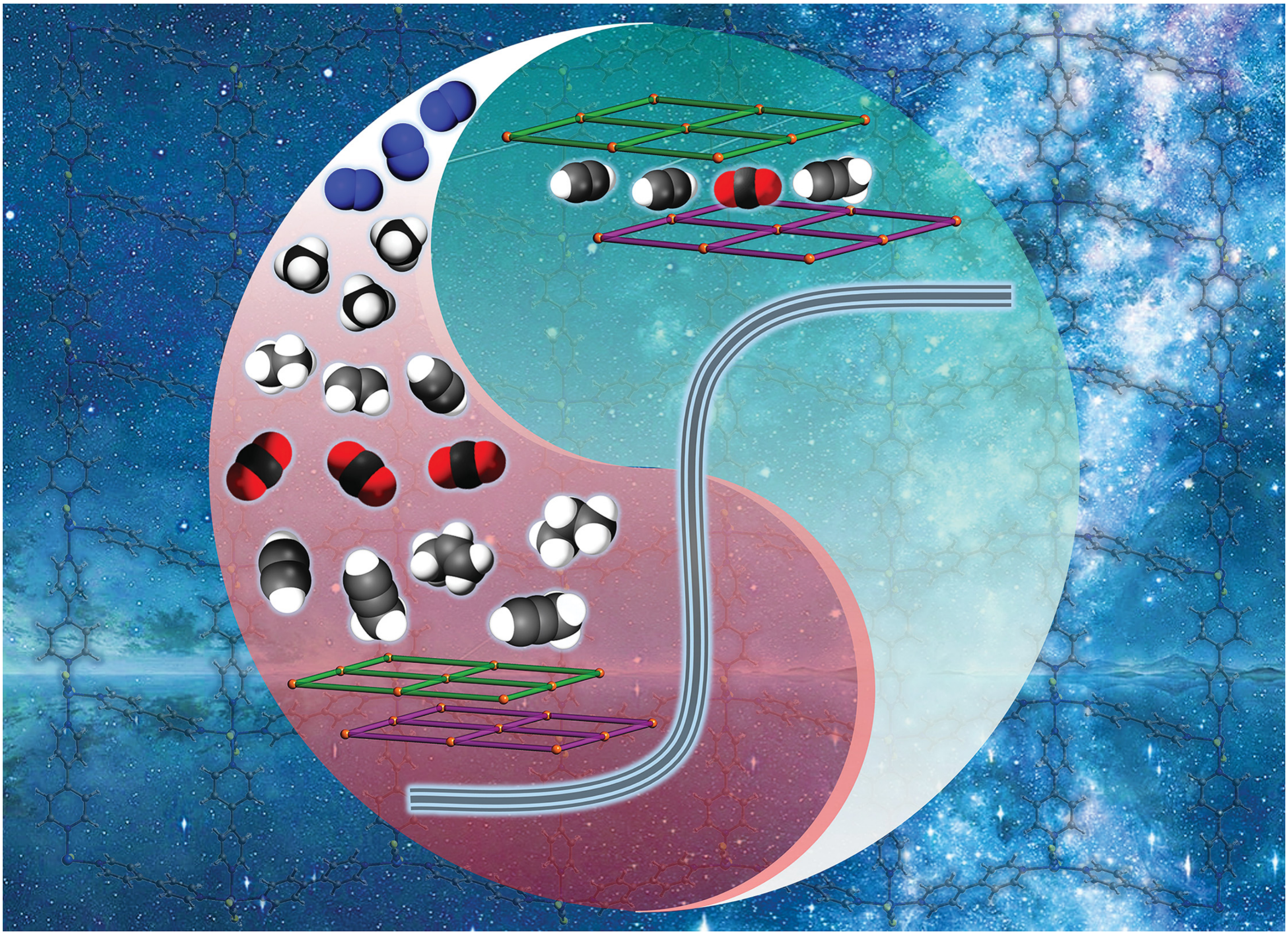

Showcasing research from the group of Professor Michael Zaworotko, Bernal Institute, Department of Chemical Sciences, University of Limerick, Limerick, Ireland and Dr Shi-Qiang Wang, Institute of Materials Research and Engineering, Agency for Science, Technology and Research, Singapore.

Adsorbate-dependent phase switching in the square lattice topology coordination network $[Ni(4,4'\text{-bipyridine})_2(NCS)_2]_n$

The sorption properties of nine gases (N_2, CH_4, CO_2, C_2H_2, C_2H_4, C_2H_6, C_3H_4, C_3H_6, and C_3H_8) on a prototypal 2D layered coordination network, $[Ni(4,4'\text{-bipyridine})_2(NCS)_2]_n$ (sql-1-Ni-NCS), were studied and reveal a diverse range of adsorbate-dependent switching pressures and sorption uptakes.

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Adsorbate-dependent phase switching in the square lattice topology coordination network $[Ni(4,4'\text{-bipyridine})_2(NCS)_2]_n$†

Shi-Qiang Wang, *[ab] Shaza Darwish[a] and Michael J. Zaworotko *[a]

Switching coordination networks (CNs) featuring stepped sorption isotherms that are accompanied by phase changes offer promise for gas storage and separation applications. However, their responsiveness to different adsorbates remains largely understudied. Herein, we report the variable switching behaviour of a previously known square lattice (sql) topology CN, $[Ni(4,4'\text{-bipyridine})_2(NCS)_2]$ (sql-1-Ni-NCS), with respect to nine gaseous adsorbates.

The increasing use of gases as fuels or chemical feedstocks has resulted in the "age of gas".[1] However, the dispersive nature of gases means that they tend to have low densities and form mixtures under ambient and typical industrial process conditions.[2] This creates several challenges for gas storage and/or separation processes with respect to the associated energy footprint and hazards.[3–6] Porous materials such as activated carbons and zeolites were deployed in the 20th century to mitigate such energy penalty,[3,4] even though their gas sorption uptakes are often modest. In the 1990s, a new class of metal–organic materials (*i.e.*, porous coordination polymers/networks, PCPs/PCNs, and metal–organic frameworks, MOFs) were introduced and it was quickly realized that their inherent modularity enables tunable pore size and chemistry.[7–11] The majority of such materials are first or second-generation CPs, *i.e.* upon sorbate removal they undergo structural collapse (first generation) or possess rigid structures like classical zeolites (second generation).[8,12] Second-generation CPs typically exhibit Langmuir (type I) sorption isotherms, which necessarily reduces working capacity for gas storage including natural gas storage.[13]

Seminal studies pioneered by Kitagawa, Férey and others introduced "third generation" flexible CPs or "soft porous crystals" in the early 2000s.[14–17] Third generation CPs exhibit structural flexibility when exposed to guest molecules and feature stepped sorption isotherms that are yet to be classified by IUPAC.[17–19] A small but growing subset of flexible CPs are the switching coordination networks (CNs) that can undergo extreme structural transition(s) between "closed" nonporous and "open" porous phases. We have classified the resulting stepped isotherms as type F-IV isotherms.[17,18] Such switching CNs can enable higher working capacity and better thermal management than rigid sorbents with type I isotherms.[13] Furthermore, switching pressure and adsorption enthalpy can be readily calculated by applying the Clausius–Clapeyron equation,[17] allowing for the strength comparison of different adsorbate–adsorbent interactions.

The switching pressure and sorption uptake of switching CNs can be influenced by various factors.[17] The effects of temperature/pressure, metal–ion and linker on switching CNs have been studied.[13,20–24] The adsorbate also plays a key role in triggering the phase transformations that accompanies switching since adsorbate–adsorbent interactions are the main driving force.[25–27] In general, nonpolar gases such as N_2 and CH_4 tend to exhibit relatively weak interactions with CNs, while hydrocarbons with unsaturated bonds and/or more carbon atoms may induce switching by providing stronger host–guest interactions (Tables S1 and S2, ESI†).[17] However, such empirical rules-of-thumb need to be experimentally verified using a systematic approach.

To our knowledge, there are around 70 switching CNs reported in the literature for which N_2 and CO_2 are the dominant adsorbates, usually studied at their boiling point temperatures of 77 K and 195 K, respectively.[17] Only a handful of switching CNs have been examined across a range of adsorbates at multiple conditions (Table S1, ESI†).[13,20–23,25–28] This situation hinders our understanding of the adsorbate dependence of switching CNs and in turn limits their potential utility. We address this matter herein through a study of the effect of nine adsorbates on the switching parameters associated with a square lattice (**sql**) topology coordination network.

Switching CNs often feature square or rhombic cavities that exploit the flexible nature of a rhombus from a mechanical

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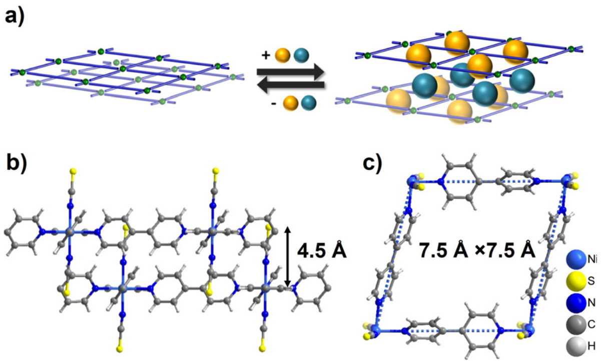

Fig. 1 (a) Schematic illustration of the switching mechanism of **sql** CNs triggered by guest sorption; (b and c) crystal structures of **sql-1-Ni-NCS**.

perspective as exemplified by **sql** CNs with general formula $[M(L)_2(A)_2]_n$ (M = divalent metal cation, L = ditopic linker ligand, A = axial counter anion).† Such CNs are modular and highlight the "node and linker" design strategy developed by Robson and Hoskins over 30 years ago.[29,30] The first reported sorption study on switching **sql** CNs was conducted on $[Cu(bpy)_2(BF_4)_2]$ (bpy = 4,4′-bipyridine), ELM-11.[31,32] It was observed to exhibit single or multi-step type F-IV sorption isotherms *via* layer expansion (Fig. 1a) when triggered by gases such as N_2, O_2, Ar, CO_2 and C_2H_2.[33–35] Recently, we studied the sorption properties of three previously known **sql** CNs $[M(bpy)_2(NCS)_2]$ (M = Fe, Co, or Ni),[36–39] **sql-1-M-NCS**, which are isostructural to the ELM family. Their CO_2 sorption isotherms under low or high temperatures/pressures were observed to exhibit single-step type F-IV isotherms and the switching pressures were found to be metal–ion controlled.[38] Amongst the three **sql-1-M-NCS** CNs, **sql-1-Ni-NCS** was found to be the "softest" switching CN based on the CO_2 gate-adsorption pressure (P_{ga}).[38] It was later found that **sql-1-Ni-NCS** exhibits even lower P_{ga} value and higher sorption uptake for C_2H_2 when compared to its CO_2 sorption.[39] These studies prompted us to study the effect of a wider range of gaseous adsorbates on **sql-1-Ni-NCS** to determine their switching pressures and sorption uptakes.

sql-1-Ni-NCS was initially synthesized hydrothermally,[40] and we have recently adopted an alternate route by heating its 1D chain CP precursor that can be obtained by water slurry.[38] **sql-1-Ni-NCS** is sustained by Ni(II) ions coordinated equatorially to bpy linker ligands with terminal NCS^- anions occupying the axial positions. The interlayer distance is 4.5 Å (Fig. 1b) and the effective dimension of the square cavity is 7.5 Å × 7.5 Å (Fig. 1c). The cavity void is blocked by the interdigitated NCS^- ligands (Fig. 1b). **sql-1-Ni-NCS** is therefore non-porous and is thermally stable up to 180 °C,[38] which is sufficient for most practical applications. In contrast to its hydrophilic analogue ELM-11, **sql-1-Ni-NCS** is hydrophobic towards humidity,[38] an important consideration given that water vapour degrades the performance of many adsorbents.

While **sql-1-Ni-NCS** is "softer" than its Fe and Co analogues, its 77 K N_2 and 195 K CH_4 sorption revealed negligible uptakes (Fig. 2). In contrast, its 195 K C_2H_4 and C_2H_6 isotherms revealed

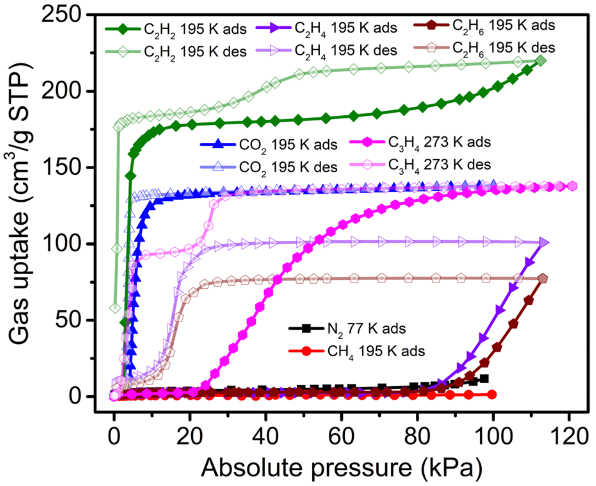

Fig. 2 77 K N_2, 195 K $CH_4/CO_2/C_2H_2/C_2H_4/C_2H_6$ and 273 K C_3H_4 sorption isotherms for sql-1-Ni-NCS.

switching behaviour but uptake did not reach saturation at 113 kPa (close to the maximum measurable pressure of the sorption instrument). The corresponding P_{ga} values for C_2H_4 and C_2H_6 were determined to be 86 and 91 kPa, respectively, much higher than those for CO_2 (4.0 kPa) and C_2H_2 (2.9 kPa) at the same temperature.[38,39] In addition, C_3H_4 (propyne) sorption on **sql-1-Ni-NCS** exhibited switching behaviour (P_{ga} = 21.5 kPa) at 273 K with a saturation uptake of 138 $cm^3\ g^{-1}$, although its C_3H_6 (propylene) and C_3H_8 (propane) sorption uptakes were negligible (Fig. S1, ESI†). This C_3H_4 uptake matches its CO_2 uptake and corresponds to three C_3H_4 molecules per formula unit (**sql-1-Ni-NCS·3C₃H₄**). Interestingly, the desorption branch of the C_3H_4 sorption isotherm featured two steps, consistent with a new phase with 2/3 of the saturation uptake (*ca.* 94 $cm^3\ g^{-1}$) between 8 and 20 kPa at 273 K. This data suggests that, before transforming to the closed phase, **sql-1-Ni-NCS·3C₃H₄** converted to **sql-1-Ni-NCS·2C₃H₄** (two C_3H_4 molecules per formula unit) during desorption. Such a phenomenon (*i.e.*, the desorption branch has more steps than the corresponding adsorption branch) is, to the best of our knowledge, reported herein for the first time in switching CNs.

To further study the C_3H_4 sorption behaviour on **sql-1-Ni-NCS**, C_3H_4 sorption isotherms were collected between 263 and 298 K with a 5 K interval (Fig. 3a and Fig. S2, ESI†). The P_{ga} values were observed to be 12.5, 16.5, 21.5, 28.0, 35.5 and 45.0 kPa at 263, 268, 273, 278, 283 and 288 K, respectively. These temperatures and P_{ga} values were fitted to the Clausius–Clapeyron equation (Fig. 3b and Fig. S3, ESI†), to calculate the adsorption enthalpy (ΔH, absolute value) of *ca.* 32.3 kJ mol^{-1}. This ΔH value is higher than those calculated for the corresponding CO_2 (28.4 kJ mol^{-1}) and C_2H_2 (28.5 kJ mol^{-1}) induced phase transformations.[38,39]

P_{ga} can be calculated at given temperatures once ΔH has been determined.[36,38,39] We therefore plotted the P_{ga} *vs.* temperature from 253 to 298 K for C_3H_4 and compared it with those for CO_2 and C_2H_2 (Fig. 4 and Table S3, ESI†). The plot reveals that the C_3H_4 switching pressure increases at elevated

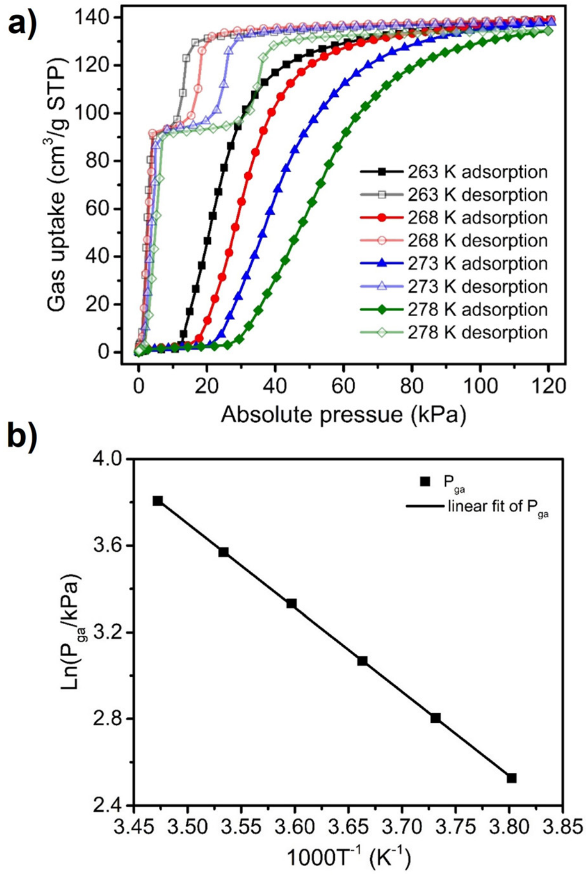

Fig. 3 (a) The C_3H_4 sorption isotherms of **sql-1-Ni-NCS** collected at different temperatures; (b) linear fit of gate adsorption pressure ($\ln P_{ga}$) and temperature ($1000/T$) using the Clausius–Clapeyron equation for **sql-1-Ni-NCS**.

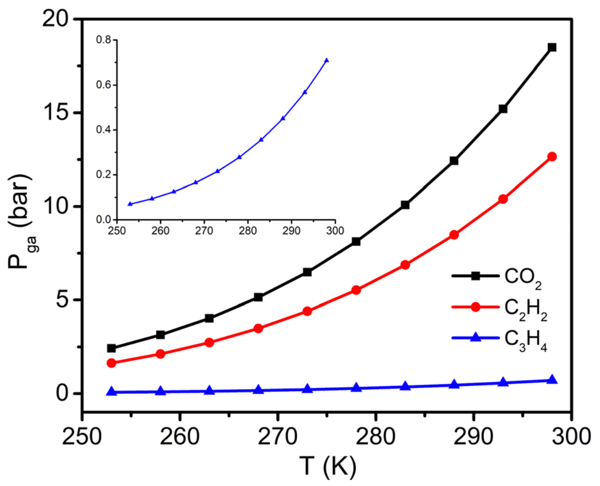

Fig. 4 Comparison of CO_2, C_2H_2, and C_3H_4 gate-adsorption pressures for **sql-1-Ni-NCS**.

temperature in a manner similar to that of its CO_2 and C_2H_2 counterparts.[38,39] However, the P_{ga} values for C_3H_4 are much lower than those for CO_2 and C_2H_2. For example, the P_{ga} value for C_3H_4 at 298 K is only 0.71 bar, while it reaches 12.66 and 18.49 bar for C_2H_2 and CO_2, respectively. Such a large difference in P_{ga} values suggests that adsorbate–adsorbent interactions strongly affect the switching pressure as reflected in their ΔH values. With respect to the sorption uptake, it is also affected by the adsorbate. For instance, the saturation uptakes of CO_2 and C_3H_4 are both 138 cm^3 g^{-1} (3 mol mol^{-1}), while C_2H_2 uptake reaches 185 cm^3 g^{-1} (4 mol mol^{-1}) at the first plateau, a 33.3% increase in capacity. The adsorbate impact upon switching easiness for the studied gases can be ordered as follows: $C_3H_4 > C_2H_2 > CO_2 > C_2H_4 > C_2H_6 > CH_4 \geq N_2$ (Fig. S4, ESI†). This order generally agrees with that reported for other switching CNs (Table S2, ESI†) and follows the trend of the boiling point and vaporisation enthalpy of the gases (Table S4, ESI†).

Structural analysis of previously reported **sql-1-M-NCS·*x*G** (Tables S5, S6 and Fig. S5, S6, ESI†) reveals that phase switching involves guest intercalation and/or inclusion phenomena and enables volume expansion of 23.5–114.9%, which can be classified into five distinct phase categories, A–E (Table S6 and Fig. S5, ESI†). The stoichiometric ratio (x) of **G: M** was found to be 2, 3 or 4. The identical stoichiometric ratio (x = 3) of C_3H_4 and CO_2 and their similar shapes prompted us to conduct molecular simulations to predict the location of C_3H_4 molecules by assuming that the crystal structure of **sql-1-Ni-NCS·3C$_3$H$_4$** is isostructural to the previously reported structure of **sql-1-Ni-NCS·3CO$_2$**.[36,38] The resulting calculations of these "category A" phases indicate that C_3H_4 molecules occupy interlayer voids and internetwork cavities (Figs S6b, ESI†) with C–H···π and π···π host–guest interactions (Fig. S7, ESI†). Future studies will focus upon *in situ* PXRD experiments to verify the nature of these structural transformations.

In summary, we herein present the sorption properties of nine gases (N_2, CH_4, CO_2, C_2H_2, C_2H_4, C_2H_6, C_3H_4, C_3H_6, and C_3H_8) of a prototypal switching **sql** CN, **sql-1-Ni-NCS**. C_3H_4 sorption was studied at eight temperatures and compared with the previously reported CO_2 and C_2H_2 sorption properties. C_3H_4 induced switching had not been previously reported for CNs, although it has been studied in a soft organic cage.[41] Our results indicate that both the switching pressure and sorption uptake are strongly influenced by the adsorbate. The switching thresholds for each adsorbate are generally compatible with the rules-of-thumb abovementioned. It should be noted that, whereas CH_4, C_3H_6 and C_3H_8 did not trigger switching of **sql-1-Ni-NCS** at 195 or 273 K and 1 bar, this does not mean that they cannot do so at lower temperatures and/or higher pressures. Overall, the primary message from this study is that nonporous structures (as determined by their crystal structures and/or 77 K N_2 sorption data) should not be discarded as candidates for sorption-based applications as first suggested by Barrer's studies on molecular compounds.[42] Future studies will explore the sorption behaviour of **sql-1-Ni-NCS** and related switching adsorbent layered materials (SALMAs) for other adsorbates including the effect of pressure.[43]

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Conflicts of interest

There are no conflicts to declare.

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