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# Acetylene storage performance of $[\text{Ni}(\text{4,4'}\text{-bipyridine})_2(\text{NCS})_2]_n$ , a switching square lattice coordination network†

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We report that the previously reported square lattice coordination network  $[\text{Ni}(\text{4,4'}\text{-bipyridine})_2(\text{NCS})_2]_n$ , sql-1-Ni-NCS, undergoes acetylene induced switching between closed (nonporous) and open (porous) phases. The resulting stepped sorption isotherms exhibit temperature controlled steps, consistent high uptake and benchmark working capacity ( $185 \text{ cm}^3 \text{ g}^{-1}$  or  $189 \text{ cm}^3$ , 1–3.2 bar, 288 K) for acetylene storage.

Acetylene ( $\text{C}_2\text{H}_2$ ) is an important chemical feedstock and is also used as a fuel for oxyacetylene torches.<sup>1</sup> However, its highly flammable and explosive nature renders its handling to be more challenging than most gases.<sup>2,3</sup> Current  $\text{C}_2\text{H}_2$  storage technology involves desensitization by dissolving  $\text{C}_2\text{H}_2$  in acetone pre-dispersed in a porous monolith that completely fills a gas cylinder.<sup>2,3</sup> The solubility of  $\text{C}_2\text{H}_2$  in acetone reaches  $470.4 \text{ cm}^3 \text{ g}^{-1}$  at 15 bar and 288 K.<sup>4</sup> Nevertheless, charging  $\text{C}_2\text{H}_2$  into acetone dramatically expands the volume of acetone and results in relatively low volumetric uptake ( $192.3 \text{ cm}^3$ ).<sup>4</sup> In addition, discharging  $\text{C}_2\text{H}_2$  releases acetone vapour,<sup>3</sup> precluding its use in production of fine chemicals and electronic materials. Solid sorbents (e.g. porous coordination networks, PCNs<sup>5,6</sup>) offer potential to address these handicaps and broaden the utility of  $\text{C}_2\text{H}_2$  in this “age of gas”.<sup>7</sup>

Switching coordination networks (CNs) can be classified as third generation CNs as they can undergo guest-induced structural transformation(s) between “closed” nonporous and “open” porous phases.<sup>8</sup> They represent a small but growing subset of flexible metal–organic frameworks (FMOFs) or soft porous crystals (SPCs).<sup>9–11</sup> Their potential utility is related to their sorption isotherms. Whereas rigid CNs typically exhibit

Langmuir (type I) isotherms, switching CNs feature stepped or type F-IV sorption isotherms,<sup>8,12</sup> making them distinctive from most metal–organic materials (MOMs<sup>13,14</sup>) by enhancing working capacity for gas storage (Fig. 1).<sup>8,12,15</sup>

With respect to  $\text{C}_2\text{H}_2$  storage, a key performance parameter is the working capacity at practically relevant gas delivery ( $P_{\text{de}}$ ) and storage ( $P_{\text{st}}$ ) pressures. We recently proposed that a pressure range of 1–15 bar might be used to define working capacity as this range is compatible with existing  $\text{C}_2\text{H}_2$ –acetone technology.<sup>4</sup> Another important but largely understudied parameter is sorption kinetics, which must be sufficiently fast for

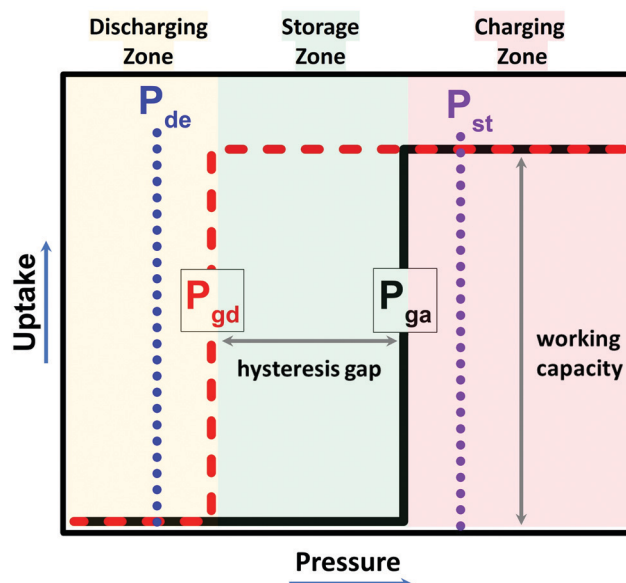


Fig. 1 Schematic illustration of a type F-IV or stepped sorption isotherm. Such isotherms can offer enhanced gas storage performance as, unlike rigid porous materials, working capacity can be 100% of uptake. Black solid line = adsorption branch; red dash line = desorption branch;  $P_{\text{ga}}$  = gate adsorption pressure;  $P_{\text{gd}}$  = gate desorption pressure,  $P_{\text{st}}$  = gas storage pressure;  $P_{\text{de}}$  = gas delivery pressure.

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gas loading and unloading. To date, more than 100 CNs have been investigated with respect to  $C_2H_2$  sorption and most are rigid CNs with high sorption uptake below 1 bar.<sup>16–27</sup> Whereas high uptake can make a sorbent suitable for  $C_2H_2$  sequestration, the type I isotherms typical of rigid sorbents are unlikely to offer a working capacity that is close or equal to their uptake as would be ideal for  $C_2H_2$  storage/delivery.<sup>4</sup> Conversely, switching CNs with a type F-IV isotherm can exhibit a working capacity that equals saturation uptake (Fig. 1). Furthermore, an appropriate hysteresis gap would enable  $C_2H_2$  to be stored at lower pressure (*i.e.* between  $P_{gd}$  and  $P_{ga}$ ) than its charging pressure (*i.e.*  $P_{ga}$  and above). A feature of switching CNs is that  $P_{ga}$  and  $P_{gd}$  can be calculated by applying the Clausius–Clapeyron equation,<sup>4,8</sup> thereby providing an opportunity to calculate  $C_2H_2$  working capacity at higher pressures and avoiding experimental explosion risks. To our knowledge, only two switching CNs, the 3D pillar-layered CN **MOF-508** and the 2D square lattice (**sql**) CN **sql-1-Cu-BF<sub>4</sub>** (**ELM-11**) have been studied for their  $C_2H_2$  storage properties.<sup>4,19,28</sup> In this contribution, we report that the **sql** CN **[Ni(bpy)<sub>2</sub>(NCS)<sub>2</sub>]**, **sql-1-Ni-NCS** (1 = bpy = 4,4'-bipyridine) exhibits  $C_2H_2$  induced switching and evaluate its  $C_2H_2$  storage performance by means of variable temperature  $C_2H_2$  sorption studies and *in situ* synchrotron PXRD studies.

**sql-1-Ni-NCS** was hydrothermally synthesized in 1999 by Zhang *et al.*<sup>29,30</sup> we have developed an alternate route by heating the 1D chain coordination polymer  $\{[Ni(bpy)(NCS)_2(H_2O)_2] \cdot bpy\}$  obtained by water slurry.<sup>31</sup> While the crystal structure (Fig. S1, ESI†) and spectroscopic properties of **sql-1-Ni-NCS** are known for two decades,<sup>29,30</sup> its sorption properties were unstudied until we reported its  $CO_2$  sorption properties at low ( $\leq 1$  bar, 195 K) and high ( $\leq 38$  bar, 273–298 K) temperatures/pressures.<sup>31</sup> Interestingly, it is the “softest” switching CN with respect to  $P_{ga}$  vs. its Fe and Co analogues.<sup>31,32</sup> This prompted us to study its  $C_2H_2$  sorption properties since  $C_2H_2$  generally offers stronger sorbent–sorbate interactions than  $CO_2$ .<sup>4,8</sup>

The 195 K  $C_2H_2$  sorption isotherm of **sql-1-Ni-NCS** reveals that the  $P_{ga}$  is 2.9 kPa (Fig. 2), below the  $P_{ga}$  for  $CO_2$  (4.0 kPa).<sup>31</sup> The  $C_2H_2$  uptake plateaus at  $185\text{ cm}^3\text{ g}^{-1}$ , which suggests 4  $C_2H_2$  molecules per formula unit (**sql-1-Ni-NCS-4C<sub>2</sub>H<sub>2</sub>**). This value is 34% higher than the  $CO_2$  saturation uptake ( $138\text{ cm}^3\text{ g}^{-1}$ ) of **sql-1-Ni-NCS-3CO<sub>2</sub>**.<sup>31</sup> A second step appeared at *ca.* 60 kPa but does not plateau before 120 kPa. At temperatures above 205 K, the second step was not observed while the initial plateau retained the same saturation uptake. The BET surface area and total pore volume of **sql-1-Ni-NCS** were calculated to be  $697.3\text{ m}^2\text{ g}^{-1}$  and  $0.41\text{ cm}^3\text{ g}^{-1}$ , respectively.  $P_{ga}/P_{gd}$  values were observed to be 2.9/1.3, 4.1/1.8, 6.8/3.0, 10.2/4.4, 14.9/6.3 and 21.3/9.0 kPa at 195, 199, 205, 210, 215 and 220 K, respectively (Fig. 2 and Fig. S2, ESI†). These temperature and  $P_{ga}/P_{gd}$  values were fitted to the Clausius–Clapeyron equation (Fig. 3a and Fig. S3, ESI†), which was used to calculate formation ( $\Delta_f H$ ) and dissociation ( $\Delta_d H$ ) enthalpies (absolute values) of *ca.* 28.5 and 27.7  $\text{kJ mol}^{-1}$ , respectively. These  $\Delta H$  values are comparable to those (28.4/28.2  $\text{kJ mol}^{-1}$ ) calculated for  $CO_2$  induced phase transition.<sup>31</sup>

$P_{ga}/P_{gd}$  can be calculated at various temperatures once  $\Delta H$  has been determined.<sup>4,8</sup> We were therefore able to calculate

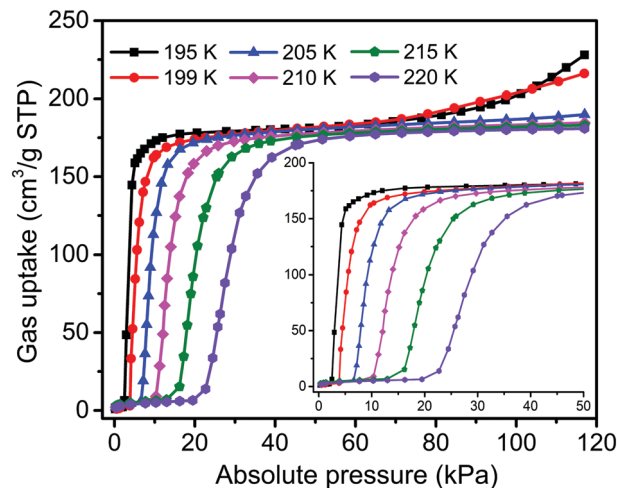


Fig. 2  $C_2H_2$  (195–220 K) adsorption isotherms for **sql-1-Ni-NCS**.

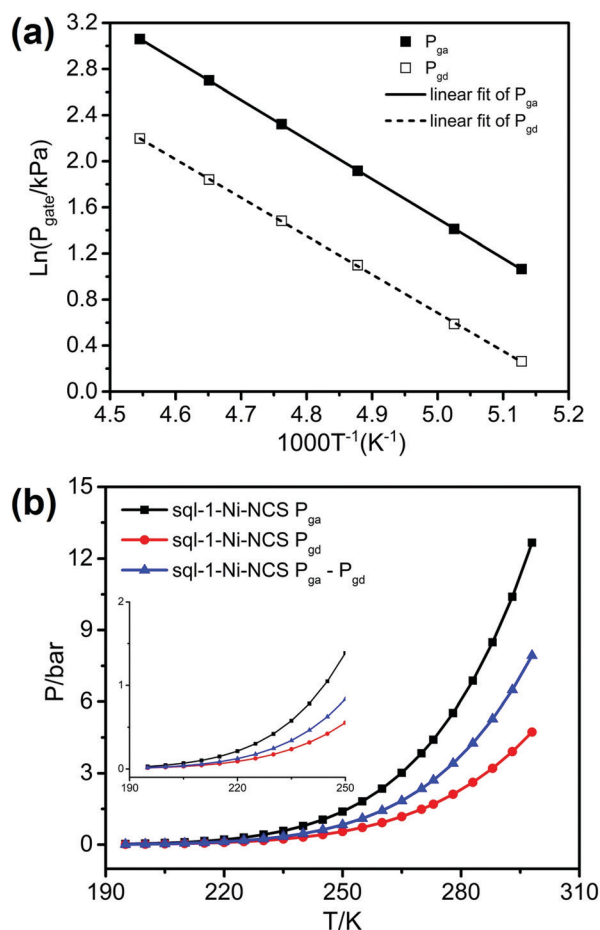


Fig. 3 (a) Linear fit of gate sorption pressure ( $\ln P_{gate}$ ) and temperature ( $1000/T$ ) using the Clausius–Clapeyron equation; (b) calculated  $P_{ga}$ ,  $P_{gd}$  and the hysteresis gap ( $P_{ga} - P_{gd}$ ) for **sql-1-Ni-NCS**.

switching pressure vs temperature from 195 to 298 K for **sql-1-Ni-NCS** (Fig. 3b and Table S1, ESI†). These plots reveal

that the  $C_2H_2$  switching pressure and the hysteresis gap between  $P_{ga}$  and  $P_{gd}$  increase at elevated temperature in a manner similar to that of its  $CO_2$  switching pressures.<sup>31</sup> For example,  $P_{ga}/P_{gd}$  were calculated to be 4.4/1.7, 8.5/3.2, and 12.7/4.7 bar at 273, 288, and 298 K, respectively. The corresponding hysteresis gaps were found to be 2.7, 5.3 and 8.0 bar at 273, 288 and 298 K, respectively. These data suggest that  $C_2H_2$  can be stored by **sql-1-Ni-NCS** at lower pressure (e.g., 3.2 bar, 288 K) than the charging pressure (e.g.,  $\geq 8.5$  bar, 288 K).

The related **sql** CN **sql-1-Cu-BF<sub>4</sub>** was reported to exhibit a type F-IV<sup>m</sup> isotherm with three complete  $C_2H_2$  sorption steps at 195 K.<sup>4,8</sup> In contrast, **sql-1-Ni-NCS** exhibited a type F-IV<sup>s</sup> isotherm with a single  $C_2H_2$  sorption step. Although the  $C_2H_2$  uptake of **sql-1-Cu-BF<sub>4</sub>** ( $245\text{ cm}^3\text{ g}^{-1}$  at the 3rd plateau) is higher than that of **sql-1-Ni-NCS** ( $185\text{ cm}^3\text{ g}^{-1}$  at the 1st plateau), its working capacity is lower between 1–15 bar under ambient temperatures. This is because only the uptake between the second and the third step of **sql-1-Cu-BF<sub>4</sub>** can be utilised in this pressure range. The working capacity ( $163\text{ cm}^3\text{ g}^{-1}$ ) of **sql-1-Cu-BF<sub>4</sub>** is therefore 66.7% of the sorption uptake.<sup>4</sup> In contrast, the uptake of **sql-1-Ni-NCS** can be fully exploited ( $185\text{ cm}^3\text{ g}^{-1}$ ) under the same conditions so its working capacity is 13.5% above that of **sql-1-Cu-BF<sub>4</sub>**. With respect to other parameters, the switching pressures ( $P_{ga}/P_{gd}$ ) and hysteresis gaps are comparable (Fig. S4 and S5, ESI†):  $P_{gd}$  values for **sql-1-Ni-NCS** are slightly (0.01–0.34 bar) lower than  $P_{gd}$  of **sql-1-Cu-BF<sub>4</sub>** in the range 195–298 K;  $P_{ga}$  values are 0.04–0.40 bar lower between 195–278 K and 0.08–1.31 bar higher between 283–298 K than those ( $P_{ga}$ ) of **sql-1-Cu-BF<sub>4</sub>**. For example, at 288 K, the  $P_{ga}/P_{gd}$  values are 8.1/3.5 and 8.5/3.2 bar for **sql-1-Cu-BF<sub>4</sub>** and **sql-1-Ni-NCS**, respectively.

To gain insight into the nature of the phase transformation induced by  $C_2H_2$ , *in situ* synchrotron PXRD experiments were conducted. As shown in Fig. 4a, the phase transformation was complete within 8 min under 0.5 bar  $C_2H_2$  at 195 K. Such sorption kinetics are adequate for practical utility and comparable with the  $CO_2$  sorption kinetics.<sup>31</sup> From a structural perspective, synchrotron PXRD refinement revealed that the unit-cell parameters of **sql-1-Ni-NCS-4C<sub>2</sub>H<sub>2</sub>** differ from those of **sql-1-Ni-NCS-3CO<sub>2</sub>** (Fig. 4b, Fig. S6 and S7, ESI†). For instance, **sql-1-Ni-NCS-3CO<sub>2</sub>** retained the same space group, *C2/c*, as the closed phase of **sql-1-Ni-NCS**, while **sql-1-Ni-NCS-4C<sub>2</sub>H<sub>2</sub>** adopted space group *P2<sub>1</sub>/n* as did the *m*-xylene loaded phase (**sql-1-Co-NCS-4MX**) previously reported by us.<sup>33</sup> The *Z* value is 4 in the closed phase and 2 in the  $C_2H_2$ -loaded phase. The normalized unit-cell volume changes from  $2264.9\text{ Å}^3$  in the closed phase to  $1818.8\text{ Å}^3$  (i.e.,  $1590.9 \times 2\text{ Å}^3$ ) in the  $C_2H_2$ -loaded phase, correspond to a 40.5% increase in unit cell volume. Attempts to solve the crystal structure of **sql-1-Ni-NCS-4C<sub>2</sub>H<sub>2</sub>** were unsuccessful, but MX molecules reside in both interlayer spaces and square cavities in **sql-1-Co-NCS-4MX** (Fig. S8, ESI†).

Volumetric working capacity for gas storage is also a key performance parameter since container volume is necessarily limited. The network density (excluding  $C_2H_2$ ) of **sql-1-Ni-NCS-4C<sub>2</sub>H<sub>2</sub>** was calculated to be  $1.02\text{ g cm}^{-3}$  (Fig. 4b), and therefore the volumetric working capacity of  $C_2H_2$  is ca.  $189\text{ cm}^3$ .

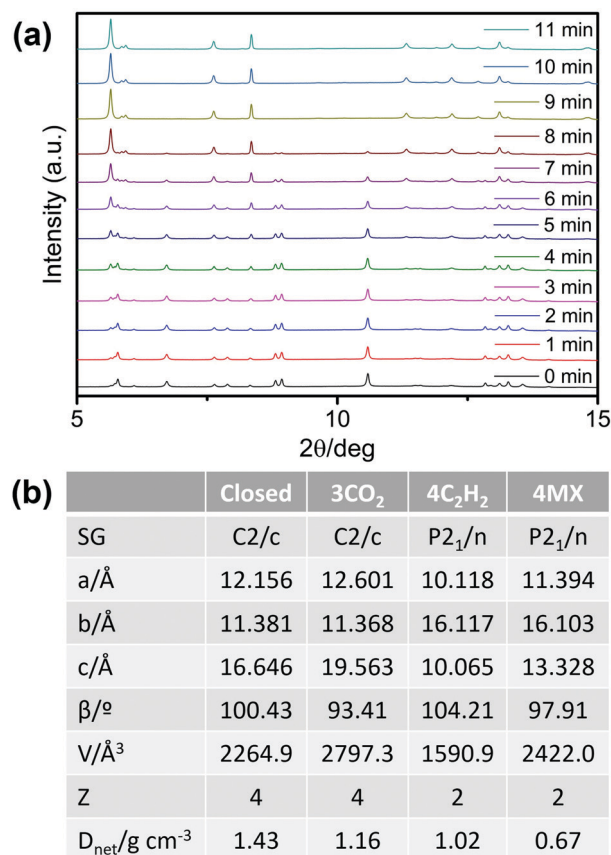


Fig. 4 (a) *In situ* synchrotron PXRD patterns for **sql-1-Ni-NCS** under 0.5 bar  $C_2H_2$  at 195 K; (b) structural parameters of **sql-1-Ni-NCS** (closed), **sql-1-Ni-NCS-3CO<sub>2</sub>**, **sql-1-Ni-NCS-4C<sub>2</sub>H<sub>2</sub>** and **sql-1-Co-NCS-4MX**.

This value is higher than **sql-1-Cu-BF<sub>4</sub>** ( $174\text{ cm}^3$ ) and **MOF-508** ( $106\text{ cm}^3$ ).<sup>4,28</sup> When compared to the industrial adsorbent acetone, which has a volumetric working capacity ( $170\text{ cm}^3$ ) between 1–15 bar at 288 K,<sup>4</sup> **sql-1-Ni-NCS** outperforms it by 11.2% at a safer working pressure range (1–3.2 bar, 288 K).

In summary, we herein report a switching transformation in a 2D **sql** CN, **sql-1-Ni-NCS**, induced through exposure to  $C_2H_2$ . The  $C_2H_2$  switching pressure,  $P_{ga}/P_{gd}$ , was controlled by temperature with retention of the saturation uptake. The type F-IV isotherm exhibited by **sql-1-Ni-NCS** enabled working capacity to be 100% of uptake capacity and the relatively high density resulted in benchmark volumetric working capacity at practically relevant conditions. When combined with other features such as fast sorption kinetics, hydrophobicity, and ease of scale-up,<sup>31</sup> **sql-1-Ni-NCS** is a promising candidate for enhancing the working capacity of gas storage and highlights the general potential that layered CNs offer for high working capacity. This is perhaps counterintuitive since such CNs are nonporous in their closed phases. Further studies to explore the storage potential of **sql-1-Ni-NCS** and related switching adsorbent layered materials (SALMAs) for other gases and vapours are in progress.

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## Conflicts of interest

There are no conflicts to declare.

## Notes and references

- 1 H. J. Arpe, *Acetylene. Industrial Organic Chemistry*, Wiley, 5th edn, 2010, pp 91–105.
- 2 R. E. Gannon, R. M. Manyik, C. Dietz, H. Sargent, R. Thribolet and R. Schaffer, *Acetylene, Kirk-Othmer Encyclopedia of Chemical Technology*, Wiley, 2003.
- 3 P. Pässler, W. Hefner, K. Buckl, H. Meinass, A. Meiswinkel, H.-J. Wernicke, G. Ebersberg, R. Müller, J. Bässler, H. Behringer and D. Mayer, *Acetylene, Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH, 2011.
- 4 S.-Q. Wang, X.-Q. Meng, M. Vandichel, S. Darwish, Z. Chang, X.-H. Bu and M. J. Zaworotko, *ACS Appl. Mater. Interfaces*, 2021, **13**, 23877–23883.
- 5 C. Janiak and J. K. Vieth, *New J. Chem.*, 2010, **34**, 2366–2388.
- 6 D. J. O'Hearn, A. Bajpai and M. J. Zaworotko, *Small*, 2021, 2006351.
- 7 S. Kitagawa, *Angew. Chem., Int. Ed.*, 2015, **54**, 10686–10687.
- 8 S.-Q. Wang, S. Mukherjee and M. J. Zaworotko, *Faraday Discuss.*, 2021, **231**, 9–50.
- 9 A. Schneemann, V. Bon, I. Schwedler, I. Senkovska, S. Kaskel and R. A. Fischer, *Chem. Soc. Rev.*, 2014, **43**, 6062–6096.
- 10 Z. Chang, D.-H. Yang, J. Xu, T.-L. Hu and X.-H. Bu, *Adv. Mater.*, 2015, **27**, 5432–5441.
- 11 S. Horike, S. Shimomura and S. Kitagawa, *Nat. Chem.*, 2009, **1**, 695–704.
- 12 Q. Y. Yang, P. Lama, S. Sen, M. Lusi, K. J. Chen, W. Y. Gao, M. Shivanna, T. Pham, N. Hosono, S. Kusaka, J. J. Perry IV, S. Ma, B. Space, L. J. Barbour, S. Kitagawa and M. J. Zaworotko, *Angew. Chem., Int. Ed.*, 2018, **57**, 5684–5689.
- 13 J. J. Perry IV, J. A. Perman and M. J. Zaworotko, *Chem. Soc. Rev.*, 2009, **38**, 1400–1417.
- 14 T. R. Cook, Y.-R. Zheng and P. J. Stang, *Chem. Rev.*, 2012, **113**, 734–777.
- 15 J. A. Mason, J. Oktawiec, M. K. Taylor, M. R. Hudson, J. Rodriguez, J. E. Bachman, M. I. Gonzalez, A. Cervellino, A. Guagliardi, C. M. Brown, P. L. Llewellyn, N. Masciocchi and J. R. Long, *Nature*, 2015, **527**, 357–361.
- 16 R. Matsuda, R. Kitaura, S. Kitagawa, Y. Kubota, R. V. Belosludov, T. C. Kobayashi, H. Sakamoto, T. Chiba, M. Takata, Y. Kawazoe and Y. Mita, *Nature*, 2005, **436**, 238–241.
- 17 D. G. Samsonenko, H. Kim, Y. Sun, G.-H. Kim, H.-S. Lee and K. Kim, *Chem. – Asian J.*, 2007, **2**, 484–488.
- 18 D. Tanaka, M. Higuchi, S. Horike, R. Matsuda, Y. Kinoshita, N. Yanai and S. Kitagawa, *Chem. – Asian J.*, 2008, **3**, 1343–1349.
- 19 S. Xiang, W. Zhou, J. M. Gallegos, Y. Liu and B. Chen, *J. Am. Chem. Soc.*, 2009, **131**, 12415–12419.
- 20 J.-P. Zhang and X.-M. Chen, *J. Am. Chem. Soc.*, 2009, **131**, 5516–5521.
- 21 S. Xiang, W. Zhou, Z. Zhang, M. A. Green, Y. Liu and B. Chen, *Angew. Chem., Int. Ed.*, 2010, **49**, 4615–4618.
- 22 Z. Zhang, S. Xiang and B. Chen, *CrystEngComm*, 2011, **13**, 5983–5992.
- 23 J. Pang, F. Jiang, M. Wu, C. Liu, K. Su, W. Lu, D. Yuan and M. Hong, *Nat. Commun.*, 2015, **6**, 7575.
- 24 S. Gao, C. G. Morris, Z. Lu, Y. Yan, H. G. W. Godfrey, C. Murray, C. C. Tang, K. M. Thomas, S. Yang and M. Schroder, *Chem. Mater.*, 2016, **28**, 2331–2340.
- 25 F. Moreau, I. da Silva, N. H. Al Smail, T. L. Easun, M. Savage, H. G. W. Godfrey, S. F. Parker, P. Manuel, S. Yang and M. Schröder, *Nat. Commun.*, 2017, **8**, 14085.
- 26 Y. He, F. Chen, B. Li, G. Qian, W. Zhou and B. Chen, *Coord. Chem. Rev.*, 2018, **373**, 167–198.
- 27 Y.-P. Li, Y. Wang, Y.-Y. Xue, H.-P. Li, Q.-G. Zhai, S.-N. Li, Y.-C. Jiang, M.-C. Hu and X. Bu, *Angew. Chem., Int. Ed.*, 2019, **58**, 13590–13595.
- 28 M. Bonneau, C. Lavenn, K. Sugimoto, A. Legrand, T. Ogawa, F.-X. Coudert, R. Réau, K.-i. Otake and S. Kitagawa, *Res. Square*, 2020, DOI: 10.21203/rs.3.rs-102861/v1.
- 29 Z. Yugen, J. Li, W. Deng, N. Masayoshi and I. Tsuneto, *Chem. Lett.*, 1999, 195–196.
- 30 Y. Zhang, L. Jianmin, M. Nishiura and T. Imamoto, *J. Mol. Struct.*, 2000, **519**, 219–224.
- 31 S.-Q. Wang, S. Darwish, D. Sensharma and M. J. Zaworotko, *Mater. Adv.*, 2022, **3**, DOI: 10.1039/D1MA00785H, accepted.
- 32 S.-Q. Wang, Q.-Y. Yang, S. Mukherjee, D. O'Nolan, E. Patyk-Kazmierczak, K.-J. Chen, M. Shivanna, C. Murray, C. C. Tang and M. J. Zaworotko, *Chem. Commun.*, 2018, **54**, 7042–7045.
- 33 S.-Q. Wang, S. Mukherjee, E. Patyk-Kazmierczak, S. Darwish, A. Bajpai, Q.-Y. Yang and M. J. Zaworotko, *Angew. Chem., Int. Ed.*, 2019, **58**, 6630–6634.

