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A metal–organic framework with suitable pore size and dual functionalities for highly efficient post-combustion CO₂ capture†

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Capturing carbon dioxide (CO₂) from flue gases with porous materials has been considered as a viable alternative technology to replace traditional liquid amine adsorbents. A large number of microporous metal–organic frameworks (MOFs) have been developed as CO₂-capturing materials. However, it is challenging to target materials with both extremely high CO₂ capture capacity and gas selectivity (so-called trade-off) along with moderate regeneration energy. Herein, we developed a novel porous material, [Cu(dpt)₂(SiF₆)_n] (termed as UTSA-120; dpt = 3,6-di(4-pyridyl)-1,2,4,5-tetrazine), which is isorecticular to the net of SIFSIX-2-Cu-i. This material exhibits simultaneously high CO₂ capture capacity (3.56 mmol g⁻¹ at 0.15 bar and 296 K) and CO₂/N₂ selectivity (~600), both of which are superior to those of SIFSIX-2-Cu-i and most other MOFs reported. Neutron powder diffraction experiments reveal that the exceptional CO₂ capture capacity at the low-pressure region and the moderate heat of CO₂ adsorption can be attributed to the suitable pore size and dual functionalities (SiF₆²⁻ and tetrazine), which not only interact with CO₂ molecules but also enable the dense packing of CO₂ molecules within the framework. Simulated and actual breakthrough experiments demonstrate that UTSA-120a can efficiently capture CO₂ gas from the CO₂/N₂ (15/85, v/v) and CO₂/CH₄ (50/50) gas mixtures under ambient conditions.

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Introduction

The concentration of atmospheric carbon dioxide (CO₂) has sharply risen from 278 ppm at the beginning of the industrial revolution to >400 ppm today, which causes global climate change.^{1,2} Efforts to reduce the increase in atmospheric CO₂ concentrations rely on the development of economical methods to capture CO₂ from flue gases and the atmosphere.³ The current state-of-the-art capture technology is to use liquid

amine chemisorbents; however, chemisorbents typically suffer from the corrosive nature of solvents, fouling of process equipment, and high energy cost for solvent regeneration. Physical adsorption based on porous materials offers promise to address the above problems. Compared with chemisorbents for complete CO₂ capture from flue gases, the CO₂ adsorption on porous materials is “physical” and weak, making these adsorbents relatively low in selectivity. Thus, physisorptive selectivity is an important parameter for evaluating these solid adsorbents' performance. Recent studies show that the cost for CO₂ capture from flue gases can be significantly reduced if the CO₂/N₂ selectivity is enhanced above 500 for an adsorbent with a CO₂ uptake capacity higher than 4 mmol g⁻¹.⁴ Therefore, both high CO₂ adsorption uptake and CO₂/N₂ selectivity are required for ideal CO₂-capturing adsorbents.

Microporous metal–organic frameworks (MOFs) represent an emerging type of porous materials as promising adsorbents for carbon capture due to their easily tunable structure, pore size, and functionality.^{5–7} Tremendous efforts have been dedicated to develop MOFs with high CO₂ adsorption capacity or separation selectivity.^{8–10} Incorporation of functional sites and fine-tuning of pore sizes/shapes in MOFs are two powerful strategies for this purpose.^{11–15} However, it is still challenging to target materials with extremely high CO₂ capture capacity/selectivity and moderate CO₂ enthalpy of adsorption simultaneously. For example, the

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MOF-74 series has a high density of open metal sites that drive a record high CO₂ uptake but displays moderately high selectivities (40–140).⁸ Some ultra-microporous MOFs exhibit full molecular sieving and then record separation selectivity but relatively low uptake of CO₂ at 0.15 bar (1.5–2.4 mmol g⁻¹) due to the small pore sizes.^{13,14} The alkylamino-functionalization within MOFs can improve both low-pressure CO₂ adsorption selectivity and capacity with high enthalpy of CO₂ adsorption (70–110 kJ mol⁻¹).¹⁵

Recent studies have shown that the SIFSIX series (SIFSIX = hexafluorosilicate (SiF₆²⁻)) are very promising candidates for CO₂-capturing adsorbents, because their pore size can be finely tuned and SiF₆²⁻ anions have moderately strong interactions with CO₂.^{13,16} Among the reported SIFSIX materials, the interpenetrated SIFSIX-2-Cu-i exhibits exceptional CO₂ uptake under ambient conditions, and moderately high CO₂/N₂ selectivity (140) and CO₂ heat of adsorption.^{4b} Reducing the pore size to ~3.5 Å in pyrazine-based SIFSIX-3 materials can afford full molecular sieving toward CO₂/N₂ separation and thus the record selectivity.¹³ However, the extremely small pore space delimits the total CO₂ uptake at 0.15 bar and the ultra-strong interactions with CO₂ in SIFSIX-3 offer relatively high regeneration energy. Evidently, simple control of the pore size in SIFSIX materials is not the best choice to target ideal materials for CO₂ capture from flue gases. We speculated that if we introduce secondary functional groups into the framework of SIFSIX-2-Cu-i to enhance the interactions with CO₂ molecules, the resulting material would have an increased CO₂ uptake at the low-pressure region, thus achieving both higher CO₂ capture capacity (especially at 0.15 bar) and selectivity.

Our experimental and simulation studies verify this hypothesis, and we herein used a functionalized organic linker of 3,6-di(4-pyridyl)-1,2,4,5-tetrazine (dpt) instead of 4,4'-dipyridylacetylene (dpa) to construct isorecticular UTSA-120 (Fig. 1). The resulting material shows a similar pore size to SIFSIX-2-Cu-i but has dual functionalities (SiF₆²⁻ and tetrazine) decorated on the pore surfaces. As expected, UTSA-120a exhibits simultaneously high CO₂ adsorption capacity (3.56 mmol g⁻¹ at 0.15 bar and 296 K) and CO₂/N₂ selectivity (~600), both of which are among the highest reported for MOF materials. In addition, UTSA-120a also shows notably lower heat of adsorption (*Q*_{st}) for CO₂ (27–31 kJ mol⁻¹) compared to the benchmark SIFSIX-3 (50–

55 kJ mol⁻¹) and liquid amines (~105 kJ mol⁻¹). This rare combination of exceptional CO₂ adsorption capacity, high CO₂/N₂ selectivity and moderate *Q*_{st} in UTSA-120a is mainly due to the suitable pore size and functionality conformation created by SiF₆²⁻ and tetrazine that enable the optimal packing of CO₂ within pore channels. Highly efficient capture of CO₂ from CO₂/N₂ (15/85) and CO₂/CH₄ (50/50) mixtures was confirmed by simulated and experimental breakthrough studies.

Results and discussion

The reaction of dpt with CuSiF₆ in methanol/water solution at room temperature for 1 day afforded a pink powder sample of [Cu(dpt)₂(SiF₆)_n] (UTSA-120). The PXRD patterns of the as-synthesized and fully activated UTSA-120 are shown in Fig. S1 (ESI[†]). The diffraction peak positions remain unchanged before and after sample activation, indicating that the UTSA-120 framework is robust upon guest removal. The PXRD patterns can be indexed to the tetragonal *I4/mmm* space group, the same as that of SIFSIX-2-Cu-i. Despite extensive attempts, we were not able to obtain single crystals large enough for single-crystal X-ray diffraction studies. Therefore, we used neutron diffraction to determine the detailed structure of activated UTSA-120a. High-resolution neutron diffraction data were collected at room temperature, and Rietveld structural refinement was performed (Fig. S2, ESI[†]).¹⁷ The obtained detailed structural information of UTSA-120a is provided in Table S1 (ESI[†]).

As depicted in Fig. 1, structural analysis revealed that UTSA-120a is composed of doubly interpenetrated nets that are isostructural to the nets in SIFSIX-2-Cu-i. The use of the longer dpt instead of dpa as a linker offers a slightly larger pore size (4.6 Å) in UTSA-120a than that in SIFSIX-2-Cu-i (4.4 Å). Most importantly, the incorporated tetrazine rings are decorated around the pore channels, and all the Lewis basic N sites point into the pores. Previous studies have well documented that functional SiF₆²⁻ or uncoordinated N-sites could effectively enhance the gas-binding affinity with CO₂.¹⁸ Thus, the synergistic effect of dual functionalities in UTSA-120a may lead to enhanced interactions with CO₂ molecules as compared to SIFSIX-2-Cu-i, thus achieving higher CO₂ capture and separation capacities.

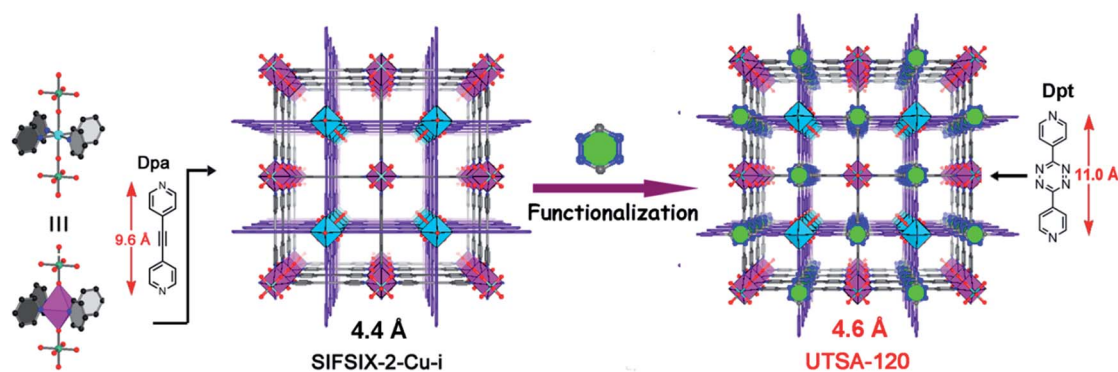


Fig. 1 Structural description of UTSA-120a, revealing its pore size (4.6 Å) and dual functionalities of SiF₆²⁻ anions and tetrazine rings around the channels. The different nets are highlighted in gray and purple for clarity. Colour code: Cu (turquoise), Si (dark green), F (red), N (blue), and C (grey).

Before evaluating UTSA-120 as a potential carbon capture adsorbent, we first examined its stability by monitoring the PXRD patterns upon sample exposure to air (Fig. 2a). When the as-synthesized sample was exposed to air for more than 6 months or to 80% humidity for 1 day, UTSA-120 could still retain its structural integrity (Fig. S3 and S4, ESI†). Even for the activated UTSA-120a sample, after exposure to air for 1 month or water vapour adsorption experiments, there is no loss of crystallinity and no obvious phase change observed (Fig. S5–S7, ESI†), indicating its excellent stability toward moisture. Next, we determined the permanent porosity of UTSA-120a using nitrogen adsorption isotherms at 77 K. As shown in Fig. S8 (ESI†) UTSA-120a can adsorb a large amount of N₂ (178 cm³ g⁻¹) at 77 K and 1 bar, and the N₂ isotherm shows a significant type I sorption behavior, characteristic of microporous materials. The Brunauer–Emmett–Teller (BET) surface area of UTSA-120a was calculated to be 638 m² g⁻¹ (Fig. S8, ESI†), comparable to that of SIFSIX-2-Cu-i (735 m² g⁻¹).

Next, we examined the single-component adsorption isotherms of CO₂, CH₄, and N₂ at 296 K up to 1 bar. As presented in Fig. 2a, UTSA-120a exhibits a rapid and high CO₂ uptake of 5.0 mmol g⁻¹ at 296 K and 1 bar. This value is comparable to the uptake of SIFSIX-2-Cu-i (5.41 mmol g⁻¹) due to their similar pore sizes. However, incorporation of functional tetrazine groups into UTSA-120a was found to enable a significantly higher CO₂ adsorption capacity than that of SIFSIX-2-Cu-i within the low-pressure region (Fig. 2b). At 0.15 bar, which is an

indicator of the CO₂ capture ability of an adsorbent from the flue gas mixture, UTSA-120a exhibits a notably enhanced CO₂ uptake (3.56 mmol g⁻¹) compared to those of SIFSIX-2-Cu-i (2.11 mmol g⁻¹) and SIFSIX-14-Cu-i (1.42 mmol g⁻¹, Fig. S9, ESI†). In comparison to other top-performing materials, the CO₂ uptake of UTSA-120a at 0.15 bar is also among the highest reported for MOF materials (Fig. 2c and Table S5, ESI†),¹⁹ outperforming most of the well-known MOFs (*i.e.*, SIFSIX-3 and UTSA-16). Conversely, UTSA-120a shows a very low CH₄ (0.93 cm³ g⁻¹) and N₂ (0.25 cm³ g⁻¹) uptake at 1 bar and 296 K (Fig. S10 and S11, ESI†). Both values are comparable to those of SIFSIX-2-Cu-i. Therefore, the incorporation of tetrazine groups into UTSA-120a can efficiently improve the CO₂ capture capacity at a low pressure of 0.15 bar, while it has no effect on CH₄ and N₂ adsorption.

Ideal adsorbed solution theory (IAST) was employed to calculate the adsorption selectivity of UTSA-120a for 15 : 85 (v/v) CO₂/N₂ and 50/50 CO₂/CH₄ gas mixtures at 296 K. As shown in Fig. 2d and S12 (ESI†), UTSA-120a exhibits an extraordinarily high selectivity of ~600 for the CO₂/N₂ mixture, and also a high CO₂/CH₄ selectivity of up to 100.

Both values are significantly higher than those observed in SIFSIX-2-Cu-i (140 and 33 for CO₂/N₂ and CO₂/CH₄). We note that the CO₂/N₂ selectivity of UTSA-120a is only lower than those of ultra-microporous MOFs that show molecular sieving for CO₂/N₂, such as Qc-5-Cu-sql and SIFSIX-3. However, the extremely small pore spaces in those MOFs limit the CO₂

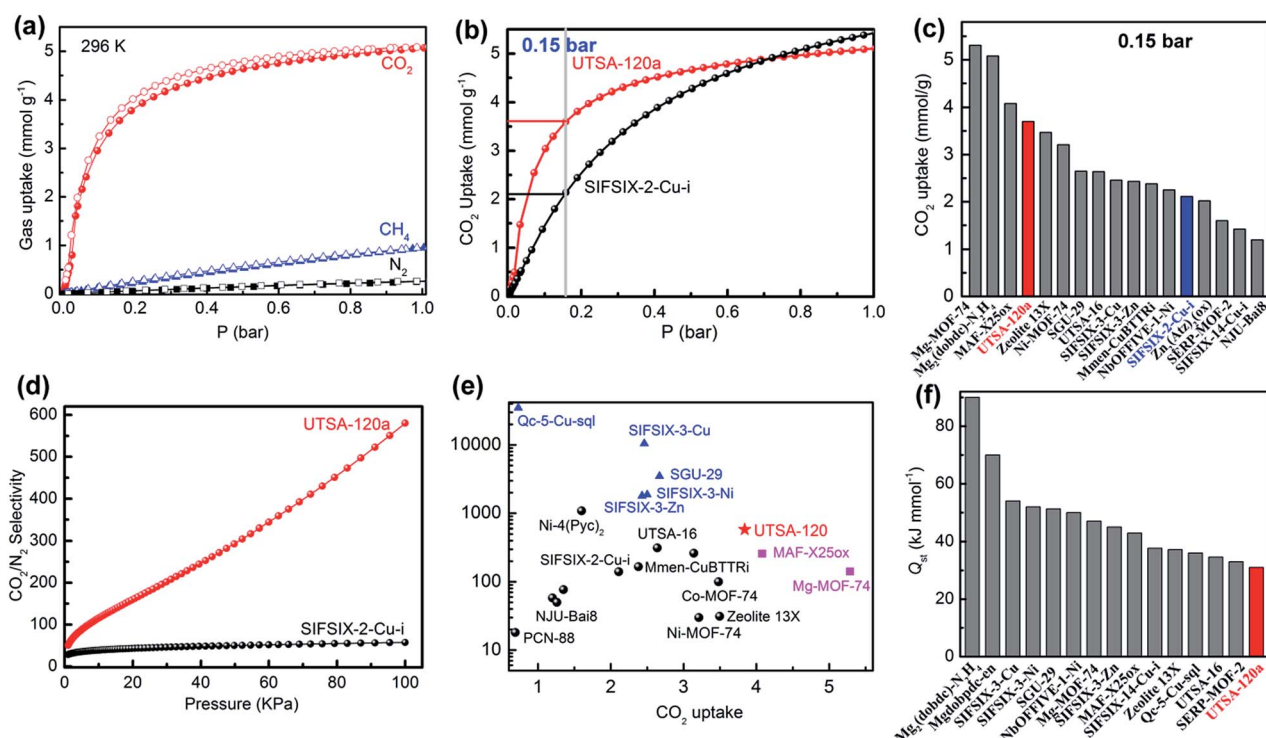


Fig. 2 (a) Gas adsorption isotherms of UTSA-120a for CO₂, CH₄ and N₂ at 296 K. Filled/empty symbols represent adsorption/desorption. (b) Comparison of CO₂ adsorption isotherms for UTSA-120a and SIFSIX-2-Cu-i at 296 K. (c) Comparison of CO₂ capture capacity for UTSA-120a and other best-performing materials at 0.15 bar and room temperature. (d) IAST selectivity of UTSA-120a (red) for CO₂/N₂ (15/85, v/v) at 296 K, as compared with SIFSIX-2-Cu-i (black). (e) A comparison of the CO₂ uptake (at 0.15 bar) and CO₂/N₂ selectivity at 1.0 bar and room temperature for UTSA-120a and other indicated MOFs. (f) Comparison of heat of CO₂ adsorption for UTSA-120a and other best-performing materials.

capture uptake at 0.15 bar, as revealed in Fig. 2e. On the other hand, although Mg-MOF-74 has the highest CO₂ capture capacity at 0.15 bar, its selectivity is relatively low (below 150). Evidently, UTSA-120a and MAF-X250x²⁰ exhibit a notable balance of both high CO₂ uptake (at 0.15 bar) and high selectivity among the indicated MOFs. In addition, UTSA-120a shows the lowest Q_{st} value among the benchmark MOFs (Fig. 2f and S14, ESI[†]) because of its suitable pore size (~4.6 Å) and the absence of ultra-strong binding sites. Therefore, this material exhibits a rare combination of exceptional CO₂ adsorption capacity, high CO₂/N₂ selectivity and moderate Q_{st} , presumably offering a lower energy input for regeneration.

To gain better insight into the enhanced CO₂ adsorption capacity at the low-pressure region and to determine CO₂ binding sites, neutron powder diffraction data were collected on a CO₂-loaded sample of UTSA-120a and Rietveld structural refinement was conducted (see Table S7 and Fig. S2 for detailed structural information of UTSA-120a·2.6CO₂, ESI[†]). As shown in Fig. 3a, the adsorbed CO₂ molecules were located within the square-shaped channels of UTSA-120a, and the carbon atom of each adsorbed CO₂ molecule interacts with one SiF₆²⁻ anion through the C··F bonding with a distance of 2.741 Å. This kind of binding site has also been determined in SIFSIX-2-Cu-i.^{4b} Unlike SIFSIX-2-Cu-i, we found that the carbon atom of each adsorbed CO₂ molecule also has a weaker interaction with uncoordinated N sites on tetrazine rings through the C··N bonding (3.701 Å). Additionally, the interpenetrated nature of the framework allows the SiF₆²⁻ pillars and tetrazine rings to be

densely arranged around the pore channel, which creates a confined pore space to organize the CO₂ molecules densely packed along the channels with a distance of 4.553 Å (Fig. 3b). Therefore, the exceptional CO₂ uptake capacity of UTSA-120a is mainly attributed to the synergistic effect of the suitable pore size and dual functionalities that enables the optimal packing of CO₂ molecules within the pores.

Transient breakthrough simulations were performed for UTSA-120a in a fixed-bed to validate the feasibility of separation of the CO₂/N₂ (15/85) mixture that mimics the fuel gas. Fig. 3c reveals the molar concentrations of CO₂/N₂ exiting the adsorber packed with UTSA-120a as a function of dimensionless time, τ , at 1 bar and 296 K. Efficient separation was realized by UTSA-120a, whereby N₂ eluted through the bed first, and then CO₂ breakthrough occurs through the fixed-bed after a certain time (τ_{break}). Attributed to both higher selectivity and CO₂ uptake capacity, the τ_{break} value of UTSA-120a is two times longer than that observed in SIFSIX-2-Cu-i (Fig. S17, ESI[†]). Similarly, Fig. 3d presents that UTSA-120a can also efficiently capture CO₂ from the 50/50 CO₂/CH₄ mixture.

Experimental breakthrough studies were further conducted in a packed column of activated UTSA-120a under flow (2.0 mL min⁻¹) of binary CO₂/N₂ (15/85) and CO₂/CH₄ (50/50) mixtures at room temperature, respectively. As illustrated in Fig. 3e and f, highly efficient separation for CO₂/N₂ and CO₂/CH₄ mixtures can be accomplished by UTSA-120a. N₂ or CH₄ pass through the sample bed rapidly, while CO₂ breakthrough occurs at 84 and 36 min g⁻¹ for CO₂/N₂ and CO₂/CH₄ mixtures,

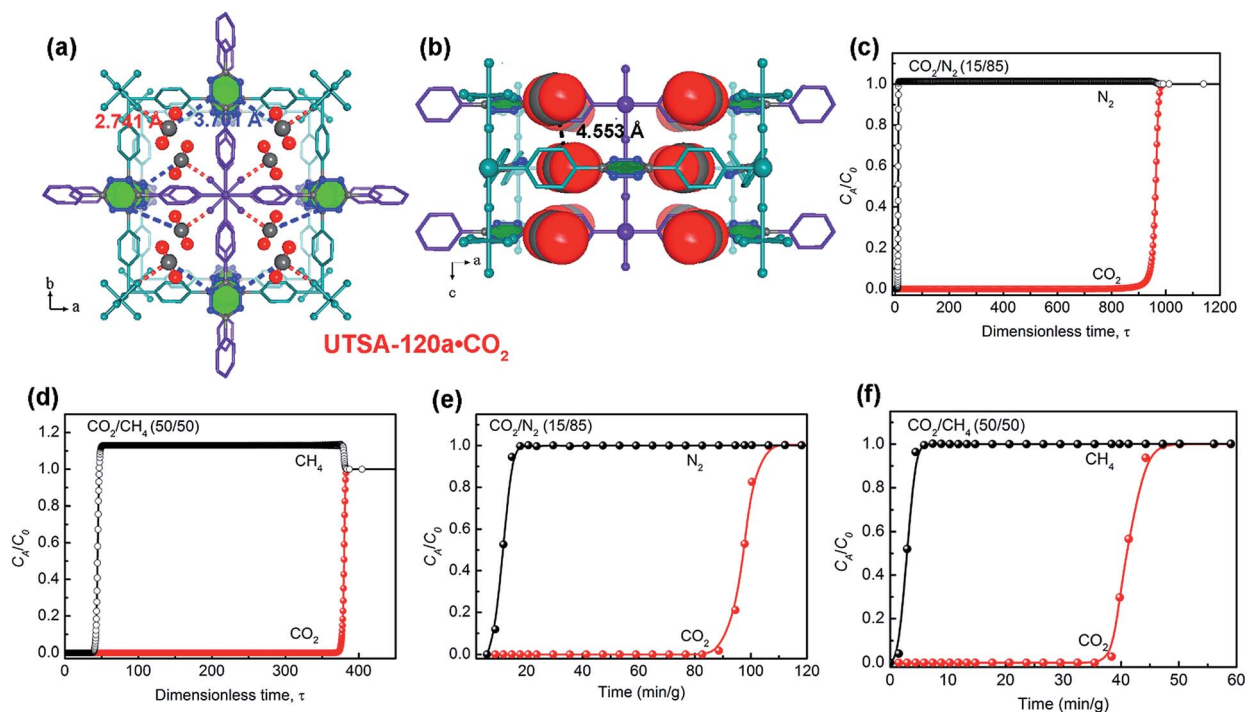


Fig. 3 (a) Neutron crystal structure of UTSA-120a·CO₂ viewed along the c and (b) b axis, determined from the Rietveld analysis (the different nets are highlighted in purple and dark green for clarity). Color code: O, red; C (in CO₂) grey. (c) Simulated column breakthrough curves for 15/85 CO₂/N₂ separation with respect to the activated UTSA-120a. (d) Simulated column breakthrough curves for CO₂/CH₄ (50/50) separation. (e) Experimental column breakthrough curves for 15/85 CO₂/N₂ and (f) 50/50 CO₂/CH₄ gas mixtures (at 298 K, 1.0 bar) with a total flow of 2 mL min⁻¹ in an absorber bed packed with UTSA-120a.

respectively. These experimental breakthrough times have the same trend as the simulated breakthrough results (850 and 370 for CO₂/N₂ and CO₂/CH₄ mixtures, respectively), indicating its excellent separation performance for CO₂ capture. The adsorption bed can be easily regenerated by He flow (20 mL min⁻¹) for 15 min at 298 K, and the separation properties of UTSA-120a can be recycled several times (Fig. S18, ESI†). As inferred from the PXRD performed on the associated samples, the framework of UTSA-120a remains stable after multiple adsorption and breakthrough experiments (Fig. S19, ESI†). It should be noted that moisture would affect gas adsorption and separation performance of porous materials under humid conditions.²¹ To further confirm the moisture stability of UTSA-120a, we measured the CO₂ adsorption properties of UTSA-120a after exposure of the sample to air for 1 month. The results revealed that the re-activated sample retains its CO₂ adsorption capacity (Fig. S20, ESI†).

Conclusions

In summary, we designed and synthesized a novel SIFSIX material (UTSA-120a) by using a functionalized organic linker of dpt instead of dpa in SIFSIX-2-Cu-i. The foregoing results revealed that UTSA-120a exhibits very high CO₂ capture capacity (3.56 mmol g⁻¹ at 0.15 bar and 296 K) and exceptional separation selectivity (~600). Both values outperform those of the isorecticular SIFSIX-2-Cu-i and most of the other reported MOFs. This exceptional separation performance is mainly attributed to the suitable pore size and dual functionalities on pore surfaces to not only interact with CO₂ molecules but also enable the dense packing of CO₂ molecules within the pores, as revealed by the UTSA-120a·2.6CO₂ structure. The rare combination of very high CO₂ adsorption capacity, exceptional CO₂/N₂ selectivity, and moderate heat of CO₂ adsorption renders UTSA-120a a very promising candidate for CO₂ capture from flue gases. Breakthrough experiments confirmed that UTSA-120a can efficiently capture CO₂ gas from the CO₂/N₂ and CO₂/CH₄ mixtures.

Experimental section

Synthesis of [Cu(dpt)₂(SiF₆)_n] (UTSA-120)

60 mg (0.25 mmol) of 3,6-di(4-pyridyl)-1,2,4,5-tetrazine (dpt) was partially dissolved in a methanol solution (30 mL). An aqueous solution of CuSiF₆ (1.0 mL, 0.247 mmol) was then added dropwise to the stirred methanol solution. A fresh pink precipitate appeared immediately, and the solution was then stirred for 24 hours at room temperature. The suspension was filtered, and the precipitate was washed with MeOH and then air dried. Bulk purity of the sample was verified by PXRD (Fig. S1, ESI†).

Gas sorption measurements

Gas adsorption isotherms were measured using a Micromeritics ASAP 2020 surface area analyzer. To remove all the guest solvents in the framework, the fresh powder sample was

first solvent-exchanged with dry methanol at least 8 times within two days. The solvent-exchanged sample was evacuated at room temperature for 24 h, at 323 K for 12 h and then at 343 K for an additional 4–5 h till the outgas rate was 5 mmHg min⁻¹ prior to measurements. The sorption measurement was maintained at 77 K with liquid nitrogen. An ice-water bath (slush) and water bath were used for adsorption isotherms at 273 and 296 K, respectively.

Neutron diffraction experiment

High-resolution neutron diffraction data were collected using a BT-1 neutron powder diffractometer at the National Institute of Standards and Technology (NIST) Center for Neutron Research. A Ge(311) monochromator with a 75° take-off angle, $\lambda = 2.0787(2)$ Å, and in-pile collimation of 60 minutes of arc was used. Data were collected over the range of 1.3–166.3° (2 θ) with a step size of 0.05°. The fully activated UTSA-120a sample was loaded in a vanadium can equipped with a capillary gas line and a packless valve. A closed-cycle He refrigerator was used for sample temperature control. The bare MOF sample was measured first, at room temperature (296 K). To probe the CO₂ adsorption location, a pre-determined amount of CO₂ was loaded into the sample at room temperature, and diffraction data were then collected. Rietveld structural refinement was performed on the neutron diffraction data using the GSAS package.²² The refinements on lattice parameters, atomic coordinates, positions/orientations of the CO₂ molecules (treated as rigid bodies), CO₂ occupancies, thermal factors, background, and profiles all converge with satisfactory *R*-factors. The structural data are summarized in Table S7.†

Breakthrough experiments

The breakthrough curves were measured on a homemade apparatus for gas mixtures CO₂/N₂ (15/85) or CO₂/CH₄ (50/50) at 298 K and 1.01 bar. In the separation experiment, the activated UTSA-120a (0.582 g) particles with diameters of 200–300 μ m were prepared and packed into a Φ 4 × 150 mm stainless steel column. The experimental set-up consisted of two fixed-bed stainless steel reactors. One reactor was loaded with the adsorbent, while the other reactor was used as a blank control group to stabilize the gas flow. The gas flows were controlled at the inlet using a mass flow meter at 2 mL min⁻¹, and a gas chromatograph (TCD – Thermal Conductivity Detector, detection limit 0.1 ppm) continuously monitored the effluent gas from the adsorption bed. Prior to every breakthrough experiment, we activated the sample by flushing the adsorption bed with helium gas for 2 hours at 323 K. Subsequently, the column was allowed to equilibrate at the measurement rate before we switched the gas flow. The adsorption bed was easily regenerated by He flow (20 mL min⁻¹) for 15 min at 298 K.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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