writing – original draft; Shaza Darwish: investigation, writing – review & editing; Debobroto Sensharma: investigation, writing – review & editing; Michael J. Zaworotko: supervision, funding acquisition, writing – review & editing.

Conflicts of interest

There are no conflicts to declare.

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