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# Crystal engineering of a new platform of hybrid ultramicroporous materials and their C<sub>2</sub>H<sub>2</sub>/CO<sub>2</sub> separation properties†

Daniel J. O'Hearn,<sup>‡a</sup> Debobroto Sensharma,<sup>‡a</sup> Asif Raza,<sup>‡a</sup> Andrey A. Bezrukov,<sup>‡a</sup> Matthias Vandichel,<sup>‡a</sup> Soumya Mukherjee<sup>‡a</sup> and Michael J. Zaworotko<sup>‡ab</sup>

Hybrid ultramicroporous materials (HUMs) comprised of combinations of organic and inorganic linker ligands are a leading class of physisorbents for trace separations involving C<sub>1</sub>, C<sub>2</sub> and C<sub>3</sub> gases. First generation HUMs are modular in nature since they can be self-assembled from transition metal cations, ditopic linkers and inorganic "pillars", as exemplified by the prototypal variant, **SIFSIX-3-Zn** (**3** = pyrazine, **SIFSIX** = SiF<sub>6</sub><sup>2-</sup>). Conversely, HUMs that utilise chelating ligands such as ethylenediamine derivatives are yet to be explored as sorbents. Herein, we report the structures and sorption properties of two HUMs based upon the chelating ligand *N*<sup>1</sup>,*N*<sup>2</sup>-bis(pyridin-4-ylmethyl)ethane-1,2-diamine (**enmepy**), [Zn(**enmepy**)(SiF<sub>6</sub>)]<sub>n</sub> (**SIFSIX-24-Zn**) and [Zn(**enmepy**)(SO<sub>4</sub>)]<sub>n</sub> (**SOFOUR-2-Zn**). These HUMs are isostructural and exhibit high C<sub>2</sub>H<sub>2</sub> uptakes of 85 cm<sup>3</sup> g<sup>-1</sup> (3.79 mmol g<sup>-1</sup>) and 79 cm<sup>3</sup> g<sup>-1</sup> (3.52 mmol g<sup>-1</sup>), and C<sub>2</sub>H<sub>2</sub>/CO<sub>2</sub> IAST selectivities of 7.4 and 8.1 (1 bar, 1:1 mixture, 298 K), respectively. Dynamic column breakthrough experiments resulted in separation factors of 5.26 and 2.05, and CO<sub>2</sub> effluent purities of 99.991 and 99.989%, respectively. Temperature programmed desorption experiments at 60 °C resulted in rapid desorption of CO<sub>2</sub>, followed by fuel grade C<sub>2</sub>H<sub>2</sub> (>98%), affording productivities of 9.45 and 7.96 L kg<sup>-1</sup> and maximum C<sub>2</sub>H<sub>2</sub> outlet purities of 99.92% and 99.66%, respectively. This study introduces the use of diamine chelating ligands in HUMs for gas separations through two parent sorbents that are prototypal for families of related materials, one of which, **SOFOUR-2-Zn**, uses the earth-friendly sulfate anion as a pillar.

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## Introduction

The first studies that confirmed permanent porosity in porous coordination networks (PCNs)<sup>1–3</sup> spawned intense interest in study of PCNs<sup>4,5</sup> for their potential utility for gas separations including purification of light hydrocarbons.<sup>6–9</sup> One class of PCN, hybrid ultramicroporous materials (HUMs), is comprised of inorganic and organic linker ligands and can exhibit highly selective physisorption.<sup>10</sup> Their performance can be attributed to their ultramicroporous (≤7.0 Å) nature, which results in tight sorbate binding, and the strong electrostatics of the inorganic anions that line the pores,<sup>11</sup> in effect creating a high density of

highly selective binding sites.<sup>5</sup> The prototypal HUM, [Zn(SiF<sub>6</sub>)(pyz)<sub>2</sub>]<sub>n</sub> (**SIFSIX-3-Zn**),<sup>12</sup> is comprised of an N-donor linker ligand, pyrazine (**3**), that links Zn<sup>2+</sup> cations to form a cationic 2D square lattice topology, **sql**, network and SiF<sub>6</sub><sup>2-</sup> (**SIFSIX**) anions that pillar the **sql** nets to form a 3D primitive cubic, **pcu**, topology network. **SIFSIX-3-Zn** was found to offer exceptional trace CO<sub>2</sub> capture properties over N<sub>2</sub> and CH<sub>4</sub>,<sup>10</sup> and its inherent modularity enabled systematic fine-tuning of composition through substitution of the metal cation, organic linker ligand and/or the **SIFSIX** pillar, affording improvements in stability and performance.<sup>10,13,14</sup> Second generation HUMs pillared by **SIFSIX** and other MF<sub>6</sub><sup>2-</sup> anions (M = Si, Ge, Sn, Ti, Zr) belong to the **MFSIX** platform.<sup>15</sup> Other HUM platforms have been based on different inorganic pillars, including **DICRO** (Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>),<sup>16,17</sup> **FOXY** (NbOF<sub>5</sub><sup>2-</sup>),<sup>18,19</sup> **MFFIVE** (AlF<sub>5</sub><sup>2-</sup>),<sup>20</sup> **mmo** topology nets (CrO<sub>4</sub><sup>2-</sup>, MoO<sub>4</sub><sup>2-</sup>, WO<sub>4</sub><sup>2-</sup>),<sup>21</sup> and, most recently, **SOFOUR** (SO<sub>4</sub><sup>2-</sup>).<sup>22</sup>

A potential application for HUMs is acetylene (C<sub>2</sub>H<sub>2</sub>) purification. C<sub>2</sub>H<sub>2</sub> is typically produced *via* oxidative coupling of CH<sub>4</sub> with CO<sub>2</sub> as a by-product.<sup>9</sup> Since C<sub>2</sub>H<sub>2</sub> and CO<sub>2</sub> have the same kinetic diameter of 3.3 Å and similar boiling/sublimation points of 188.4 and 194.7 K, respectively,<sup>5,6</sup> sorptive separation is

<sup>a</sup>Department of Chemical Sciences, Bernal Institute, University of Limerick, Limerick V94 T9PX, Ireland. E-mail: matthias.vandichel@ul.ie; soumya.mukherjee@ul.ie; xtal@ul.ie

<sup>b</sup>SSPC, Science Foundation Ireland Research Centre for Pharmaceuticals, University of Limerick, Limerick V94 T9PX, Ireland

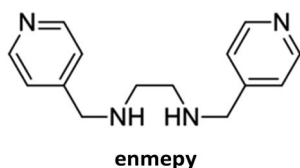
† Electronic supplementary information (ESI) available: Synthesis, gas sorption, modelling details, crystallographic information. CCDC 2206134. For ESI and crystallographic data in CIF or other electronic format see DOI: <https://doi.org/10.1039/d4sc03029j>

‡ These authors contributed equally to this work.

challenging. Industrially, purification is typically achieved using organic solvents, which is inefficient and requires multiple steps to reach the required levels of purity. HUMs such as **SIFSIX-dps-Cu**,<sup>23</sup> **UTSA-300a**,<sup>24</sup> and **DICRO-4-Ni-i**,<sup>25</sup> selectively adsorb  $C_2H_2$  *via* strong  $C_2H_2$  binding sites in which F atoms serve as hydrogen bond acceptors, particularly when spaced optimally (*ca.* 7 Å) to interact with both ends of a  $C_2H_2$  molecule.<sup>6</sup> Recently, the linker ligand bpe, 1,2-bis(4-pyridyl)ethane, afforded a layered flexible HUM, **sql-SIFSIX-bpe-Zn**, the activated phase of which, **sql-SIFSIX-bpe-Zn-β**, set a new benchmark for  $C_2H_2$  adsorption enthalpy ( $Q_{st}$ ) of 67.5 kJ mol<sup>-1</sup>.<sup>26</sup> This strong binding was attributed to induced fit of  $C_2H_2$  molecules by enzyme-like adaptable sorbent binding sites and **sql-SIFSIX-bpe-Zn-β** was found to be highly  $C_2H_2$ -selective over both ethylene and  $CO_2$ .

Although families of pillared HUMs composed of linear or angular ditopic linker ligands are the most commonly studied HUM variants, other ligand types are possible. HUMs with 4,6-connected **fsc** topology are composed of tetratopic ligands where the ligand serves as a 4-c node and the metal ion serves as a 6-c node. Examples of ligands and their respective **fsc** topology HUMs are as follows: metalloligand  $[Cu_2(3\text{-pyridin-4-yl} \text{ acrylate})_4]$  in **fsc-2-SIFSIX**,<sup>27</sup> tetra-(pyridin-4-yl)porphyrin in **CPM-131**,<sup>28</sup> "FTPFs" **Cu-Nb-M** ( $M = Zn, Fe, Ni$ ),<sup>29</sup> 1,2,4,5-tetra(pyridin-4-yl)benzene (tepb) in **ZJU-280** (**SIFSIX-22-Cu**),<sup>30</sup> **SIFSIX-22-Zn**,<sup>22,31</sup> **SOFOUR-1-Zn**,<sup>22</sup> and **TIFSIX-Cu-TPB** (**TIFSIX-6-Cu**).<sup>32</sup> These materials have been studied for  $CO_2$  capture,<sup>27</sup> electrocatalysis,<sup>29</sup>  $C_2H_2/C_2H_4$  separation,<sup>30</sup> and  $C_2H_2/CO_2$  separation.<sup>22,26</sup> Since the ligand serves as a 4-c node, such PCNs are also amenable to pillar substitution as exemplified by replacement of the **SIFSIX** pillar in **SIFSIX-22-Zn** by  $SO_4^{2-}$  (**SOFOUR**) in **SOFOUR-1-Zn**<sup>22</sup> and **SOFOUR-DPDS-Ni** (4-DPDS = 4,4'-dipyridyldisulfide),<sup>33</sup> and the use of other fluorinated pillars, *e.g.*  $TiF_6^{2-}$ ,  $SnF_6^{2-}$ ,  $GeF_6^{2-}$ ,  $ZrF_6^{2-}$  and  $TaF_7^{2-}$ , while retaining **fsc** topology.<sup>34</sup> The  $SO_4^{2-}$  pillar has also been used in HUMs such as  $CuSO_4(1,4\text{-bin})_{1.5}$  (1,4-bin = 1,4-bisimidazole naphthalene),<sup>35</sup> and **SOFOUR-TEPE-Zn** (TEPE = 1,1,2,2-tetra(pyridin-4-yl) ethene).<sup>36</sup>

Nevertheless, the availability of linker ligands suitable for HUMs remains somewhat limited in scope and derivatives of chelating ligands such as ethylenediamine (**en**), which represent a potentially inexpensive and versatile class of ligand, are to our knowledge unexplored. This is despite **en** and its derivatives representing 7.27% (55 046 entries) of coordination compounds archived in the Cambridge Structural Database (CSD version 5.45, September 2024).<sup>37</sup> In this contribution, we report a successful crystal engineering approach to preparing the prototypal members of two HUM platforms comprising a pyridyl functionalised chelating **en** ligand, **enmepy**, and their sorption properties in the context of  $C_2H_2/CO_2$  gas separations.



## Results and discussion

### CSD analysis

In order to design and characterise new HUM platforms based on **en** derivatives, we first looked for reports of **en** chelates pillared by  $MF_6$  anions ( $M = Si, Ge, Sn, Ti, Zr, Hf$ ). Database mining of the CSD for coordination compounds containing both an **en** (or derivative) chelate and a coordinated **MFSIX** anion afforded just five hits (Table S1 and Fig. S1a†): two  $ZrF_6^{2-}$  complex anions ( $[(ZrF_6)_2(ZrF_5(OH)_2)_2]^{6-}$  and  $[(ZrF_6)_2]^{4-}$ ); three 1D chains involving **SIFSIX** or  $TiF_6^{2-}$  (**TIFSIX**) linkers ( $[Cu(en)_2(SiF_6)]_n$  and  $[Cu(en)_2(TiF_6)]_n$ ). No apparent porosity was present or studied in these compounds.<sup>38,39</sup> This lack of sorption candidates prompted us to look at the earth-friendly inorganic pillar **SOFOUR** and our search (Fig. S1b†) resulted in 25 hits (20 distinct compounds, Table S2;† corresponding to chelating ligands listed in Fig. S2†).  $[Cu(en)(OH)_2(SO_4)]_n$  and  $[Zn(en)_2(SO_4)]_n$  are 1D chains with no apparent or permanent porosity.<sup>40–45</sup> However,  $[Zn(enmepy)(SO_4)]_n$  (CSD refcode ZOMNOG, hereinafter referred to as **SOFOUR-2-Zn**) is composed of the chelating **en** derivative  $N^1,N^2$ -bis(pyridin-4-ylmethyl)ethane-1,2-diamine (**enmepy**) and  $Zn^{2+}$  cations that form a **sql** network pillared by **SOFOUR** to afford a 3D **pcu** network. Even though **SOFOUR-2-Zn** contains 1D ultramicropores, no gas sorption data was reported.<sup>46</sup> We then searched for other structures containing **enmepy** chelates that form **sql** nets similar to **SOFOUR-2-Zn**. This search, which used the query in Fig. S3,† afforded 62 hits, manual inspection of which revealed 31 **sql** nets (see Table S3†). The majority (22) are not pillared, with axial positions metal cations coordinated by terminal ligands. The remaining entries were found to be pillared by either 1,4-benzenedicarboxylate derivatives,<sup>47,48</sup>  $MO_4^{2-}$  ( $M = Cr, Mo$ ) or, in the case of **SOFOUR-2-Zn**, **SOFOUR**.<sup>46</sup> The earth friendly characteristics of **SOFOUR** over  $CrO_4^{2-}$  and  $MoO_4^{2-}$ , motivated us to characterise the sorption properties of **SOFOUR-2-Zn** along with its new **SIFSIX** variant,  $[Zn(enmepy)(SiF_6)]_n$  (**SIFSIX-24-Zn**).

### Crystal structures

**SOFOUR-2-Zn** was previously reported in 2014, crystallising in the monoclinic space group  $C2$ .<sup>46</sup> Each octahedral  $Zn^{2+}$  cation is chelated by amino groups of one **enmepy** and two pyridyl groups from two different **enmepy** ligands to fill its equatorial positions (Fig. 1a), thereby generating a 2D cationic network with **sql** topology (Fig. 1b). In each axial position, a **SOFOUR** anion serves as a pillar to adjacent **sql** layers so as to form a **pcu** topology network with an intermetallic distance between **sql** layers of 6.74 Å (Fig. 1c). The **sql** layers stack such that triangular 1D channels containing hydrate molecules run parallel to the crystallographic *c*-axis (Fig. 1b). The calculated void space is 40.9% of unit cell volume after removal of hydrate molecules (mercury contact surface, probe radius 1.2 Å).<sup>49</sup>

**SIFSIX-24-Zn** was prepared by reacting **enmepy** with  $ZnSiF_6$ . Crystals suitable for single crystal X-ray diffraction, SCXRD, were obtained by diffusion of a methanolic solution of **enmepy** layered onto an ethylene glycol solution of  $ZnSiF_6$  (see ESI† for details). SCXRD data revealed that **SIFSIX-24-Zn** had crystallised



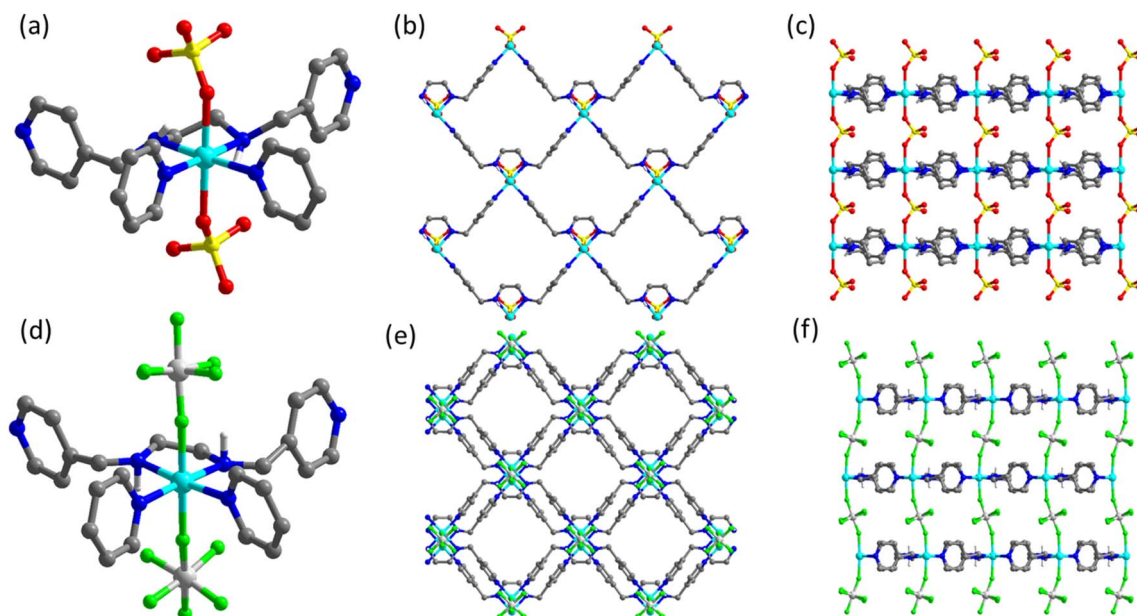


Fig. 1 Crystal structures of SIFSIX-24-Zn and SOFOUR-2-Zn (C–H atoms omitted for clarity, C = grey, H = white, N = blue, O = red, F = green, S = yellow, Si = light beige, Zn = cyan). (a) The octahedral coordination environment around  $\text{Zn}^{2+}$  in SOFOUR-2-Zn, (b) SOFOUR-2-Zn packing viewed along  $a$ -axis, (c) SOFOUR-2-Zn crystal packing viewed along  $c$ -axis, (d) the octahedral coordination environment around  $\text{Zn}^{2+}$  in SIFSIX-24-Zn, (e) SIFSIX-24-Zn crystal packing viewed along  $b$ -axis, (f) SIFSIX-24-Zn crystal packing viewed along  $c$ -axis.

in the chiral orthorhombic space group  $C222_1$ . The equatorial environment of the  $\text{Zn}^{2+}$  cations is similar to that of SOFOUR-2-Zn but the SIFSIX pillars form shorter bonds with the Zn cation at the axial positions ( $\text{Zn-F} = 2.148(5)$  Å vs.  $\text{Zn-O} = 2.223$  Å, Fig. 1d). SIFSIX-24-Zn formed the same **sql** layers found in SOFOUR-2-Zn, resulting in the **pcu** network illustrated in Fig. 1e and f. The larger SIFSIX anion resulted in intermetallic distance between layers of  $7.5759(16)$  Å ( $0.833$  Å longer than SOFOUR-2-Zn, Fig. 1f). SIFSIX-24-Zn possesses similar 1D pores to SOFOUR-2-Zn but with diffuse electron density which was accounted for by the PLATON SQUEEZE<sup>50</sup> procedure in the final structure refinement. The void space (Mercury contact surface, probe radius  $1.2$  Å) was calculated to be  $37.9\%$  of unit cell volume. Further crystallographic details are presented in Table S4†.

In both SOFOUR-2-Zn and SIFSIX-24-Zn, all **enmepy** ligands within a **sql** layer orient in the same direction, precluding a crystallographic inversion centre. The stacking of **sql** layers differs between the two compounds. In SOFOUR-2-Zn, each layer is identical and orients in the same direction, whereas in SIFSIX-24-Zn, the layers alternate in direction and chirality and a pseudo centre of symmetry is present. Though this detail may seem inconsequential for gas adsorption, it impacts pore shape as becomes apparent when examining crystal packing (Fig. 1). The chirality of the **sql** layers formed by **enmepy** has been explored by Wen *et al.*, where homochiral batches of crystals could be obtained when using a homochiral template during crystallisation.<sup>51–53</sup> The SIFSIX-24-Zn crystal used for SCXRD study was found to be a racemic twin with a Flack parameter of  $0.5$  (Table S4†).<sup>46,47</sup>

## Gas sorption

**Pure gas sorption studies.** In order to perform sorption studies, bulk samples of SOFOUR-2-Zn and SIFSIX-24-Zn were prepared by mixing methanolic solutions of **enmepy** with aqueous solutions of  $\text{ZnSO}_4$  and  $\text{ZnSiF}_6$ , respectively, at room temperature, to obtain microcrystalline powders (see ESI† for synthetic details) with Powder X-ray diffraction (PXRD) patterns matching those calculated from SCXRD data (Fig. S4†). Thermogravimetric analysis (TGA) of SOFOUR-2-Zn and SIFSIX-24-Zn indicated loss of solvent molecules at  $90$  and  $75$  °C, respectively, and thermal stability up to approximately  $300$  °C and  $200$  °C, respectively (Fig. S5†). Following activation at  $60$  °C under dynamic vacuum, both materials exhibited type-I isotherms for  $\text{CO}_2$  at  $195$  K, with saturation uptakes of  $135$   $\text{cm}^3$   $\text{g}^{-1}$  and  $178$   $\text{cm}^3$   $\text{g}^{-1}$ , respectively (Fig. 2a), and apparent BET surface areas of  $452$   $\text{m}^2$   $\text{g}^{-1}$  and  $590$   $\text{m}^2$   $\text{g}^{-1}$ , respectively (Fig. S6 and S7†). The Horvath-Kawazoe differential pore volume plots from  $195$  K  $\text{CO}_2$  isotherms for both compounds were centred around  $5.0$  Å, classifying them as ultra-microporous (Fig. S8†). SIFSIX-24-Zn exhibited a minor inflection in the  $195$  K  $\text{CO}_2$  isotherm in the absolute pressure range  $100$ – $200$  mmHg. Similarly, SOFOUR-2-Zn revealed inflections at  $350$ – $400$  mmHg in the  $\text{CO}_2$  at  $195$  K isotherm (Fig. 2a), and at  $5$ – $10$  mm Hg in the  $\text{N}_2$  at  $77$  K isotherm (Fig. S9†). Such an inflection was not observed in the  $273$  K and  $298$  K  $\text{CO}_2$  and  $\text{C}_2\text{H}_2$  isotherms (Fig. S10 and S11†). At  $298$  K, the  $\text{CO}_2$  uptakes of SOFOUR-2-Zn and SIFSIX-24-Zn at  $1$  bar were observed to be  $41$   $\text{cm}^3$   $\text{g}^{-1}$  ( $1.78$   $\text{mmol g}^{-1}$ ) and  $40$   $\text{cm}^3$   $\text{g}^{-1}$  ( $1.79$   $\text{mmol g}^{-1}$ ), respectively (Fig. 2b). The  $Q_{\text{st}}$  values for  $\text{CO}_2$ ,  $22.1$   $\text{kJ mol}^{-1}$  and  $16.8$   $\text{kJ mol}^{-1}$ , respectively, at low loading (Fig. 2c and S12†) are





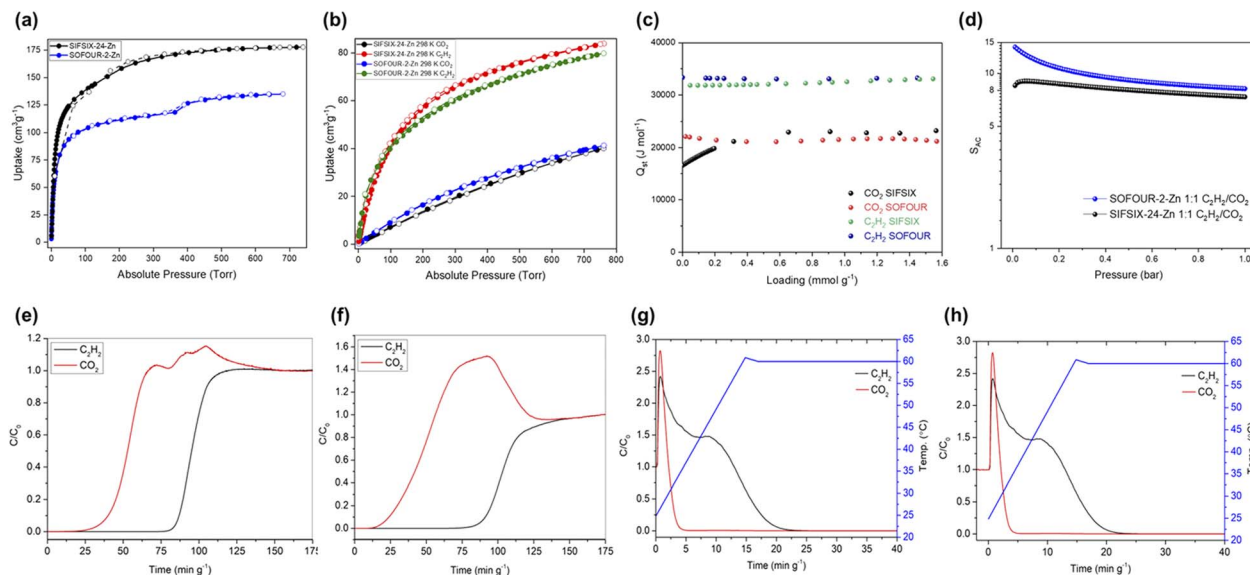


Fig. 2 Gas sorption properties of SIFSIX-24-Zn and SOFOUR-2-Zn: (a) 195 K  $\text{CO}_2$ ; (b) 298 K  $\text{C}_2\text{H}_2$  and  $\text{CO}_2$ ; (c)  $Q_{\text{st}}$  for  $\text{C}_2\text{H}_2$  and  $\text{CO}_2$ ; (d) IAST selectivity for  $\text{C}_2\text{H}_2$  over  $\text{CO}_2$  at 298 K and 1 : 1 (v/v) mixture; (e) breakthrough curve at 298 K for 1 : 1  $\text{C}_2\text{H}_2/\text{CO}_2$  mixture for SOFOUR-22-Zn; (f) breakthrough curve at 298 K for 1 : 1  $\text{C}_2\text{H}_2/\text{CO}_2$  mixture for SIFSIX-24-Zn; (g) temperature programmed desorption after breakthrough experiment for SOFOUR-2-Zn; (h) temperature programmed desorption after breakthrough experiment for SIFSIX-24-Zn.

exceptionally low. In contrast, the uptakes for  $\text{C}_2\text{H}_2$  at 298 K were relatively high, 79 and  $84 \text{ cm}^3 \text{ g}^{-1}$ , or  $3.52$  and  $3.75 \text{ mmol g}^{-1}$ , respectively (Fig. 2b), with  $Q_{\text{st}}$  values of  $33.3 \text{ kJ mol}^{-1}$  and  $31.8 \text{ kJ mol}^{-1}$ , respectively, at low loading.<sup>54</sup> Evidently both these sorbents exhibit a relatively high pure component uptake for  $\text{C}_2\text{H}_2$  over  $\text{CO}_2$  at 298 K, which is in the range that could break the usual trade-off between uptake and selectivity.<sup>55,56</sup> PXRD patterns measured after activation and adsorption experiments showed retention of the crystal structures of both materials (Fig. S13†).

Since single-component gas sorption isotherms revealed significantly higher  $\text{C}_2\text{H}_2$  uptakes relative to  $\text{CO}_2$ , ideal adsorbed solution theory (IAST) was applied using the pyIAST Python package<sup>57</sup> to determine the selectivity for  $\text{C}_2\text{H}_2$  in a 1 : 1  $\text{C}_2\text{H}_2/\text{CO}_2$  mixture,  $S_{\text{AC}}$ . We found moderate selectivities for SOFOUR-2-Zn and SIFSIX-24-Zn of 8.2 and 7.3 at 1 bar and 298 K, respectively (Fig. 2d and S14†). Although these selectivity numbers are lower than benchmark physisorbents such as ZNU-1 (56.6),<sup>58</sup>  $\text{Zn}_2(\text{bpy})(\text{btec})$  (33.3),<sup>59</sup>  $\text{sql-16-Cu-NO}_3\text{-}\alpha$  (27.8),<sup>60</sup> and  $\text{Ni}_3(\text{HCOO})_6$  (22),<sup>61</sup> they are higher than HUMs such as TIFSIX-2-Ni-i (6.1),<sup>62</sup> and NboFFIVE-3-Ni (6.0)<sup>56</sup> (see Table S5† for a list of leading  $\text{C}_2\text{H}_2/\text{CO}_2$  selective PCNs). Combining both IAST selectivity and adsorption capacity recorded at 298 K, the separation potentials for both sorbents were found to be similar at 1 bar and 298 K:  $0.78 \text{ mmol g}^{-1}$  for SOFOUR-2-Zn, and  $0.76 \text{ mmol g}^{-1}$  for SIFSIX-24-Zn (Fig. S15†).

The water vapour sorption isotherm of SOFOUR-2-Zn reveals a sigmoidal adsorption profile with a total uptake approaching 30 wt% at 95% R.H. (relative humidity), followed by desorption with low hysteresis. In contrast, SIFSIX-24-Zn shows a sudden decrease in uptake at ca. 90% R.H., followed by high desorption hysteresis, typical of moisture-induced phase degradation (Fig. S16†). Accelerated stability tests conducted by incubating

activated samples at 40 °C and 75% R.H. show retention of the porous phase of SOFOUR-2-Zn over 5 days, whereas significant new peaks are observed in SIFSIX-24-Zn within 90 hours of exposure (Fig. S17†), indicating that the  $\text{SO}_4^{2-}$  pillar enhances framework stability relative to  $\text{SiF}_6^{2-}$ .

**Dynamic column breakthrough testing.** Encouraged by the single-component gas sorption data, we performed dynamic column breakthrough (DCB) experiments on microcrystalline samples of SOFOUR-2-Zn and SIFSIX-24-Zn. A 1 : 1  $\text{C}_2\text{H}_2/\text{CO}_2$  mixture was passed through a column packed with activated sample under a total flow rate of 1.0 sccm and the effluent composition was monitored using mass spectrometry. For SOFOUR-2-Zn (Fig. 2e),  $\text{CO}_2$  breakthrough occurred at 25.4 min  $\text{g}^{-1}$ , followed by  $\text{C}_2\text{H}_2$  at 81.0 min  $\text{g}^{-1}$  (55.6 min  $\text{g}^{-1}$  later). During this interval, the minimum effluent purity of  $\text{CO}_2$  was measured to be 99.989% and the saturation uptakes were  $47.1 \text{ cm}^3 \text{ g}^{-1}$  and  $23.2 \text{ cm}^3 \text{ g}^{-1}$  for  $\text{C}_2\text{H}_2$  and  $\text{CO}_2$ , respectively, resulting in a separation factor ( $\alpha_{\text{AC}}$ ) of 2.05. For SIFSIX-24-Zn (Fig. 2f),  $\text{CO}_2$  breakthrough occurred at 14.2 min  $\text{g}^{-1}$  with a minimum effluent purity of 99.991% and  $\text{C}_2\text{H}_2$  breakthrough occurred at 78.6 min  $\text{g}^{-1}$  (64.4 min  $\text{g}^{-1}$  later). Minor fluctuations were observed at the onset of gas breakthrough in all experiments due to a pressure drop across the powdered sorbent bed. The saturation uptakes for  $\text{C}_2\text{H}_2$  and  $\text{CO}_2$  were determined to be  $53.0 \text{ cm}^3 \text{ g}^{-1}$  and  $10.1 \text{ cm}^3 \text{ g}^{-1}$ , respectively (Table S6†), resulting in higher  $\alpha_{\text{AC}}$  of 5.26, putting SIFSIX-24-Zn in the same performance range as TIFSIX-4-Cu in terms of separation factor and pure component  $\text{C}_2\text{H}_2$  uptake ( $5.4$  and  $3.85 \text{ mmol g}^{-1}$ , respectively).<sup>56</sup>

Temperature Programmed Desorption (TPD) experiments were conducted after completion of the adsorption branches in DCB experiments for both SOFOUR-2-Zn and SIFSIX-24-Zn (Fig. 2g and h) by replacing the inlet gas mixture flow with 20



sccm of He and applying a temperature ramp of  $5\text{ }^{\circ}\text{C min}^{-1}$  from  $25\text{ }^{\circ}\text{C}$  to  $60\text{ }^{\circ}\text{C}$ . Desorption was continued until no further adsorbate was detected. We found that  $60\text{ }^{\circ}\text{C}$  was sufficient to regenerate both HUMs. Similar TPD curves were obtained for both **SOFOUR-2-Zn** and **SIFSIX-24-Zn**, characterised by rapid decreases in effluent  $\text{CO}_2$  concentration, while  $\text{C}_2\text{H}_2$  continued to be released with increasing temperature for a period prior to desorption. Fuel grade  $\text{C}_2\text{H}_2$  ( $>98\%$  purity) was eluted in the interval between 5 and 27  $\text{min g}^{-1}$  for **SIFSIX-24-Zn**, and between 4 and 20  $\text{min g}^{-1}$  for **SOFOUR-2-Zn**, corresponding to productivities of  $9.45\text{ L kg}^{-1}$  and  $7.69\text{ L kg}^{-1}$  of fuel grade  $\text{C}_2\text{H}_2$  respectively, and peak  $\text{C}_2\text{H}_2$  purities of 99.66 and 99.92%, respectively (Table S7†). These results are similar to literature values in terms of peak  $\text{C}_2\text{H}_2$  purity for **TIFSIX-2-Cu-i**,<sup>63</sup> **SIFSIX-22-Zn** and **SOFOUR-1-Zn**,<sup>22</sup> which are all 99.9% or higher. The productivities for fuel grade  $\text{C}_2\text{H}_2$  in a 1 : 1  $\text{C}_2\text{H}_2/\text{CO}_2$  mixture are  $9.45\text{ L kg}^{-1}$  and  $7.69\text{ L kg}^{-1}$  for **SIFSIX-24-Zn** and **SOFOUR-2-Zn**, respectively. This is much higher than previously reported values of  $3.3\text{ L kg}^{-1}$  and  $3.1\text{ L kg}^{-1}$ , for **SIFSIX-22-Zn** and **SOFOUR-1-Zn**, respectively.<sup>22</sup> **SOFOUR-2-Zn** and **SIFSIX-24-Zn** also produced significant amounts of high purity  $\text{C}_2\text{H}_2$  (99.5%). For **SIFSIX-24-Zn**,  $>99.5\%$   $\text{C}_2\text{H}_2$  eluted over the interval 5.8 to 23.9  $\text{min g}^{-1}$ , resulting in a productivity of  $8.75\text{ L kg}^{-1}$ , only  $0.7\text{ L kg}^{-1}$  less than the production of fuel-grade  $>98\%$   $\text{C}_2\text{H}_2$ , but for **SOFOUR-2-Zn**,  $>99.5\%$   $\text{C}_2\text{H}_2$  was eluted only between 5.3 and 9.4  $\text{min g}^{-1}$  resulting in a significantly lower productivity of  $3.01\text{ L kg}^{-1}$ . These values are lower than the benchmark of  $53.8\text{ L kg}^{-1}$  for  $>99.5\%$   $\text{C}_2\text{H}_2$  set by **ZNU-1**.<sup>58</sup> Additional DCB experiments conducted using a humid  $\text{C}_2\text{H}_2/\text{CO}_2$  mixture showed that separation performance was largely unaffected by moisture in both **SOFOUR-2-Zn** and **SIFSIX-24-Zn** over a complete adsorption cycle, despite the poor stability of **SIFSIX-24-Zn** towards moisture (Fig. S18†).

Based on pure component isotherms and IAST calculations, both **SOFOUR-2-Zn** and **SIFSIX-24-Zn** should have roughly the same performance. However, DCB experiments revealed that despite showing comparable  $\text{C}_2\text{H}_2$  uptakes in mixed-gas conditions, **SIFSIX-24-Zn** is better in terms of separation factor (2.05 vs. 5.26 for **SOFOUR-2-Zn** and **SIFSIX-24-Zn**, respectively). Production of high purity ( $>99.5\%$ )  $\text{C}_2\text{H}_2$  was also higher for **SIFSIX-24-Zn** than for **SOFOUR-2-Zn**, although, fuel-grade ( $>98\%$ ) productivity was similar for both. The differences might be attributed to the weaker  $Q_{\text{st}}$  for  $\text{CO}_2$  of **SIFSIX-24-Zn**,  $16.8\text{ kJ mol}^{-1}$  ( $\Delta Q_{\text{st}}$  for  $\text{C}_2\text{H}_2/\text{CO}_2 = 15.0\text{ kJ mol}^{-1}$ ), vs.  $22.1\text{ kJ mol}^{-1}$  ( $\Delta Q_{\text{st}}$  for  $\text{C}_2\text{H}_2/\text{CO}_2 = 11.2\text{ kJ mol}^{-1}$ ) for **SOFOUR-2-Zn**.

### Sorbate binding sites

To better understand the nature of the  $\text{C}_2\text{H}_2$  and  $\text{CO}_2$  binding sites, density functional theory (DFT) calculations were performed for **SOFOUR-2-Zn** and **SIFSIX-24-Zn** (see ESI† for computational methodology). In **SOFOUR-2-Zn**, the  $\text{C}_2\text{H}_2$  molecule orients along one of the channel walls, forming simultaneous hydrogen bonds from both C–H hydrogen atoms to  $\text{SO}_4^{2-}$  oxygen atoms, with  $\text{O}\cdots\text{H}$  distances of 2.57 Å and 2.62 Å (Fig. 3). In **SIFSIX-24-Zn**, hydrogen bonds are bifurcated, with the H-atoms being shared between two F-atoms of the same

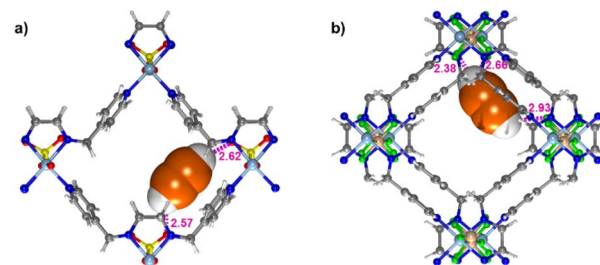


Fig. 3 Ball and stick models of (a) the  $\text{C}_2\text{H}_2$  binding site for **SOFOUR-2-Zn**; (b) the  $\text{C}_2\text{H}_2$  binding site for **SIFSIX-24-Zn**. Short contacts are highlighted as dashed magenta bonds and distances are given in Å.

**SIFSIX** pillar, with distances of 2.38 and 2.66 Å on one end, and 2.93 Å with a contact of 3.66 Å on the other end (Fig. 3). These multi-site short contacts provide a clear basis for the selective  $\text{C}_2\text{H}_2$  binding observed in both materials. In contrast,  $\text{CO}_2$  binding sites are primarily governed by electrostatic interactions between the  $\text{CO}_2$  carbon and electronegative pillar F and O atoms respectively (Fig. S19†). DFT-derived enthalpy values associated with gas adsorption are presented in Table S8.†

## Conclusions

The previously reported material  $[\text{Zn}(\text{enmepyl})(\text{SO}_4)]_n$  (**SOFOUR-2-Zn**),<sup>46</sup> illustrates the potential utility of **en** based ligands for design of new HUMs with potential utility in gas separations. Pillar substitution using a crystal engineering approach enabled us to isolate  $[\text{Zn}(\text{enmepyl})(\text{SiF}_6)]_n$  (**SIFSIX-24-Zn**), the prototypal member of a new platform of **MFSIX** HUMs. Pure component gas sorption studies and dynamic column breakthrough experiments revealed strong performance for the separation of  $\text{C}_2\text{H}_2$  from  $\text{CO}_2$  for both HUMs with appreciable amounts of fuel grade  $\text{C}_2\text{H}_2$  ( $>98\%$ ) as shown by temperature programmed desorption of the sorbed gases from a 1 : 1 mixture of  $\text{C}_2\text{H}_2/\text{CO}_2$ . Productivities of  $9.45\text{ L kg}^{-1}$  and  $7.69\text{ L kg}^{-1}$  were measured for **SIFSIX-24-Zn** and **SOFOUR-2-Zn**, respectively, and **SIFSIX-24-Zn** produced high purity  $\text{C}_2\text{H}_2$  ( $>99.5\%$ ). This study demonstrates for the first time that chelating ethylenediamine based ligands can sustain facile to synthesise HUMs with strong gas separation properties. Both HUM platforms are inherently modular and their scope in terms of composition and properties are under further investigation in our laboratory. We anticipate that **SIFSIX-24-Zn** and **SOFOUR-2-Zn** will serve as prototypes for families of second-generation sorbents through metal and/or pillar substitution, as well as ligand modification.

## Data availability

The data supporting the findings of this study are available in the ESI† or from the authors upon request.

## Author contributions

Project conceptualisation: D. J. O., D. S., S. M. and M. J. Z.; synthesis and characterisation: D. J. O., A. R. and A. A. B.; single component gas sorption: D. S., A. R. and D. J. O.; dynamic



column breakthrough and temperature programmed desorption: D. S. and S. M.; molecular modelling: M. V.; single crystal X-ray crystallography: D. J. O.; Cambridge Structural Database analysis: D. J. O. and A. R.; writing – original draft: D. J. O., D. S., S. M., A. A. B., and M. J. Z.; writing – review & editing: all authors; funding acquisition: M. J. Z. and M. V.; supervision: S. M., M. J. Z. and M. V. D. J. O., D. S. and A. R. contributed equally to this work.

## Conflicts of interest

There are no conflicts to declare.

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