

Cite this: *Chem. Sci.*, 2023, 14, 1472

All publication charges for this article have been paid for by the Royal Society of Chemistry

# Fluorido-bridged robust metal–organic frameworks for efficient C<sub>2</sub>H<sub>2</sub>/CO<sub>2</sub> separation under moist conditions†

Yi-Ming Gu,<sup>ab</sup> You-You Yuan,<sup>c</sup> Cai-Lin Chen,<sup>d</sup> Sheng-Sheng Zhao,<sup>a</sup> Tian-Jun Sun,<sup>a</sup> Yu Han,<sup>d</sup> Xiao-Wei Liu,<sup>d</sup> Zhiping Lai<sup>\*,d</sup> and Shu-Dong Wang<sup>\*,a</sup>

The modern technology for acetylene production is inevitably accompanied by the contamination of carbon dioxide and moisture impurities. Metal–organic frameworks (MOFs), with rational configurations of fluorine as the hydrogen-bonding acceptor (HBA), exhibit excellent affinities to capture acetylene from the gas mixtures. Currently, most research studies feature anionic fluorine groups as structural pillars (e.g., SiF<sub>6</sub><sup>2-</sup>, TiF<sub>6</sub><sup>2-</sup>, NbOF<sub>5</sub><sup>2-</sup>), whereas *in situ* insertion of fluorine into metal clusters is rather challenging. Herein, we report a unique fluorine-bridged Fe-MOF, *i.e.*, DNL-9(Fe), which is assembled by mixed-valence Fe<sup>II</sup>Fe<sup>III</sup> clusters and renewable organic ligands. The fluorine species in the coordination-saturated structure offer superior C<sub>2</sub>H<sub>2</sub>-favored adsorption sites facilitated by hydrogen bonding, with a lower C<sub>2</sub>H<sub>2</sub> adsorption enthalpy than other reported HBA-MOFs, demonstrated by static/dynamic adsorption tests and theoretical calculations. Importantly, DNL-9(Fe) shows exceptional hydrochemical stability under aqueous, acidic, and basic conditions, and its intriguing performance for C<sub>2</sub>H<sub>2</sub>/CO<sub>2</sub> separation was even maintained at a high relative humidity of 90%.

Received 5th December 2022

Accepted 2nd January 2023

DOI: 10.1039/d2sc06699h

rsc.li/chemical-science

## Introduction

Acetylene (C<sub>2</sub>H<sub>2</sub>) is a vital building block for the synthesis of various chemical commodities. Its modern production methods, *e.g.*, pyrolysis, partial combustion, or thermal cracking of hydrocarbons, inevitably contaminate the product gas with carbon dioxide (CO<sub>2</sub>) and moisture (H<sub>2</sub>O).<sup>1–3</sup> These impurities pose a challenge in producing high-purity C<sub>2</sub>H<sub>2</sub> in isolation for end-users, given the similarities in kinetic diameter (*i.e.*, 3.3 Å) and polarizability (*i.e.*, 33.3 *versus* 29.1 × 10<sup>25</sup> cm<sup>−3</sup>) between C<sub>2</sub>H<sub>2</sub> and CO<sub>2</sub>, along with the presence of vapor/moisture *via* physisorption-based pressure swing adsorption (PSA) and vacuum swing adsorption (VSA) processes.<sup>4–7</sup>

Metal–organic frameworks (MOFs) are promising sorbents for C<sub>2</sub>H<sub>2</sub> separation owing to their tailorability in pores, surface chemistry and building units.<sup>8–12</sup> Particularly, the introduction of fluorine (F) into the backbone of MOFs is found to effectively enhance C<sub>2</sub>H<sub>2</sub> adsorption, boost C<sub>2</sub>H<sub>2</sub>/CO<sub>2</sub> separation properties and the resistance to moisture, with fluorine species serving as the hydrogen bonding acceptor (HBA).<sup>13–19</sup> Two main strategies are reported to achieve the aim: (i) employing anionic fluorine groups, such as SiF<sub>6</sub><sup>2-</sup>, TiF<sub>6</sub><sup>2-</sup>, FeF<sub>5</sub><sup>2-</sup> and NbOF<sub>5</sub><sup>2-</sup>, to construct anion-pillared MOFs;<sup>13–16</sup> (ii) utilizing fluorinated organic linkers to form fluorine-containing MOFs like FMOF-1, FMOFCu and MOFF-5.<sup>17–19</sup> Although a few MOFs prepared by the above approaches have shown promise for C<sub>2</sub>H<sub>2</sub>/CO<sub>2</sub> separation, the fluorous reagents are relatively expensive. Also, most anion-pillared MOFs reveal high adsorption enthalpies for C<sub>2</sub>H<sub>2</sub>, *e.g.*, over 35 kJ mol<sup>−1</sup>, which in turn, will cause an energy penalty during desorption. Besides, it is also fairly difficult to introduce highly coordinated fluorine moieties into MOFs, *e.g.*, the fluorination of metal nodes (Scheme 1).<sup>20–22</sup> The high liganacy of fluorine bonded with metal nodes as well as the hydrophobic micro environment, however, may protect the sites from being attacked by water molecules.<sup>13</sup>

We herein report a unique Fe-MOF, *i.e.*, DNL-9(Fe) (Dalian National Laboratory for Clean Energy, China), constructed from Fe<sup>II</sup>Fe<sup>III</sup> clusters and biomass-derived 2,5-furandicarboxylic acid (FDCA) linkers. This material possesses a high coordination liganacy of bridged and terminal fluorine with metal nodes,

<sup>a</sup>Dalian National Laboratory for Clean Energy, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian, 116023, China. E-mail: wangsd@dicp.ac.cn

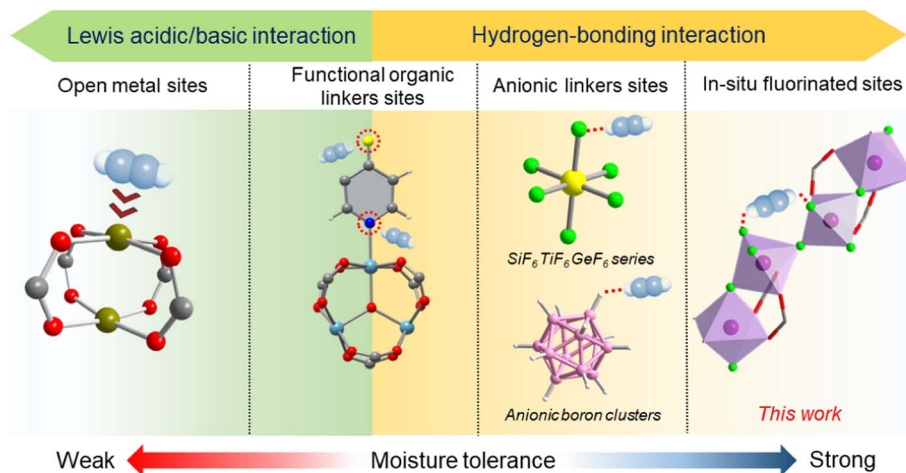
<sup>b</sup>University of Chinese Academy of Sciences, Beijing 100049, China

<sup>c</sup>Core Laboratory, King Abdullah University of Science and Technology (KAUST), Thuwal, 23955-6900, Saudi Arabia

<sup>d</sup>Advanced Membranes and Porous Materials Center, Division of Physical Sciences and Engineering, King Abdullah University of Science and Technology (KAUST), Thuwal, 23955-6900, Saudi Arabia. E-mail: zhiping.lai@kaust.edu.sa; xiaowei.liu@kaust.edu.sa

† Electronic supplementary information (ESI) available: Full experimental details, characterization, additional adsorption measurement, theoretical calculations, supplementary summary. CCDC 2050430. For ESI and crystallographic data in CIF or other electronic format see DOI: <https://doi.org/10.1039/d2sc06699h>





**Scheme 1** Schematic showing state-of-art synthesis strategies for MOFs to achieve efficient  $C_2H_2/CO_2$  separation. Gray, C; red, O; white: H; green, F; yellow: Si/Ti/Ge; pink: B; else: metal or functional group atoms.

which is very rarely reported in MOFs.<sup>20,21,23</sup> Hydrogen bonding could then be steadily formed between the framework and  $C_2H_2$  molecules, *e.g.*,  $C-H\cdots F$  and  $C-H\cdots O_F$  (from furan rings), thus enhancing  $C_2H_2$  capture. Consequently, these features endow DNL-9(Fe) with great potential to separate  $C_2H_2$  from other gas impurities under moist conditions in the current production technology. The prominent  $C_2H_2/CO_2$  performance of DNL-9(Fe) was then confirmed by a plethora of static/dynamic adsorption measurements and theoretical calculations. Furthermore, our work also demonstrated the exceptional hydrochemical stability of DNL-9(Fe) under aqueous, acidic, and basic conditions, and its excellent  $C_2H_2/CO_2$  separation property was even maintained at a high relative humidity of 90%.

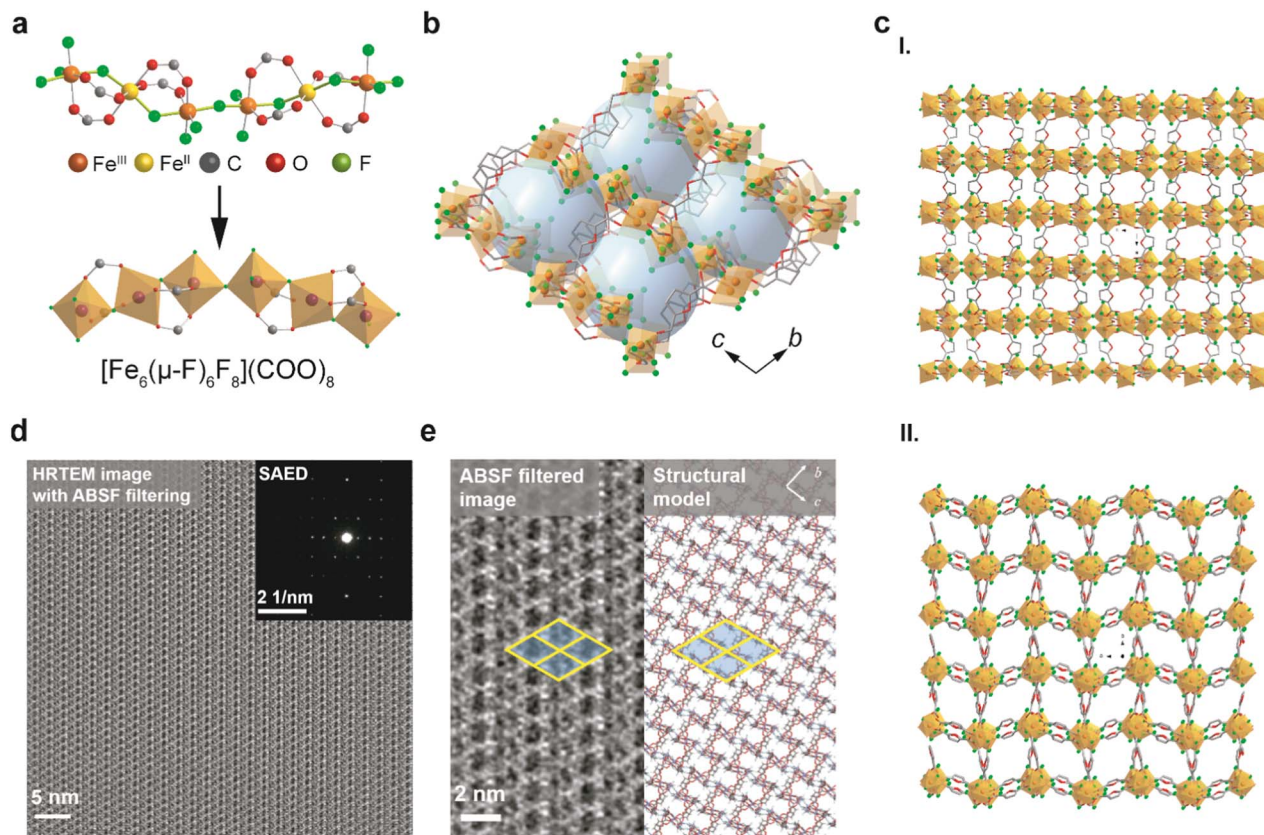
## Results and discussion

To decode the fine structure of DNL-9(Fe), we obtained its single-crystal (Fig. S1<sup>†</sup>), and details of the crystallographic information are given in Table S1.<sup>†</sup> Also, the following X-ray fluorescence (XRF) measurement and elemental analysis determined the chemical composition of the structure, with calculated formula basically matching with that obtained from the single crystal (Table S2<sup>†</sup>). Fig. 1a and b illustrate the orthogonal structure of DNL-9(Fe) with a  $P2_12_12_1$  space group, in which the chain-linked metal molecules precisely pack in an alternating helical pattern, and carboxylate groups of the FDCA ligands bridge helical  $Fe_6(\mu-F)_6F_8$  clusters to ultimately form a chiral topology framework with pore channels running along different axes (Fig. 1c). There are two sets of  $\mu-F$  and terminal F linkers that connect each hexa-coordinated Fe atom, *i.e.*,  $Fe-F-Fe$  and  $Fe-F$ ; distinct from oxygen linkages, this is seldom explored in MOFs.<sup>20,21,23</sup> The saturated Fe units were divided into mixed-valence  $Fe^{II}(\mu-O)_4\alpha-(\mu-F)_2$  and  $Fe^{III}(\mu-O)_2\alpha-(\mu-F)\beta-(\mu-F)_2$  characters, due to the reducing environment arising from the decomposition of *N,N*-dimethylformamide (DMF) (product gases are analyzed in Fig. S2<sup>†</sup>). As shown in Fig. 1d and e, the

ordered structure of DNL-9(Fe) was observed by high resolution transmission electron microscopy (HRTEM). The acquired HRTEM image shows the visible microporous channels, with the structure in agreement with the simulated model decoded from the single crystal measurement. The zero-field Mössbauer spectrum of the sample recorded at 298 K exhibits quadrupole doublets, which could indicate the oxidation state of specific Fe centers as well as the protonation state of the atom bridge (Fig. 2a).<sup>24</sup> The two distinct doublets are characteristics of hyperfine parameters typical of high-spin  $Fe^{II}$  with isomer shift  $\delta = 1.252 \text{ mm s}^{-1}$  and quadrupole splitting  $|\Delta E_Q| = 2.993 \text{ mm s}^{-1}$ , whereas the other two can be assigned to high-spin  $Fe^{III}$  with isomer shift  $\delta = 0.445 \text{ mm s}^{-1}$  and quadrupole splitting  $|\Delta E_Q| = 0.612 \text{ mm s}^{-1}$ . Furthermore, it also demonstrates that  $Fe^{(II \text{ or } III)}-F$  species, rather than normal oxo-bridged complexes, *e.g.*,  $Fe-O-Fe$  with  $\delta = 0.45-0.52 \text{ mm s}^{-1}$  and  $|\Delta E_Q| = 1.27-1.80 \text{ mm s}^{-1}$  at 298 K, or hydroxo-bridged complexes, *e.g.*,  $Fe-OH-Fe$  with  $\delta = 0.45-0.52 \text{ mm s}^{-1}$  and  $|\Delta E_Q| = 0.25-0.56 \text{ mm s}^{-1}$  under the same conditions, that were reported before, are coordinated with iron atoms.<sup>25</sup> As a result, the configuration of  $\mu-F$  influences the asymmetry of electron distribution, causing a large quadrupole splitting.<sup>21,26</sup> The presence of bridged and terminal fluorine atoms is also verified in the solid state  $^{19}F$  Nuclear Magnetic Resonance ( $^{19}F$ -NMR) analyses (Fig. S3<sup>†</sup>).<sup>27,28</sup> The relative areas of the Mössbauer doublets further reveal the existence of  $Fe^{II}$  (33.31%) and  $Fe^{III}$  (66.69%), consistent with the single crystal data.

Fig. S4<sup>†</sup> shows the powder X-ray diffraction (PXRD) patterns of DNL-9(Fe), indicating good purity and crystallinity. Fig. S5<sup>†</sup> presents the argon adsorption isotherm at 87 K, which suggests a type I isotherm for a microporous structure with Brunauer-Emmett-Teller (BET) area and micropore volume being  $1135 \text{ m}^2 \text{ g}^{-1}$  and  $0.38 \text{ cm}^3 \text{ g}^{-1}$  for the guest-free MOF, respectively; the average pore size of the solvent-free channels is around  $5.5 \text{ \AA}$ , in line with the crystallographic value from the single-crystal structure. Fig. S6 and Table S4<sup>†</sup> show that the adsorption of  $N_2$  at 77 K gives a bit smaller BET area ( $1113 \text{ m}^2 \text{ g}^{-1}$ ) and





**Fig. 1** (a) The structure of the fluorine coordination and the helical chain of DNL-9(Fe); (b) the framework viewed along the *a*-axis (balls indicate cavities), (c) the structure of DNL-9(Fe) viewed along the (I) *b*-axis and (II) *c*-axis; (d) low-dose motion-corrected high-resolution TEM (HRTEM) image of DNL-9(Fe) denoised by using ABSF filtering; inset: the SAED pattern. (e) Enlarged HRTEM image (left) matched with the structural model of DNL-9(Fe) viewing along the *a*-axis (right).

a slightly larger average pore size (5.8 Å) for the MOF. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) profiles of DNL-9(Fe) verified its decent thermal stability up to *ca.* 250 °C, with no phase transformation confirmed by structure comparisons (Fig. S7a†). The obvious weight loss in 50–200 °C in the TGA curve is due to the desorption of H<sub>2</sub>O molecules, as evidenced by the broad peak in a similar temperature range in the mass spectra (Fig. S7b and c†). SEM images reveal the layered morphology of the samples (Fig. S8†).

Fig. 2b and S14–S16† display C<sub>2</sub>H<sub>2</sub> and CO<sub>2</sub> single gas adsorption isotherms at 288, 298 and 308 K over 0–1 bar, which are well-fitted within the dual-site Langmuir–Freundlich (DSLFL) model. In the tests, DNL-9(Fe) adsorbs far more C<sub>2</sub>H<sub>2</sub> than CO<sub>2</sub>; at 298 K and 1 bar, the adsorption capacity of C<sub>2</sub>H<sub>2</sub> reaches 5.42 mol kg<sup>-1</sup>, twice as much of CO<sub>2</sub>, which is among the best results reported.<sup>14,29,30</sup> The adsorption enthalpies (Fig. 2b) are 26.1–28.0 kJ mol<sup>-1</sup> for C<sub>2</sub>H<sub>2</sub> and 25.6–26.5 kJ mol<sup>-1</sup> for CO<sub>2</sub>, both exhibiting a decrease with increasing gas loadings, indicating the presence of preferential adsorption sites in MOFs. The ideal adsorbed solution theory (IAST) selectivities were then calculated for equimolar C<sub>2</sub>H<sub>2</sub>/CO<sub>2</sub> mixtures (Fig. S17; fitting parameters: Table S6†),<sup>31</sup> which grow from 1.06 to 2.68 (1 bar and 288 K) with decreasing temperature and increasing

pressure. This is important because, in the narrow channels of DNL-9(Fe), more adsorption of C<sub>2</sub>H<sub>2</sub>, either at lower temperatures or higher pressures, will prohibit the coexisting adsorption of CO<sub>2</sub>, thus benefiting the selectivities.

Dispersion-corrected density functional theory (DFT-D3) calculations were performed to gain molecular insights into the gas adsorption behavior in DNL-9(Fe). Fig. 2c reveals the preferential binding sites for C<sub>2</sub>H<sub>2</sub> and CO<sub>2</sub> in DNL-9(Fe), facilitated by hydrogen bonding. C<sub>2</sub>H<sub>2</sub> has two such sites: the primary one is formed through F<sup>δ-</sup>⋯H<sub>C<sub>2</sub>H<sub>2</sub></sub> (F<sup>δ-</sup>, terminal fluorine atom binding with metal; H<sub>C<sub>2</sub>H<sub>2</sub></sub><sup>δ+</sup>, hydrogen atom from acetylene), with interaction distances of 2.40–2.52 Å; the other one stems from the interaction of O<sub>F</sub>⋯H<sub>C<sub>2</sub>H<sub>2</sub></sub> (O<sub>F</sub><sup>δ-</sup>, O atom from furan rings) with distances of 2.55 Å (Fig. S20a†). The second site involves competitive adsorption, as O atoms from CO<sub>2</sub> (O<sub>CO<sub>2</sub></sub><sup>δ-</sup>) could also bind with H atoms from furan rings (H<sub>F</sub><sup>δ+</sup>), forming hydrogen bonding of H<sub>F</sub>⋯O<sub>CO<sub>2</sub></sub> with distances of 2.92–3.20 Å. In all, C<sub>2</sub>H<sub>2</sub> was found to have a lower static binding energy with the framework than CO<sub>2</sub> (–31.78 *vs.* –28.56 kJ mol<sup>-1</sup>), matching with the trend in adsorption enthalpies.

To verify the above theoretical findings in experiments, FT-IR analysis was carried out; Fig. 2d presents the spectra of blank DNL-9(Fe), and the samples adsorbed with C<sub>2</sub>H<sub>2</sub>, CO<sub>2</sub> or water. The signals observed in the curves, *e.g.*, ν(≡C–H) = 3226–3234



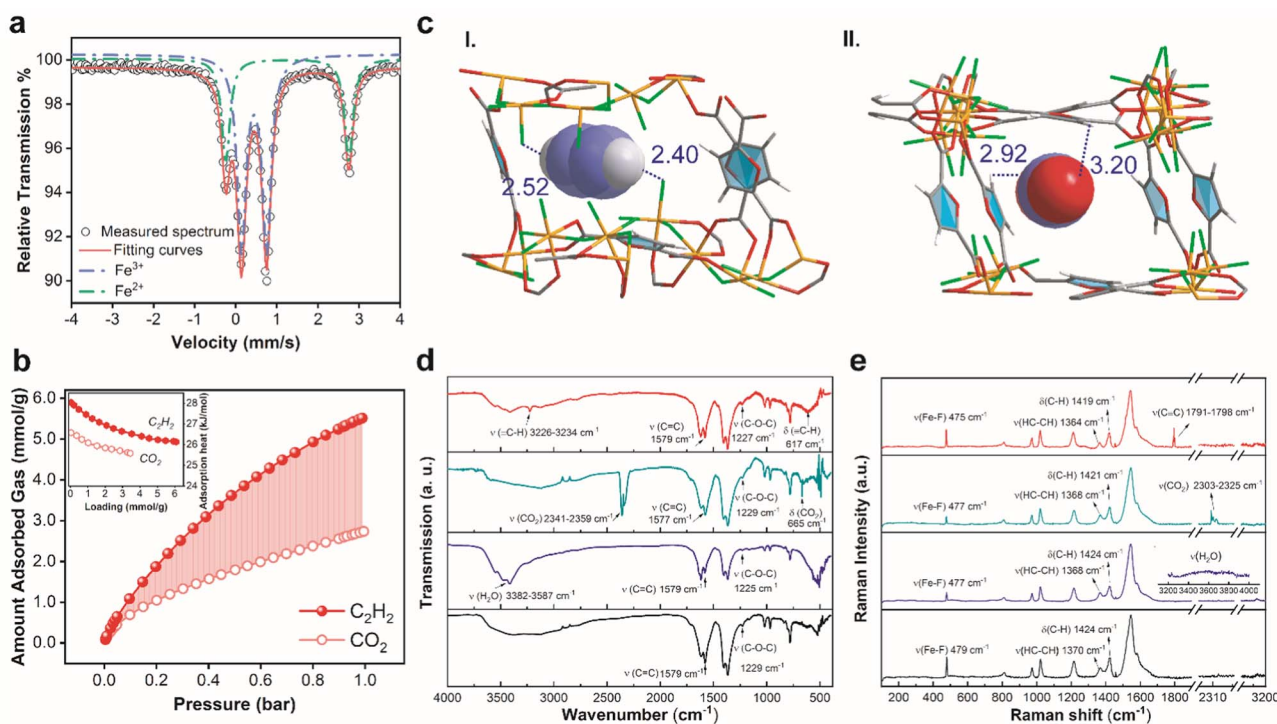


Fig. 2 (a)  $^{57}\text{Fe}$  Mössbauer spectrum of DNL-9(Fe) at room temperature. Green and purple dash lines indicate fitted adsorption doublets assigned to  $\text{Fe}^{\text{II}}$  and  $\text{Fe}^{\text{III}}$ , respectively. The hollow circles denote the measured spectrum and the red curve represents summed fitted spectra; (b) pure gas adsorption isotherms and enthalpies (inset) of  $\text{C}_2\text{H}_2$  and  $\text{CO}_2$  at 298 K; (c) the adsorption status of (I)  $\text{C}_2\text{H}_2$  and (II)  $\text{CO}_2$  molecule in MOF via DFT-D3 optimization; unit: Å. Green, F; red, O; grey, C; yellow, Fe; white, H; (d) FT-IR spectra of DNL-9(Fe). Samples from bottom to top: blank MOF,  $\text{H}_2\text{O}$ -,  $\text{CO}_2$ - and  $\text{C}_2\text{H}_2$ -adsorbed (1 bar, 298 K) MOF, referenced to the KBr pellet; (e) Raman spectra of DNL-9(Fe). Samples from bottom to top: blank MOF,  $\text{H}_2\text{O}$ -,  $\text{CO}_2$ - and  $\text{C}_2\text{H}_2$ -adsorbed (1 bar, 298 K) MOF.

$\text{cm}^{-1}$  and  $\nu(\text{C}=\text{O}) = 2341\text{--}2359\text{ cm}^{-1}$ ,<sup>32</sup> prove the presence of  $\text{C}_2\text{H}_2$  and  $\text{CO}_2$  adsorbed in MOFs. Compared to the reference and  $\text{CO}_2$  loaded sample, adsorption of  $\text{C}_2\text{H}_2$  led the bands of  $\nu(\text{C}-\text{O}-\text{C})$  to shift from 1229 to  $1227\text{ cm}^{-1}$ , driven by the interactions between furans ( $\text{O}_F$ ) and  $\text{C}_2\text{H}_2$  via H-bonding of  $\text{O}_F \cdots \text{H}_{\text{C}_2\text{H}_2}$ , as described in the above DFT findings. Raman spectra (Fig. 2e) were also recorded, where signals for the adsorption of gas molecules were clearly present. Besides, the peak seen at  $479\text{ cm}^{-1}$  in the blank sample was attributed to the stretching of Fe-F, rather than  $\nu(\text{Fe}-\text{O}) = 520\text{--}550\text{ cm}^{-1}$ , normally found in other Fe-MOFs.<sup>32</sup> The peak moved to lower values of 477 and  $475\text{ cm}^{-1}$  with the adsorption of  $\text{CO}_2$  and  $\text{C}_2\text{H}_2$ , which indicates that the fluorine regions could preferentially trap  $\text{C}_2\text{H}_2$ , possibly through the H-bonding of  $\text{F}_{\text{II}} \cdots \text{H}_{\text{C}_2\text{H}_2}$  as stated above. Similar trends were also witnessed in the shifts of  $\nu(\text{HC}-\text{CH})$  and  $\delta(\text{C}-\text{H})$  bands (in furan rings), implying that  $\text{C}_2\text{H}_2$  had superior competitive adsorption to  $\text{CO}_2$ , via the interactions with the ligands.

Meanwhile, Fig. 2d and e also suggest that the changes in the profiles of FT-IR and Raman were generally weaker, upon contacting the framework with water compared to  $\text{C}_2\text{H}_2$  and  $\text{CO}_2$ . Fig. S10† shows the water sorption isotherm of DNL-9(Fe) at 298 K, where the uptake was nominal with a relative pressure  $<0.2$ . Afterwards, it increased gradually until close to saturation, with the final uptake approaching 19 wt%. We also evaluated the initial differential adsorption heat of  $\text{H}_2\text{O}$  on DNL-9(Fe) to be ca.

$43.5\text{ kJ mol}^{-1}$ , which is lower than that of other FDCA-based MOFs, e.g., MIL-160 ( $54\text{ kJ mol}^{-1}$ ),<sup>33</sup> and PCN-233 ( $62\text{--}77\text{ kJ mol}^{-1}$ ).<sup>34</sup> DFT calculations further reveal that the dominant water adsorption occurred in the cavity near the furan linker in DNL-9(Fe), with the corresponding  $\text{O}_F^{\text{I}} \cdots \text{H}_W^{\text{I}}$  distance of  $2.02\text{ Å}$ , and a  $\text{F}_{\text{II}}^{\text{I}} \cdots \text{H}_W^{\text{II}}$  distance of  $2.01\text{ Å}$  (Fig. S20b†). This configuration generated a binding strength of  $-47.5\text{ kJ mol}^{-1}$ , notably smaller than that of MIL-160(Al) and PCN-233 (FeNi),<sup>34</sup> and comparable to that of another famous fluorinated MOF, i.e., FMOF-1 ( $-46.0\text{ kJ mol}^{-1}$ ).<sup>35</sup> Importantly, we also exposed DNL-9(Fe) to water, acidic/basic (pH = 2, 10) aqueous solutions, and typical organic solvents (MeOH, EtOH, MeCN). Fig. S4 and S9† show that the structural and adsorption properties of DNL-9(Fe) almost remain the same, demonstrating the exceptional hydrochemical stability of the material.

Next, experimental breakthrough tests were carried out to examine the separation performance of DNL-9(Fe) in practical scenarios, where equimolar  $\text{C}_2\text{H}_2/\text{CO}_2$  mixtures were passed through a homemade apparatus (Fig. S11†) with a total flow rate of  $5\text{ ml min}^{-1}$  under dry or wet (ca. 90% RH) conditions at 298 K and 1 bar. An efficient separation was readily achieved in the dry atmosphere (Fig. 3a), in which  $\text{CO}_2$  first broke the column at about 21 min, and after a long period of ca. 47 min,  $\text{C}_2\text{H}_2$  came out, whilst under the humid condition, the breakthrough curves only shifted a bit to earlier moments, resulting from the competitive adsorption of water. The efficient separation of



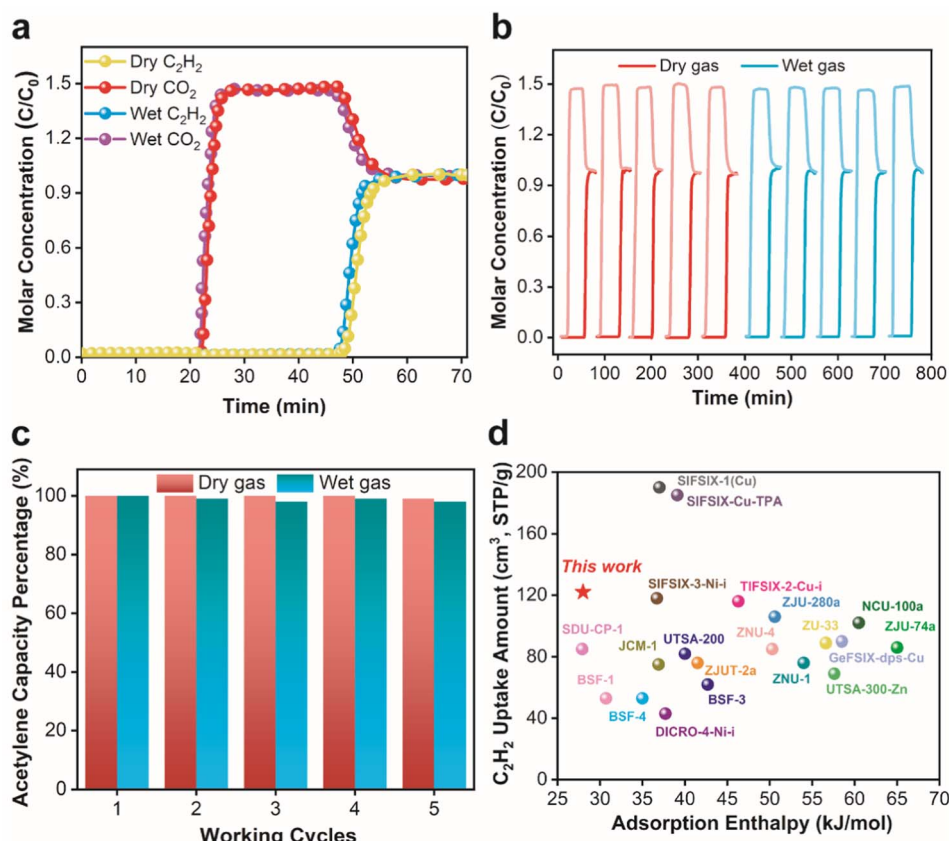


Fig. 3 (a) Experimental breakthrough curves for binary C<sub>2</sub>H<sub>2</sub>/CO<sub>2</sub> mixtures (50/50, v/v) on DNL-9(Fe) under dry and wet (ca. 90% RH) conditions; the cycling tests under dry and moist conditions at 298 K and 1 bar. (b) Breakthrough curves of C<sub>2</sub>H<sub>2</sub> (dark) and CO<sub>2</sub> (light), (c) the recovery degree of C<sub>2</sub>H<sub>2</sub> capacity; (d) comparison of the adsorption capacity (from static adsorption isotherms) and adsorption enthalpy of C<sub>2</sub>H<sub>2</sub> for state-of-art HBA-type MOF materials. All the above: at 298 K and 1 bar.

C<sub>2</sub>H<sub>2</sub>/CO<sub>2</sub> could also be witnessed at higher temperatures under consistent conditions, albeit also with left moves of breakthrough points primarily due to lower gas uptakes at 308 K and 318 K (Fig. S13<sup>†</sup>). C<sub>2</sub>H<sub>2</sub>/CO<sub>2</sub> breakthrough selectivity was then calculated to be 2.48, which agrees with the IAST selectivities at 298 K and 1 bar. At extremely low pressures (*i.e.*, below 0.05 bar), the similar initial slopes of uptake for C<sub>2</sub>H<sub>2</sub> and CO<sub>2</sub> also encourage us to study the adsorption kinetics for an efficient separation in DNL-9(Fe) (Fig. S18 and S19<sup>†</sup>). Table S8<sup>†</sup> shows the calculated diffusion coefficients of C<sub>2</sub>H<sub>2</sub> ( $4.40 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$ ) and CO<sub>2</sub> ( $8.63 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$ ) under the same conditions: the much lower diffusion rate of C<sub>2</sub>H<sub>2</sub> than CO<sub>2</sub> at 0.005 bar is due to the diffusion limitation rising from the intermolecular H-bonding interaction between C<sub>2</sub>H<sub>2</sub> molecules and the framework.

Fig. 3b and c show the cycling tests for the separation under dry and wet conditions, where over 97% of C<sub>2</sub>H<sub>2</sub> capacities were recovered in all cycles, when simply activating the adsorbent under a dynamic vacuum at ca. 0.00001 bar (0.007 Torr, absolute pressure) for 2 h at 298 K before each cycle. This is a gift from the mild gas adsorption enthalpies because of the fluorinated and saturated framework. Upon five cycles, C<sub>2</sub>H<sub>2</sub> adsorption capacities were up to 3.83–3.91 mol kg<sup>-1</sup>, even with

the competitive adsorption of CO<sub>2</sub> and moisture. Again, Fig. S4 and S5<sup>†</sup> demonstrate that the MOF structure remained intact after the cycling tests either under dry conditions or even at a high relative humidity of 90%, with no obvious degradation in the structural crystallinity and surface area. Fig. 3d compares the adsorption capacity and enthalpy of C<sub>2</sub>H<sub>2</sub> of DNL-9(Fe) and other state-of-art HBA-type anionic MOFs reported under the same conditions. Also with a moderate C<sub>2</sub>H<sub>2</sub>/CO<sub>2</sub> selectivity compared with other benchmark MOFs (Table S10<sup>†</sup>), DNL-9(Fe) presents a high C<sub>2</sub>H<sub>2</sub> capacity, and the lowest C<sub>2</sub>H<sub>2</sub> adsorption enthalpy compared to other HBA-type MOFs.<sup>14,29,30</sup> The latter is significant in real scenes, as it may mitigate the demands of the equipment to withstand heating, and cut down energy consumption for sorbent regeneration. Besides, Table S11<sup>†</sup> summarizes the C<sub>2</sub>H<sub>2</sub>/CO<sub>2</sub> separation performance of benchmark MOFs, including C<sub>2</sub>H<sub>2</sub> static adsorption and normalized breakthrough capacity, as well as the separation time per weight of adsorbent. Clearly, DNL-9(Fe) has above-average static and normalized breakthrough capacity for C<sub>2</sub>H<sub>2</sub> among all MOFs, and is superior to most HBA-containing MOFs. Overall, with the above-mentioned intriguing separation performance, as well as being prepared from cheap components (iron nodes and bio-derived massive ligands) and convenient synthesis methods,



DNL-9(Fe) is a rather promising candidate sorbent for acetylene purification in real-world applications.

## Conclusions

In summary, we here reported a new fluorinated MOF, *i.e.*, DNL-9(Fe), serving as an HBA for efficient C<sub>2</sub>H<sub>2</sub>/CO<sub>2</sub> separation. This material has bridged and terminal fluorine species directly bonded with the metal. The static/dynamic adsorption tests show that the MOF displays a prominent C<sub>2</sub>H<sub>2</sub>/CO<sub>2</sub> separation performance either under dry conditions or at a high relative humidity of 90%, as well as a low adsorption enthalpy with a robust structure which is particularly beneficial for practical applications, *e.g.*, in the vacuum swing adsorption (VSA) processes. DFT calculations suggest multiple C<sub>2</sub>H<sub>2</sub>-favored adsorption sites with MOF-C<sub>2</sub>H<sub>2</sub> hydrogen-bonding interactions in DNL-9(Fe), which is further proved by the FT-IR and Raman measurements. All results manifest that DNL-9(Fe) is very promising to be utilized as a sorbent for acetylene purification in industry.

## Data availability

All experimental supporting data and procedures are available in the ESI.†

## Author contributions

Y.-M. G., Y.-Y. Y. and C.-L. C. contributed equally to this work. Conceptualization: Y.-M. G., X.-W. L. and S.-D. W. Methodology: Y.-M. G. and X.-W. L. Investigation: Y.-M. G., Y.-Y. Y., C.-L. C., S.-S. Z., T.-J. S. and Y. H. Validation: X.-W. L., Z. L. and S.-D. W. Visualization: Y.-M. G., Y.-Y. Y. and C.-L. C. Writing – original draft: Y.-M. G. and X.-W. L. Writing – review & editing: X.-W. L., Z. L. and S.-D. W. Supervision: X.-W. L., Z. L. and S.-D. W.

## Conflicts of interest

The authors declare that they have no competing interests.

## Acknowledgements

Y.-M. G., T.-J. S. and S.-D. W. are grateful to the National Natural Science Foundation of China for funding (No. 21776266). X.-W. L. and Z. L. appreciate the funding (BAS/1/1375-01-01 and FCC/1/1972-88-01) from King Abdullah University of Science and Technology (KAUST). The authors also thank Prof. Alexandre Rykov at the Center for Advanced Mössbauer Spectroscopy in DICP, for Mössbauer spectroscopy measurement and analysis; and Dr Wen-Guang Yu and Dr Pei-Fang Yan for the help in TGA-DSC and IGA adsorption measurements.

## Notes and references

1 Y. Ye, S. Xian, H. Cui, K. Tan, L. Gong, B. Liang, T. Pham, H. Pandey, R. Krishna, P. C. Lan, K. A. Forrest, B. Space,

- T. Thonhauser, J. Li and S. Ma, *J. Am. Chem. Soc.*, 2022, **144**, 1681–1689, DOI: [10.1039/d2qj01989b](https://doi.org/10.1039/d2qj01989b).
- 2 P. Pässler, W. Hefner, K. Buckl, H. Meinass, A. Meiswinkel, H.-J. Wernicke, G. Ebersberg, R. Müller, J. Bässler, H. Behringer and D. Mayer, in *Ullmann's Encyclopedia of Industrial Chemistry*, 2011, DOI: [10.1002/14356007.a01\\_097.pub4](https://doi.org/10.1002/14356007.a01_097.pub4).
- 3 J. Liu, J. W. Lam and B. Z. Tang, *Chem. Rev.*, 2009, **109**, 5799–5867, DOI: [10.1021/cr900149d](https://doi.org/10.1021/cr900149d).
- 4 V. I. Savchenko, A. V. Nikitin, I. V. Sedov, A. V. Ozerskii and V. S. Arutyunov, *Chem. Eng. Sci.*, 2019, **207**, 744–751, DOI: [10.1016/j.ces.2019.07.012](https://doi.org/10.1016/j.ces.2019.07.012).
- 5 J. R. Li, R. J. Kuppler and H. C. Zhou, *Chem. Soc. Rev.*, 2009, **38**, 1477–1504, DOI: [10.1039/B802426J](https://doi.org/10.1039/B802426J).
- 6 Y.-M. Gu, H.-F. Qi, T.-T. Sun, X.-W. Liu, S. Qadir, T.-J. Sun, D.-F. Li, S.-S. Zhao, D. Fairen-Jimenez and S.-D. Wang, *Chem. Mater.*, 2022, **34**, 2708–2716, DOI: [10.1021/acs.chemmater.1c04168](https://doi.org/10.1021/acs.chemmater.1c04168).
- 7 B. Wang, L. H. Xie, X. Q. Wang, X. M. Liu, J. P. Li and J. R. Li, *Green Energy Environ.*, 2018, **3**, 191–228, DOI: [10.1016/j.gee.2018.03.001](https://doi.org/10.1016/j.gee.2018.03.001).
- 8 L. Yang, S. Qian, X. Wang, X. Cui, B. Chen and H. Xing, *Chem. Soc. Rev.*, 2020, **49**, 5359–5406, DOI: [10.1039/C9CS00756C](https://doi.org/10.1039/C9CS00756C).
- 9 Z. J. Zhang, S. C. Xiang and B. L. Chen, *CrystEngComm*, 2011, **13**, 5983–5992, DOI: [10.1039/C1CE05437F](https://doi.org/10.1039/C1CE05437F).
- 10 N. Xu, J. B. Hu, L. Y. Wang, D. Luo, W. Q. Sun, Y. Q. Hu, D. M. Wang, X. L. Cui, H. B. Xing and Y. B. Zhang, *Chem. Eng. J.*, 2022, **450**, 138034, DOI: [10.1016/j.cej.2022.138034](https://doi.org/10.1016/j.cej.2022.138034).
- 11 P. Z. Moghadam, A. Li, X. W. Liu, R. Bueno-Perez, S. D. Wang, S. B. Wiggin, P. A. Wood and D. Fairen-Jimenez, *Chem. Sci.*, 2020, **11**, 8373–8387, DOI: [10.1039/d0sc01297a](https://doi.org/10.1039/d0sc01297a).
- 12 M. Ding, R. W. Flaig, H. L. Jiang and O. M. Yaghi, *Chem. Soc. Rev.*, 2019, **48**, 2783–2828, DOI: [10.1039/C8CS00829A](https://doi.org/10.1039/C8CS00829A).
- 13 A. Cadiau, Y. Belmabkhout, K. Adil, P. M. Bhatt, R. S. Pillai, A. Shkurenko, C. Martineau-Corcoc, G. Maurin and M. Eddaoudi, *Science*, 2017, **356**, 731–735, DOI: [10.1126/science.aam8310](https://doi.org/10.1126/science.aam8310).
- 14 H. Li, C. Liu, C. Chen, Z. Di, D. Yuan, J. Pang, W. Wei, M. Wu and M. Hong, *Angew. Chem., Int. Ed.*, 2021, **60**, 7547–7552, DOI: [10.1002/anie.202013988](https://doi.org/10.1002/anie.202013988).
- 15 J. Wang, Y. Zhang, Y. Su, X. Liu, P. Zhang, R. B. Lin, S. Chen, Q. Deng, Z. Zeng, S. Deng and B. Chen, *Nat. Commun.*, 2022, **13**, 200, DOI: [10.1038/s41467-021-27929-7](https://doi.org/10.1038/s41467-021-27929-7).
- 16 J. Wang, Y. Zhang, P. Zhang, J. Hu, R. B. Lin, Q. Deng, Z. Zeng, H. Xing, S. Deng and B. Chen, *J. Am. Chem. Soc.*, 2020, **142**, 9744–9751, DOI: [10.1021/jacs.0c02594](https://doi.org/10.1021/jacs.0c02594).
- 17 C. Yang, X. Wang and M. A. Omary, *J. Am. Chem. Soc.*, 2007, **129**, 15454–15455, DOI: [10.1021/ja0775265](https://doi.org/10.1021/ja0775265).
- 18 C. A. Fernandez, J. Liu, P. K. Thallapally and D. M. Strachan, *J. Am. Chem. Soc.*, 2012, **134**, 9046–9049, DOI: [10.1021/ja302071t](https://doi.org/10.1021/ja302071t).
- 19 T. H. Chen, I. Popov, W. Kaveevivitchai, Y. C. Chuang, Y. S. Chen, A. J. Jacobson and O. S. Miljanic, *Angew. Chem., Int. Ed.*, 2015, **54**, 13902–13906, DOI: [10.1002/anie.201505149](https://doi.org/10.1002/anie.201505149).



- 20 Z. Shi, Y. Tao, J. Wu, C. Zhang, H. He, L. Long, Y. Lee, T. Li and Y. B. Zhang, *J. Am. Chem. Soc.*, 2020, **142**, 2750–2754, DOI: [10.1021/jacs.9b12879](https://doi.org/10.1021/jacs.9b12879).
- 21 S. Dammers, T. P. Zimmermann, S. Walleck, A. Stammer, H. Bogge, E. Bill and T. Glaser, *Inorg. Chem.*, 2017, **56**, 1779–1782, DOI: [10.1021/acs.inorgchem.6b03093](https://doi.org/10.1021/acs.inorgchem.6b03093).
- 22 A. Ebadi Amooghini, H. Sanaeepur, R. Luque, H. Garcia and B. Chen, *Chem. Soc. Rev.*, 2022, **51**, 7427–7508, DOI: [10.1039/D2CS00442A](https://doi.org/10.1039/D2CS00442A).
- 23 W. J. Shi, Y. Z. Li, J. Chen, R. H. Su, L. Hou, Y. Y. Wang and Z. Zhu, *Chem. Commun.*, 2021, **57**, 12788–12791, DOI: [10.1039/D1CC05196B](https://doi.org/10.1039/D1CC05196B).
- 24 J. L. Lee, S. Biswas, C. Sun, J. W. Ziller, M. P. Hendrich and A. S. Borovik, *J. Am. Chem. Soc.*, 2022, **144**, 4559–4571, DOI: [10.1021/jacs.1c12888](https://doi.org/10.1021/jacs.1c12888).
- 25 D. M. Kurtz, *Chem. Rev.*, 2002, **90**, 585–606, DOI: [10.1021/cr00102a002](https://doi.org/10.1021/cr00102a002).
- 26 U. Bossek, H. Hummel, T. Weyhermüller, E. Bili and K. Wieghardt, *Angew. Chem., Int. Ed.*, 1996, **34**, 2642–2645, DOI: [10.1002/anie.199526421](https://doi.org/10.1002/anie.199526421).
- 27 J. M. Miller, *Prog. Nucl. Magn. Reson. Spectrosc.*, 1996, **28**, 255–281, DOI: [10.1016/0079-6565\(95\)01024-6](https://doi.org/10.1016/0079-6565(95)01024-6).
- 28 N. Bouzidia, B. Hamdi and A. Ben Salah, *Chem. Res. Chin. Univ.*, 2016, **32**, 519–526, DOI: [10.1007/s40242-016-6012-y](https://doi.org/10.1007/s40242-016-6012-y).
- 29 K. J. Chen, H. S. Scott, D. G. Madden, T. Pham, A. Kumar, A. Bajpai, M. Lusi, K. A. Forrest, B. Space, J. J. Perry and M. J. Zaworotko, *Chem*, 2016, **1**, 753–765, DOI: [10.1016/j.chempr.2016.10.009](https://doi.org/10.1016/j.chempr.2016.10.009).
- 30 Q. L. Qian, X. W. Gu, J. Y. Pei, H. M. Wen, H. Wu, W. Zhou, B. Li and G. D. Qian, *J. Mater. Chem. A*, 2021, **9**, 9248–9255, DOI: [10.1039/D0TA11340A](https://doi.org/10.1039/D0TA11340A).
- 31 A. L. Myers and J. M. Prausnitz, *AIChE J.*, 1965, **11**, 121–127, DOI: [10.1002/aic.690110125](https://doi.org/10.1002/aic.690110125).
- 32 K. I. Hadjiivanov, D. A. Panayotov, M. Y. Mihaylov, E. Z. Ivanova, K. K. Chakarova, S. M. Andonova and N. L. Drenchev, *Chem. Rev.*, 2021, **121**, 1286–1424, DOI: [10.1021/acs.chemrev.0c00487](https://doi.org/10.1021/acs.chemrev.0c00487).
- 33 A. Cadiou, J. S. Lee, D. Damasceno Borges, P. Fabry, T. Devic, M. T. Wharmby, C. Martineau, D. Foucher, F. Taulelle, C. H. Jun, Y. K. Hwang, N. Stock, M. F. De Lange, F. Kapteijn, J. Gascon, G. Maurin, J. S. Chang and C. Serre, *Adv. Mater.*, 2015, **27**, 4775–4780, DOI: [10.1002/adma.201502418](https://doi.org/10.1002/adma.201502418).
- 34 Y.-M. Gu, H.-F. Qi, S. Qadir, X.-W. Liu, T.-J. Sun, S.-S. Zhao, Z. Lai and S.-D. Wang, *ACS Sustainable Chem. Eng.*, 2021, **9**, 17310–17318, DOI: [10.1021/acssuschemeng.1c06207](https://doi.org/10.1021/acssuschemeng.1c06207).
- 35 K. Tan, N. Nijem, Y. Gao, S. Zuluaga, J. Li, T. Thonhauser and Y. J. Chabal, *CrystEngComm*, 2015, **17**, 247–260, DOI: [10.1039/C4CE01406E](https://doi.org/10.1039/C4CE01406E).

