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# Spatial disposition of square-planar mononuclear nodes in metal–organic frameworks for C<sub>2</sub>H<sub>2</sub>/CO<sub>2</sub> separation†

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The efficient separation of acetylene (C<sub>2</sub>H<sub>2</sub>) from its mixture with carbon dioxide (CO<sub>2</sub>) remains a challenging industrial process due to their close molecular sizes/shapes and similar physical properties. Herein, we report a microporous metal–organic framework (JNU-4) with square-planar mononuclear copper(II) centers as nodes and tetrahedral organic linkers as spacers, allowing for two accessible binding sites per metal center for C<sub>2</sub>H<sub>2</sub> molecules. Consequently, JNU-4 exhibits excellent C<sub>2</sub>H<sub>2</sub> adsorption capacity, particularly at 298 K and 0.5 bar (200 cm<sup>3</sup> g<sup>−1</sup>). Detailed computational studies confirm that C<sub>2</sub>H<sub>2</sub> molecules are indeed predominantly located in close proximity to the square-planar copper centers on both sides. Breakthrough experiments demonstrate that JNU-4 is capable of efficiently separating C<sub>2</sub>H<sub>2</sub> from a 50 : 50 C<sub>2</sub>H<sub>2</sub>/CO<sub>2</sub> mixture over a broad range of flow rates, affording by far the largest C<sub>2</sub>H<sub>2</sub> capture capacity (160 cm<sup>3</sup> g<sup>−1</sup>) and fuel-grade C<sub>2</sub>H<sub>2</sub> production (105 cm<sup>3</sup> g<sup>−1</sup>, ≥98% purity) upon desorption. Simply by maximizing accessible open metal sites on mononuclear metal centers, this work presents a promising strategy to improve the C<sub>2</sub>H<sub>2</sub> adsorption capacity and address the challenging C<sub>2</sub>H<sub>2</sub>/CO<sub>2</sub> separation.

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## 1. Introduction

Acetylene (C<sub>2</sub>H<sub>2</sub>) is one of the most essential feedstocks in petrochemical industries with a global market of 5.6 billion US\$ in 2018 and projected to reach 11.42 billion US\$ in 2023.<sup>1</sup> It is manufactured by hydrocarbon cracking or partial nature gas combustion, in which carbon dioxide (CO<sub>2</sub>) is an inevitable byproduct.<sup>2</sup> Thus, the removal of CO<sub>2</sub> is a must-do step before further production of value-added chemicals. Yet, the C<sub>2</sub>H<sub>2</sub>/CO<sub>2</sub> separation is a challenging task owing to their very close molecular sizes/shapes (C<sub>2</sub>H<sub>2</sub>, 3.34 Å × 3.32 Å × 5.70 Å; CO<sub>2</sub>, 3.33 Å × 3.18 Å × 5.36 Å, Fig. S1†) and similar physical properties (boiling points: C<sub>2</sub>H<sub>2</sub>, 189.3 K; CO<sub>2</sub>, 194.7 K).<sup>3</sup> The industrial purification of C<sub>2</sub>H<sub>2</sub> from CO<sub>2</sub> is carried out by cryogenic distillation and liquid absorption,<sup>4–7</sup> both of which are highly energy-intensive and often associated with potential safety hazards.

Adsorptive separation enables efficient gas purification and is deemed an energy-saving alternative technology. Porous materials that can selectively adsorb one type of molecule over others have recently aroused great interest and are deemed promising to replace traditional industrial practices. For instance, metal–organic frameworks (MOFs), a.k.a. porous coordination polymers (PCPs), are porous crystalline solids constructed from the self-assembly of organic linkers and metal ions/clusters.<sup>8–20</sup> Although recently emerged, MOFs stand out in gas separation studies and the reticular chemistry enables exquisite control over pore size and surface chemistry to realize preferential binding or even molecular sieving effects.<sup>21–28</sup> With regard to C<sub>2</sub>H<sub>2</sub>/CO<sub>2</sub> separation, however, the trade-off between adsorption capacity and selectivity still poses a daunting challenge for materials scientists.

Surface engineering with electronegative elements (*e.g.*, N, O, and F) usually facilitates the binding of C<sub>2</sub>H<sub>2</sub> over CO<sub>2</sub> due to their difference in the quadrupole moments (−13.4 × 10<sup>−40</sup> and +20.5 × 10<sup>−40</sup> C m<sup>2</sup> for CO<sub>2</sub> and C<sub>2</sub>H<sub>2</sub>, respectively) and electrostatic potentials (Fig. S1†).<sup>29–48</sup> For example, a highly fluorinated MOF material SIFSIX-Cu-TPA exhibits a very large C<sub>2</sub>H<sub>2</sub> adsorption of 185 cm<sup>3</sup> g<sup>−1</sup> at 298 K and 1 bar with a moderate C<sub>2</sub>H<sub>2</sub>/CO<sub>2</sub> selectivity of 5.4.<sup>31</sup> This approach, however, may not necessarily favor C<sub>2</sub>H<sub>2</sub> adsorption as the overall mismatch of electrostatic potentials between the framework surface and C<sub>2</sub>H<sub>2</sub> molecule could disrupt and even reverse the selectivity.<sup>49</sup>

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On the other hand, a more reliable approach is surface engineering with open metal sites (OMSs) to preferentially bind  $C_2H_2$  molecules *via*  $\pi$ -complexation.<sup>50–56</sup> Most of the reported clusters in MOFs offer one accessible OMS per metal, such as mononuclear square-pyramidal,<sup>57</sup> dinuclear paddle-wheel,<sup>58</sup> and trinuclear  $\mu_3$ -oxo clusters.<sup>59</sup> It is interesting to point out that a simple square-planar mononuclear center may be able to provide as many as two binding sites for  $C_2H_2$  molecules. The material UTSA-74a is constructed with both square-planar and tetrahedral mononuclear zinc centers. Although the square-planar zinc center can provide two accessible binding sites, the tetrahedral one has no accessible binding sites due to the rigid coordination geometry.<sup>51</sup> The material NKMOF-1-Ni is a rare MOF example constructed with square-planar mononuclear centers.<sup>60</sup> As strong as it may seem in the binding of  $C_2H_2$  over  $CO_2$  ( $C_2H_2/CO_2$  selectivity = 249.3), its  $C_2H_2$  adsorption capacity ( $85.7\text{ cm}^3\text{ g}^{-1}$ ) is relatively low, likely due to the short Ni...Ni distance (5.75 Å) allowing only one  $C_2H_2$  molecule in between. Intuitively, by employing organic linkers of right size and geometry as spacers, it is plausible to realize the maximum utilization of binding sites of square-planar metal centers, and therefore, achieve not only high  $C_2H_2/CO_2$  selectivity but also large  $C_2H_2$  adsorption capacity (Scheme 1).

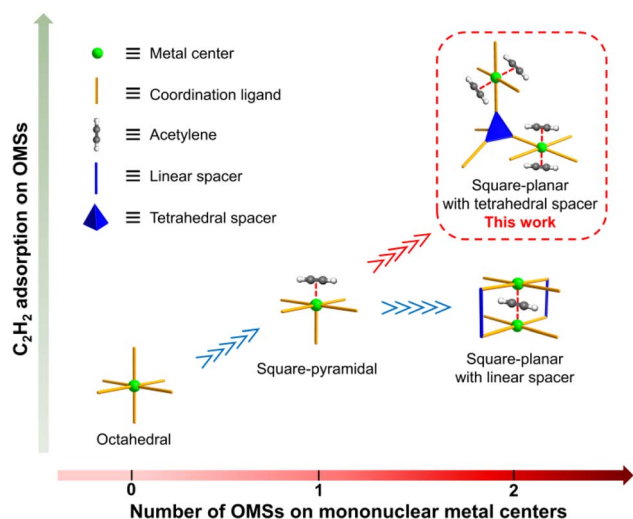
Herein we report a microporous MOF (termed JNU-4, JNU = Jinan University) featuring a 4,4-connected **pts** topology with square-planar mononuclear copper(II) centers spaced by tetrahedral organic linkers. Structural analysis shows that every copper center has both OMSs orientated toward the channels, and thus, spatially accessible for  $C_2H_2$  molecules. As a result, the activated JNU-4 (JNU-4a) exhibits excellent  $C_2H_2$  adsorption capacity, particularly at 298 K and 0.5 bar ( $200\text{ cm}^3\text{ g}^{-1}$ ). Computational studies confirm that  $C_2H_2$  molecules indeed preferentially occupy both OMSs of the square-planar copper centers, and the simulated adsorption data are consistent with the experimental results. Breakthrough measurements demonstrate that JNU-4a is capable of efficiently separating

$C_2H_2$  from  $C_2H_2/CO_2$  mixtures over a broad range of flow rates, realizing by far the largest  $C_2H_2$  capture capacity and fuel-grade  $C_2H_2$  production even under humid conditions.

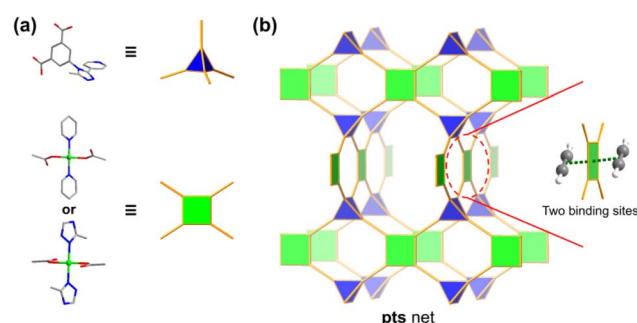
## 2. Results and discussion

### 2.1. Structure and porosity analysis

JNU-4 was synthesized according to a modified procedure previously reported by Krautscheid.<sup>61</sup> The solvothermal reaction of 5-(3-methyl-5-(pyridin-4-yl)-4H-1,2,4-triazol-4-yl)-1,3-benzenedicarboxylic acid ( $H_2$ MPTBDC) and  $Cu(NO_3)_2 \cdot 3H_2O$  in a mixture of acetonitrile, water, and nitric acid yielded dark blue crystals of JNU-4. Single crystal X-ray diffraction (SCXRD) data reveal that the as-synthesized JNU-4 crystallized in the monoclinic  $P2_1/c$  space group. There are two crystallographically independent Cu(II) atoms in the asymmetric unit, both of which are in four-coordination with the oxygen/nitrogen atoms of MPTBDC linkers, affording  $Cu(COO)_2(N\text{-pyridine})_2$  and  $Cu(COO)_2(N\text{-triazole})_2$  of similar square planar geometry. One Cu atom coordinates with two O atoms from carboxylate groups and two N atoms from pyridine groups, while the other coordinates with two O atoms from carboxylate groups and two N atoms from triazole groups. The tetrahedral MPTBDC linkers and the square planar copper centers are further linked to generating a three-dimensional (3D) MOF with a 4,4-connected **pts** topology network. The copper centers are sufficiently spaced by the organic linkers and the two binding sites are potentially accessible for  $C_2H_2$  molecules (Fig. 1 and S2†). The phase purity of the bulk JNU-4 was verified by comparison of the simulated and experimental powder X-ray diffraction (PXRD) patterns (Fig. S3†). The  $N_2$  adsorption/desorption measurements of JNU-4a (see the ESI† for the detailed activation method) at 77 K display a reversible type I adsorption isotherm with a saturated adsorption of  $400\text{ cm}^3\text{ g}^{-1}$ , characteristic of a microporous material (Fig. 2a). The pore size distribution (PSD) calculated using Non-Localized Density Functional Theory (NL-DFT) methods shows two main peaks centered at 4.8 and 9.3 Å (Fig. 2a inset), which are arguably in the right range for realizing



**Scheme 1** A simple concept to enhance  $C_2H_2$  adsorption *via* spatial disposition of square-planar mononuclear metal centers with tetrahedral spacers.



**Fig. 1** (a) MPTBDC organic linker as a tetrahedral building unit,  $Cu(COO)_2(N\text{-pyridine})_2$  and  $Cu(COO)_2(N\text{-triazole})_2$  complexes as square-planar 4-connected building units, respectively. (b) Simplified **pts** topology of JNU-4, highlighting that every copper center has both OMSs orientated toward the channels accessible for  $C_2H_2$  interaction. Color code: green, Cu; red, O; blue, N; gray, C.  $C_2H_2$  molecules are shown in a ball-and-stick model depicted in gray.



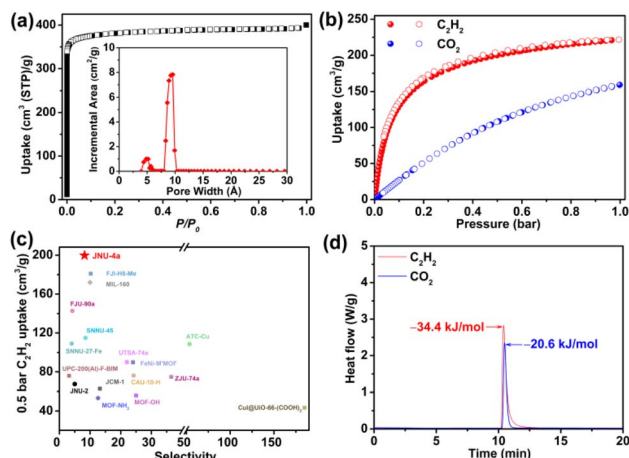


Fig. 2 (a)  $\text{N}_2$  adsorption/desorption isotherms of JNU-4a at 77 K. Filled/empty squares represent adsorption/desorption. (Inset) Calculated pore-size distribution using the Non-Localized Density Functional Theory (NL-DFT) method. (b)  $\text{C}_2\text{H}_2$  and  $\text{CO}_2$  single-component adsorption/desorption isotherms of JNU-4a at 298 K up to 1 bar. (c) Comparison of  $\text{C}_2\text{H}_2$  gravimetric uptake in JNU-4a and some representative MOF materials at room temperature (0.5 bar and 1 bar). (d) Differential scanning calorimetry of JNU-4a upon introducing  $\text{C}_2\text{H}_2$  or  $\text{CO}_2$  at a flow rate of  $20 \text{ mL min}^{-1}$  under ambient conditions (298 K and 1 bar).

both high  $\text{C}_2\text{H}_2$  adsorption and  $\text{C}_2\text{H}_2/\text{CO}_2$  selectivity.<sup>62</sup> The Brunauer–Emmett–Teller surface area of JNU-4a was calculated to be  $1533 \text{ m}^2 \text{ g}^{-1}$  and the pore volume to be  $0.62 \text{ cm}^3 \text{ g}^{-1}$  at  $P/P_0 = 0.9$  (Fig. S4†), which matches well with the crystal structure ( $0.60 \text{ cm}^3 \text{ g}^{-1}$ ), indicating that the sample can be fully desolvated while maintaining the structural integrity. The high surface area, suitable pore size, and square planar mononuclear centers of JNU-4a encouraged us to further investigate its  $\text{C}_2\text{H}_2$  adsorption and  $\text{C}_2\text{H}_2/\text{CO}_2$  separation. The OMS density of JNU-4a is about  $4.8 \text{ mmol cm}^{-3}$  (Table S5†), which is mediocre compared to other MOFs, likely due to its high specific surface area ( $1533 \text{ m}^2 \text{ g}^{-1}$ ) and large pore volume ( $0.62 \text{ cm}^3 \text{ g}^{-1}$ ).

## 2.2. Gas adsorption

Hence, we collected single-component  $\text{C}_2\text{H}_2$  and  $\text{CO}_2$  adsorption isotherms at different temperatures. As expected, JNU-4a manifests a steep adsorption curve with an adsorption capacity of  $222 \text{ cm}^3 \text{ g}^{-1}$  at 298 K and 1 bar (Fig. 2b and S5†), which is superior to most of the top-performing materials, such as SIFSIX-Cu-TPA ( $185 \text{ cm}^3 \text{ g}^{-1}$ ),<sup>31</sup> FJU-90a ( $180 \text{ cm}^3 \text{ g}^{-1}$ ),<sup>32</sup> SIFSIX-3-Ni ( $73.9 \text{ cm}^3 \text{ g}^{-1}$ ),<sup>33</sup> ZJU-74a ( $85.7 \text{ cm}^3 \text{ g}^{-1}$ ),<sup>50</sup> UTSA-74a ( $108 \text{ cm}^3 \text{ g}^{-1}$ ),<sup>51</sup> UPC-200(Al)-F-BIM ( $144.5 \text{ cm}^3 \text{ g}^{-1}$ ),<sup>34</sup> FeNi-MOF ( $96 \text{ cm}^3 \text{ g}^{-1}$ ),<sup>52</sup> SNNU-27-Fe ( $182.4 \text{ cm}^3 \text{ g}^{-1}$ ),<sup>62</sup> JCM-1 ( $75 \text{ cm}^3 \text{ g}^{-1}$ ),<sup>35</sup> and JNU-1 ( $64 \text{ cm}^3 \text{ g}^{-1}$ ),<sup>63</sup> and slightly lower than that for FJI-H8-Me ( $229 \text{ cm}^3 \text{ g}^{-1}$ ).<sup>64</sup> For an equimolar  $\text{C}_2\text{H}_2/\text{CO}_2$  separation, the  $\text{C}_2\text{H}_2$  uptake value at a partial pressure of 0.5 bar is considered an essential indicator of its separation potential. JNU-4a exhibits a gravimetric  $\text{C}_2\text{H}_2$  adsorption capacity of  $200 \text{ cm}^3 \text{ g}^{-1}$ . To the best of our knowledge, this value is higher than those of reported top-performance porous materials for  $\text{C}_2\text{H}_2/\text{CO}_2$  separation (Fig. 2c), including MIL-160 ( $172 \text{ cm}^3 \text{ g}^{-1}$ ),<sup>65</sup> Co-

MOF-74 ( $174 \text{ cm}^3 \text{ g}^{-1}$ ),<sup>55</sup> SIFSIX-Cu-TPA ( $168.8 \text{ cm}^3 \text{ g}^{-1}$ ),<sup>31</sup> and FJI-H8-Me ( $180 \text{ cm}^3 \text{ g}^{-1}$ ).<sup>64</sup> By contrast, the  $\text{CO}_2$  adsorption capacity of JNU-4a at 0.5 bar is  $109 \text{ cm}^3 \text{ g}^{-1}$ , which is almost half of that for  $\text{C}_2\text{H}_2$  under similar conditions. We further employed ideal adsorption solution theory (IAST)<sup>66</sup> to simulate the adsorption behavior for a 50:50  $\text{C}_2\text{H}_2/\text{CO}_2$  gas mixture. As shown in Fig. S6–S8,† JNU-4a shows a moderate IAST selectivity of  $\text{C}_2\text{H}_2$  over  $\text{CO}_2$ , reaching up to 8.2 at 298 K and 1 bar, which is higher than that of many benchmark materials studied for  $\text{C}_2\text{H}_2/\text{CO}_2$  separation, such as FJU-90a (4.3),<sup>32</sup> MUF-17 (6.0),<sup>36</sup> SIFSIX-21-Ni (7.8),<sup>38</sup> UPC-200(Al)-F-BIM (3.15),<sup>34</sup> and SNNU-27-Fe (3.6).<sup>62</sup>

## 2.3. Adsorption enthalpy

To quantitatively depict the large adsorption difference between  $\text{C}_2\text{H}_2$  and  $\text{CO}_2$  on JNU-4a, their isosteric heat of adsorption ( $Q_{\text{st}}$ ) values were calculated from the fitting of single-component gas adsorption isotherms collected at different temperatures. As shown in Fig. S9–S11,† the  $Q_{\text{st}}$  for  $\text{C}_2\text{H}_2$  at zero coverage was calculated to be  $26.8 \text{ kJ mol}^{-1}$ , significantly higher than that for  $\text{CO}_2$  ( $19.7 \text{ kJ mol}^{-1}$ ). To further experimentally quantify the  $Q_{\text{st}}$  for  $\text{C}_2\text{H}_2$  and  $\text{CO}_2$  on JNU-4a, we performed differential scanning calorimetry measurements of heat flow upon introducing  $\text{C}_2\text{H}_2$  or  $\text{CO}_2$  at a flow rate of  $20 \text{ mL min}^{-1}$ , respectively, at 298 K and 1 bar (Fig. 2d). The obtained experimental  $Q_{\text{st}}$  for  $\text{C}_2\text{H}_2$  and  $\text{CO}_2$  is  $34.4 \text{ kJ mol}^{-1}$  and  $20.6 \text{ kJ mol}^{-1}$ , respectively, indicative of a significantly stronger binding affinity for  $\text{C}_2\text{H}_2$  than  $\text{CO}_2$ . It is worth mentioning that the  $Q_{\text{st}}$  for  $\text{C}_2\text{H}_2$  on JNU-4a is lower than those on UTSA-300 ( $57.6 \text{ kJ mol}^{-1}$ ),<sup>67</sup> SIFSIX-3-Ni ( $36.7 \text{ kJ mol}^{-1}$ ),<sup>33</sup> and most of the benchmark MOFs with high-density OMSs, such as ATC-Cu ( $79.1 \text{ kJ mol}^{-1}$ ),<sup>56</sup> NKMOF-1-Ni ( $60.3 \text{ kJ mol}^{-1}$ ),<sup>60</sup> ZJU-74a ( $45 \text{ kJ mol}^{-1}$ ),<sup>50</sup> and CuI@UiO-66-(COOH)<sub>2</sub> ( $74.5 \text{ kJ mol}^{-1}$ )<sup>54</sup> (Fig. S12†). Such a low  $Q_{\text{st}}$  value implies that JNU-4a could be regenerated under mild conditions, which would be highly beneficial for energy-efficient  $\text{C}_2\text{H}_2/\text{CO}_2$  separation. To prove the easy regeneration and recyclability of JNU-4a, we carried out twenty continuous gas adsorption/desorption measurements for  $\text{C}_2\text{H}_2$  and  $\text{CO}_2$  without applying heat at the degassing stage. As expected, no obvious loss of  $\text{C}_2\text{H}_2$  and  $\text{CO}_2$  adsorption capacity was observed (Fig. S13 and S14†).

## 2.4. Computational studies

To corroborate the adsorption capacity and the preferred  $\text{C}_2\text{H}_2$  binding sites in JNU-4a, grand canonical Monte Carlo (GCMC) simulations were first carried out at 298 K.<sup>68,69</sup> The experimental and simulated isotherms are in reasonably good agreement, particularly for  $\text{C}_2\text{H}_2$  at low pressures and for  $\text{CO}_2$  over the entire pressure range (Fig. 3a). The density distribution and radial distribution functions of  $\text{C}_2\text{H}_2$  and  $\text{CO}_2$  at 298 K and 1 bar further reveal that  $\text{C}_2\text{H}_2$  molecules are indeed predominantly located on both sides of  $\text{Cu}(\text{COO})_2(\text{N-triazole})_2$  (site I) and  $\text{Cu}(\text{COO})_2(\text{N-pyridine})_2$  (site II), whereas  $\text{CO}_2$  molecules were observed only at site I (Fig. 3b, c and S15†). To describe the detailed interactions of gas molecules at both sites, dispersion-corrected density functional theory (DFT-D) calculations were



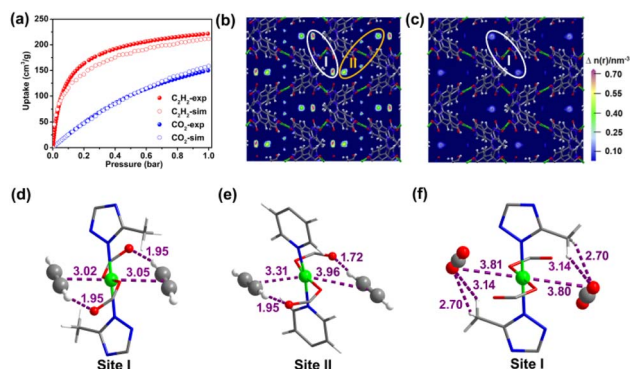


Fig. 3 (a) Experimental and simulated adsorption isotherms of  $\text{C}_2\text{H}_2$  (red) and  $\text{CO}_2$  (blue) at 298 K and up to 1 bar. (b) GCMC simulated adsorption density distributions of  $\text{C}_2\text{H}_2$  in JNU-4a at 298 K and 1 bar. (c) GCMC simulated adsorption density distributions of  $\text{CO}_2$  in JNU-4a at 298 K and 1 bar. (d) DFT-D-calculated binding configurations of  $\text{C}_2\text{H}_2$  at site I. (e) DFT-D-calculated binding configurations of  $\text{C}_2\text{H}_2$  at site II. (f) DFT-D-calculated binding configurations of  $\text{CO}_2$  at site I (green, Cu; dark gray, C; blue, N; red, O; white, H).  $\text{C}_2\text{H}_2$  and  $\text{CO}_2$  are represented in ball-and-stick models in (d)–(f), and the distance unit is Å.

then carried out. As shown in Fig. 3d–f, two  $\text{C}_2\text{H}_2$  molecules at site I interact with  $\text{Cu}^{2+}$  through  $\pi$ -complexation with distances of 3.02 and 3.05 Å, respectively, which are comparable to the sum of the van der Waals radii of carbon (1.70 Å) and copper (1.40 Å) atoms. Additionally, one of the H atoms of  $\text{C}_2\text{H}_2$  molecules is bound by uncoordinated carboxylate O atoms through C–H $\cdots$ O interaction with a distance of 1.95 Å (Fig. 3d). At site II, two  $\text{C}_2\text{H}_2$  molecules interact with  $\text{Cu}^{2+}$  with distances of 3.31 and 3.96 Å, respectively, and both  $\text{C}_2\text{H}_2$  molecules have an H atom bound by uncoordinated carboxylate O atoms through C–H $\cdots$ O interaction with distances of 1.72 and 1.95 Å (Fig. 3e). By contrast, both  $\text{CO}_2$  molecules at site I interact side-on with  $\text{Cu}^{2+}$  through Cu $\cdots$ O=C=O interaction with distances of 3.80 and 3.81 Å, respectively, and the same interacting O atoms are also bound by H atoms of methyl groups through C=O $\cdots$ H interaction with distances of 2.70 and 3.14 Å, respectively (Fig. 3f). The static binding energies ( $\Delta E$ ) for  $\text{C}_2\text{H}_2$  were calculated to be 41.7 and 33.2 kJ mol $^{-1}$  at site I and site II, respectively, which is much higher than that for  $\text{CO}_2$  at site I (29.87 kJ mol $^{-1}$ ). The overall large difference between  $\text{C}_2\text{H}_2$  and  $\text{CO}_2$  in their static binding energies on JNU-4a is in good agreement with their respective experimental  $Q_{\text{st}}$  values. Thus, not only was the square planar copper center successfully integrated into the framework but also the two OMSs of copper clusters were proved accessible for  $\text{C}_2\text{H}_2$  binding due to the right-sized organic linker as a spacing unit. The unprecedented maximum utilization of OMSs of the square planar metal center in JNU-4a enables both strong binding of  $\text{C}_2\text{H}_2$  molecules and large  $\text{C}_2\text{H}_2$  adsorption capacity, which prompted us to further investigate its  $\text{C}_2\text{H}_2/\text{CO}_2$  separation performance.

## 2.5. Breakthrough experiments

Column breakthrough experiments were first performed on JNU-4a for a 50:50  $\text{C}_2\text{H}_2/\text{CO}_2$  mixture at a flow rate of 4

mL min $^{-1}$  at 298 K. As shown in Fig. 4a, a clean separation of  $\text{C}_2\text{H}_2/\text{CO}_2$  was observed with a large separation window;  $\text{CO}_2$  quickly broke through the column after 42 min g $^{-1}$ , whereas the retention time of  $\text{C}_2\text{H}_2$  on the column was 79 min g $^{-1}$ , almost doubled that of  $\text{CO}_2$ . Moreover, the breakthrough curve for  $\text{CO}_2$  exhibited a typical but very strong rolling-up at 42 min g $^{-1}$ , with a  $C/C_0$  value rising to 2.0, indicating that a great deal of the adsorbed  $\text{CO}_2$  was displaced by  $\text{C}_2\text{H}_2$  until breakthrough equilibrium, which can be rationalized by their large binding energy difference. Based on the breakthrough curves, the amount of  $\text{C}_2\text{H}_2$  and  $\text{CO}_2$  captured on the breakthrough column was estimated to be 160 cm $^3$  g $^{-1}$  and 12.5 cm $^3$  g $^{-1}$ , respectively. Notably, such a captured amount of  $\text{C}_2\text{H}_2$  is by far the highest among all reported porous materials (Fig. 4b and S17 $^\dagger$ ), including MIL-160 (152 cm $^3$  g $^{-1}$  or 142 cm $^3$  g $^{-1}$  in a different report),<sup>65,70</sup> FeNi-M'MOF (66.7 cm $^3$  g $^{-1}$ ),<sup>52</sup> CuI@UiO-66-(COOH) $_2$  (64.7 cm $^3$  g $^{-1}$ ),<sup>54</sup> and ZJU-74 (81.5 cm $^3$  g $^{-1}$ ).<sup>50</sup> With the captured amount of  $\text{C}_2\text{H}_2$  and  $\text{CO}_2$ , the separation factor was estimated to be 12.8, which is consistent with the IAST selectivity, and higher than that of most of the top-performing porous materials, such as CuI@UiO-66-(COOH) $_2$  (3.4),<sup>54</sup> FeNi-M'MOF (1.7),<sup>52</sup> FJU-90a (2.1),<sup>32</sup> NKMOF-1-Ni (2.6),<sup>60</sup> and SNNU-45 (2.9)<sup>37</sup> (Fig. S17 and S18 $^\dagger$ ).

Although many MOF materials have been studied for  $\text{C}_2\text{H}_2/\text{CO}_2$  separation, only a few of them reported  $\text{C}_2\text{H}_2$  purity and

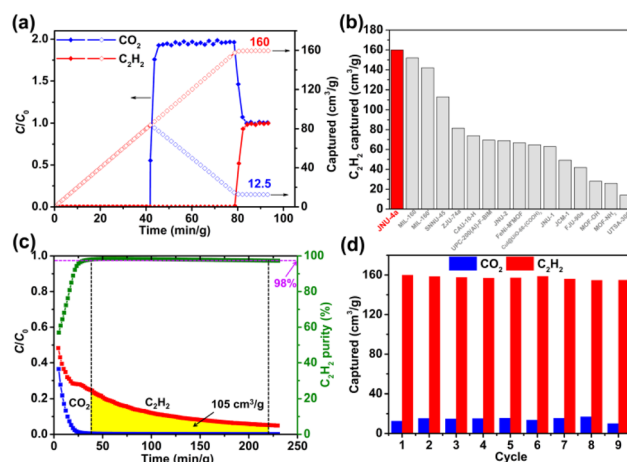


Fig. 4 (a) Breakthrough curves (left y-axis) of  $\text{C}_2\text{H}_2$  and  $\text{CO}_2$  on JNU-4a for an equimolar mixture of  $\text{C}_2\text{H}_2/\text{CO}_2$  (4.0 mL min $^{-1}$ ) at 298 K. Empty squares depict the estimated amount of  $\text{C}_2\text{H}_2$  and  $\text{CO}_2$  captured on the breakthrough column (right y-axis). (b) Comparison of the estimated amount of  $\text{C}_2\text{H}_2$  captured on the breakthrough column for an equimolar mixture of  $\text{C}_2\text{H}_2/\text{CO}_2$  (JNU-4a and other top-performing materials). (c) Desorption curves of  $\text{C}_2\text{H}_2$  and  $\text{CO}_2$  after breakthrough equilibrium with helium gas (10.0 mL min $^{-1}$ ) sweeping at 298 K. Solid green squares represent the ratios of  $\text{C}_2\text{H}_2/\text{CO}_2$  in the desorbed gas mixture. The yellow area highlights  $\text{C}_2\text{H}_2$  with over 98% purity (105 cm $^3$  g $^{-1}$ ) collectible during the desorption. (d) Continuous breakthrough experiments on JNU-4a for an equimolar mixture of  $\text{C}_2\text{H}_2/\text{CO}_2$  at 298 K and the estimated amount of  $\text{C}_2\text{H}_2$  and  $\text{CO}_2$  captured on the breakthrough column of nine cycles. *In situ* regeneration was carried out with helium gas (10.0 mL min $^{-1}$ ) sweeping at 298 K.



productivity. The high separation factor of JNU-4a prompted us to conduct desorption experiments. Indeed, fuel-grade  $C_2H_2$  (98% purity) can be achieved upon desorption and the productivity was estimated to be  $105\text{ cm}^3\text{ g}^{-1}$  (Fig. 4c and S19<sup>†</sup>), which is sustainably higher than those of reported porous materials.<sup>33,44,49,71,72</sup> To further evaluate the recyclability of JNU-4a, continuous breakthrough experiments were carried with helium sweeping at room temperature as the regeneration method (Fig. 4d and S20–S22<sup>†</sup>). Benefitting from its low  $Q_{\text{st}}$ , JNU-4a maintained the high  $C_2H_2$  capture capacity after nine cycles, highlighting the easy regeneration and good recyclability of JNU-4a for  $C_2H_2/CO_2$  separation. A high diffusion rate is crucial for industrial applications, which will drastically reduce the operation time.<sup>73</sup> Volumetric adsorption kinetics was first studied on a BEL MAX II sorption analyzer; both  $C_2H_2$  and  $CO_2$  exhibit a relatively high diffusion rate with diffusion constants ( $D/r^2$ ) calculated to be  $3.00 \times 10^{-3}$  and  $2.59 \times 10^{-3}$ , respectively (Fig. S29a and b<sup>†</sup>). The data were consistent with the time-dependent gravimetric adsorption performed on a thermogravimetric analyzer; both  $C_2H_2$  and  $CO_2$  can reach adsorption saturation in a short time period (Fig. S29c<sup>†</sup>). To investigate the influence of the flow rate on the separation performance, column breakthrough experiments were carried out for a 50 : 50  $C_2H_2/CO_2$  mixture at different flow rates (up to  $10.0\text{ mL min}^{-1}$ ) (Fig. S23–S25<sup>†</sup>). The breakthrough times of  $C_2H_2$  and  $CO_2$  were reduced with the increase of flow rates, while the amount of the captured  $C_2H_2$  was estimated to be  $158.0\text{ cm}^3\text{ g}^{-1}$ ,  $162.4\text{ cm}^3\text{ g}^{-1}$ , and  $168.3\text{ cm}^3\text{ g}^{-1}$  at flow rates of  $6.0\text{ mL min}^{-1}$ ,  $8.0\text{ mL min}^{-1}$ , and  $10.0\text{ mL min}^{-1}$ , respectively. The results suggest that the higher flow rate may increase the amount of  $C_2H_2$  captured on the breakthrough column owing to the buildup of pressures.

In industrial  $C_2H_2/CO_2$  separation, the feed gases may contain water vapor, which will likely affect the separation performance of MOF materials with OMSSs. Continuous single-component adsorption/desorption experiments were carried out on JNU-4a with moisturized  $C_2H_2$  (10% relative humidity, RH). As shown in Fig. S26 and S27,<sup>†</sup> no obvious loss of adsorption capacity was observed after ten cycles of adsorption/desorption. Furthermore, we conducted eight cycles of continuous breakthrough experiments for an equimolar  $C_2H_2/CO_2$  mixture with a flow rate of  $6.0\text{ mL min}^{-1}$  under humid conditions (10% RH) (Fig. 5a), and also no obvious loss of capture capacity was observed. The amount of  $C_2H_2$  captured on the breakthrough column was estimated to be  $145\text{ cm}^3\text{ g}^{-1}$  (Fig. 5b). Based on desorption curves, about  $85\text{ cm}^3$  of fuel-grade  $C_2H_2$  can be retrieved for 1 g of JNU-4a (Fig. 5c). Although lower than the productivity under dry conditions, it is still much higher than those of reported porous materials, including SIFSIX-3-Ni ( $56\text{ cm}^3\text{ g}^{-1}$ , 99.9%),<sup>33</sup> SIFSIX-dps-Cu ( $55.6\text{ cm}^3\text{ g}^{-1}$ , 99.9%),<sup>71</sup> ZNU-1 ( $53.8\text{ cm}^3\text{ g}^{-1}$ , 99.5%),<sup>44</sup> JXNU-11( $Fe_2Ni$ ) ( $44.3\text{ cm}^3\text{ g}^{-1}$ , 95%),<sup>72</sup> and Cd-NP ( $27.8\text{ cm}^3\text{ g}^{-1}$ , 99.99%)<sup>49</sup> (Fig. 5d). Many MOFs with OMSSs have been reported to be poisoned by water vapor, and it is worth pointing out that JNU-4a may be capable of efficiently separating  $C_2H_2/CO_2$  even under humid conditions.

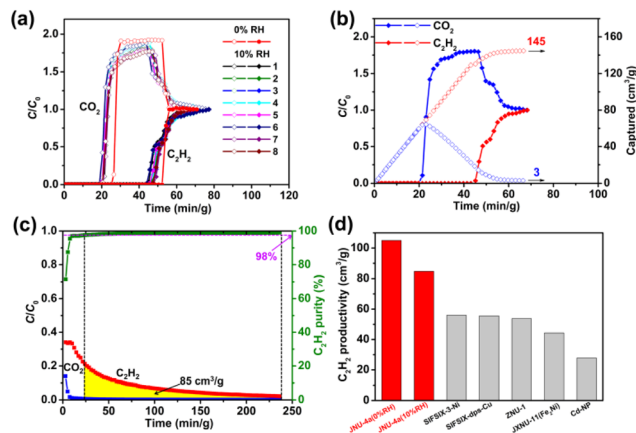


Fig. 5 (a) Continuous breakthrough curves of  $C_2H_2$  and  $CO_2$  on JNU-4a for an equimolar  $C_2H_2/CO_2$  mixture ( $6.0\text{ mL min}^{-1}$ ) under dry (0% RH) and humid conditions (10% RH). *In situ* regeneration was carried out with helium gas ( $10.0\text{ mL min}^{-1}$ ) sweeping at 298 K. (b) One set of breakthrough curves (left y-axis) of  $C_2H_2$  and  $CO_2$  on JNU-4a for an equimolar  $C_2H_2/CO_2$  mixture ( $6.0\text{ mL min}^{-1}$ ) under humid conditions (10% RH). Empty squares depict the estimated amount of  $C_2H_2$  and  $CO_2$  captured on the breakthrough column (right y-axis). (c) Desorption curves of  $C_2H_2$  and  $CO_2$  after breakthrough equilibrium with helium gas ( $10.0\text{ mL min}^{-1}$ ) sweeping at 298 K. Solid green squares represent the ratios of  $C_2H_2/CO_2$  in the desorbed gas mixture. The yellow area represents  $C_2H_2$  with over 98% purity ( $85\text{ cm}^3\text{ g}^{-1}$ ) collectible during the desorption. (d) Comparison of the  $C_2H_2$  productivity estimated from desorption curves for an equimolar  $C_2H_2/CO_2$  mixture.

### 3. Conclusion

We have implemented a simple concept of two accessible OMSSs per metal in MOFs by employing square-planar mononuclear centers as nodes and tetrahedral organic linkers as spacers. The 4,4-connected **pts** topology network (JNU-4) exhibits excellent  $C_2H_2$  adsorption capacity, particularly at 298 K and 0.5 bar ( $200\text{ cm}^3\text{ g}^{-1}$ ). Computational modeling studies reveal that  $C_2H_2$  molecules indeed preferentially occupy both OMSSs of the square-planar centers. Breakthrough experiments demonstrate by far the largest  $C_2H_2$  capture capacity ( $160\text{ cm}^3\text{ g}^{-1}$ ) from a 50 : 50  $C_2H_2/CO_2$  mixture and fuel-grade  $C_2H_2$  production ( $105\text{ cm}^3\text{ g}^{-1}$ ,  $\geq 98\%$ ) upon desorption. This work illustrates a straightforward design strategy to maximize the accessible OMSSs in MOFs for  $C_2H_2$  adsorption. Further optimization of the spacing linkers with the assistance of computational simulations would be key to advancing in this direction to address the challenging  $C_2H_2/CO_2$  separation.

### Data availability

The data that support the plots within this paper and other finding of this study are available from the corresponding authors upon reasonable request.

### Author contributions

W. L. and D. L. conceived and designed the research. H. Z., W. L., and D. L. co-wrote the manuscript. H. Z. and X.-J. X. planned



and executed the synthesis, characterization, and gas separation studies. Y. W. performed the theoretical simulations. D. L. and R.-J. W. carried out the structural analyses. All authors participated in and contributed to the preparation of the manuscript.

## Conflicts of interest

There are no conflicts to declare.

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