

A Fine-Tuned Fluorinated MOF Addresses the Needs for Trace CO₂ Removal and Air Capture Using Physisorption

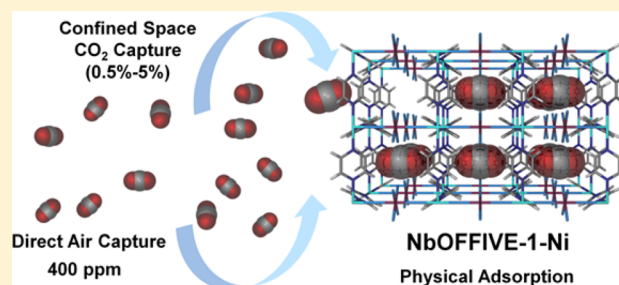
Prashant M. Bhatt,[†] Youssef Belmabkhout,[†] Amandine Cadiou,[†] Karim Adil,[†] Osama Shekhah,[†] Aleksander Shkurenko,[†] Leonard J. Barbour,[‡] and Mohamed Eddaoudi^{*,†}

[†]Functional Materials Design, Discovery & Development Research Group (FMD3), Advanced Membranes & Porous Materials Center, Division of Physical Sciences and Engineering, King Abdullah University of Science and Technology (KAUST), Thuwal 23955-6900, Kingdom of Saudi Arabia

[‡]Department of Chemistry and Polymer Science, University of Stellenbosch, Stellenbosch 7600, South Africa

S Supporting Information

ABSTRACT: The development of functional solid-state materials for carbon capture at low carbon dioxide (CO₂) concentrations, namely, from confined spaces (<0.5%) and in particular from air (400 ppm), is of prime importance with respect to energy and environment sustainability. Herein, we report the deliberate construction of a hydrolytically stable fluorinated metal–organic framework (MOF), **NbOFFIVE-1-Ni**, with the appropriate pore system (size, shape, and functionality), ideal for the effective and energy-efficient removal of trace carbon dioxide. Markedly, the CO₂-selective **NbOFFIVE-1-Ni** exhibits the highest CO₂ gravimetric and volumetric uptake (ca. 1.3 mmol/g and 51.4 cm³ (STP) cm⁻³) for a physical adsorbent at 400 ppm of CO₂ and 298 K. Practically, **NbOFFIVE-1-Ni** offers the complete CO₂ desorption at 328 K under vacuum with an associated moderate energy input of 54 kJ/mol, typical for the full CO₂ desorption in conventional physical adsorbents but considerably lower than chemical sorbents. Noticeably, the contracted square-like channels, affording the close proximity of the fluorine centers, permitted the enhancement of the CO₂–framework interactions and subsequently the attainment of an unprecedented CO₂ selectivity at very low CO₂ concentrations. The precise localization of the adsorbed CO₂ at the vicinity of the periodically aligned fluorine centers, promoting the selective adsorption of CO₂, is evidenced by the single-crystal X-ray diffraction study on **NbOFFIVE-1-Ni** hosting CO₂ molecules. Cyclic CO₂/N₂ mixed-gas column breakthrough experiments under dry and humid conditions corroborate the excellent CO₂ selectivity under practical carbon capture conditions. Pertinently, the notable hydrolytic stability positions **NbOFFIVE-1-Ni** as the new benchmark adsorbent for direct air capture and CO₂ removal from confined spaces.



INTRODUCTION

Mitigating the amount of the CO₂ released in the atmosphere, directly correlated to the global warming, remains an ongoing challenge that requires a concerted worldwide effort from academia, industry, and governments alike. Inopportunistly, worldwide energy needs have doubled fossil fuel consumption in the last two decades,^{1–11} as a result of the eminent economic growth and the enhanced quality of living in emerging countries, thus provoking the manifest and amplified global carbon dioxide emission. The foreseen deployment of a relatively cleaner alternative energy sources, e.g., solar, renewable, and nuclear, to meet the increasing global energy demand while lessening or eliminating the CO₂ emission as a result of deserting the dominant use of the fossil fuel is still universally debated and implausible in the near future.^{1–11} In view of that and while preparing for the looked-for fossil-fuel-free transition, it is evidently necessary to develop new technologies and materials for effective and energy-efficient carbon dioxide (CO₂) capture at a wide range of concentrations. Explicitly, point-source carbon capture and storage

(CCS) can be regarded as a plausible solution sanctioning the sustainable use of fossil fuels in power, steel, and cement production plants, whereas direct air capture (DAC) can address and remediate CO₂ emissions from mobile sources such as automobiles and airplanes.^{1–11} Markedly, DAC offers a great prospective to remotely capture the emitted CO₂ at a different distant location and time.

It is noteworthy that CO₂ capture from air using the chemical adsorption technology has been deployed for over seven decades to maintain a safe level of CO₂ in confined spaces such as space shuttles and submarines, where access to fresh air is limited.^{12,13} Nevertheless, the CO₂ concentrations and the associated CO₂ quantities captured by DAC (400 ppm of CO₂, worldwide average of 54 kg/person/day) and point-source CCS (7–15% CO₂, worldwide average of 38 kg/person/day) entail a relatively larger scale footprint and/or an excessive energy penalty compared to the requisites for CO₂ capture in

Received: May 24, 2016

Published: July 8, 2016

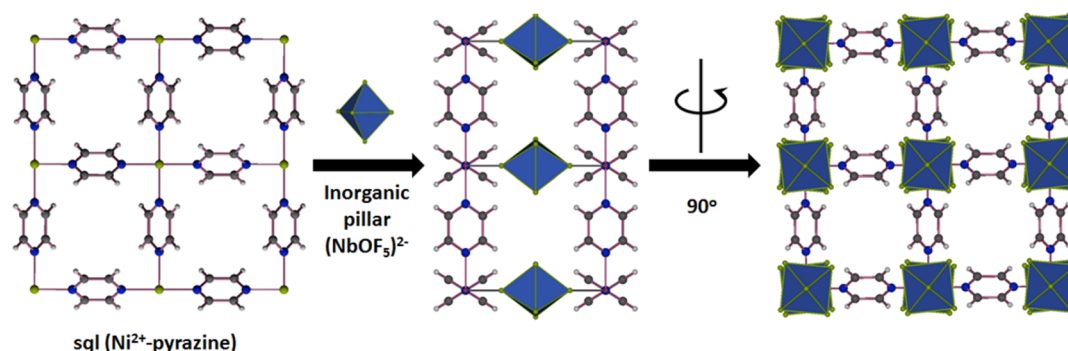


Figure 1. Structural representation of NbOFFIVE-1-Ni: left, the 2-periodic square-grid layer constructed by linking Ni(II) with pyrazine ligands; middle, pillaring of square-grid layers by the $(\text{NbOF}_5)_2^{2-}$ inorganic pillars; right, square-shaped channels in the resultant 3-periodic pcu-MOF, NbOFFIVE-1-Ni.

confined spaces (1–5% CO_2 and 1 kg/person/day).^{1–11} Perceptibly, the cost associated with the CO_2 capture in confined spaces is not a disturbing concern because the compulsory objective is the effective removal of CO_2 and the subsequent procurement of the indispensable clean air.

Noticeably, the low CO_2 concentration in air (400 ppm) and the compulsory low CO_2 level in confined spaces (<0.5%) position chemical adsorbents, such as aqueous alkylamine solutions and lithium hydroxide (LiOH) (80–120 kJ/mol), as the conventional benchmark materials, with a high CO_2 selectivity even in the presence of water vapor, for carbon capture in diluted CO_2 concentrations.⁸ Nevertheless, large-scale spread of the chemically driven separation approach is hampered by the prohibitive high-energy requirement for the CO_2 desorption/regeneration process. Markedly, there is a need to develop a new generation of highly CO_2 -selective physical adsorbent materials with a moderate CO_2 heat of adsorption, i.e., below 60 kJ/mol.^{3,14–17} Consequently, such a looked-for adsorbent will pave the way to affordable, effective, and energy-efficient recovery of CO_2 and will render the DAC competitive and self-sustainable. Considerately, the aerospace industry recognized the advantages of the physisorption-based separation and recently shifted their efforts to the utilization of recyclable physical adsorbents, such as the zeolite 5A (Ca^{2+}) and the SAPO-34 (Sr^{2+}), for the capture of CO_2 in confined spaces.^{18,19} Typically, the aforementioned physical adsorbents exhibit a moderate CO_2 heat of adsorption of 45–50 kJ/mol and a recyclable CO_2 uptake of 9–15 $\text{cm}^3(\text{STP})/\text{g}$ (1.7–2.9 wt %) at 1300 ppm. Nonetheless, their overall performance is inadequate and ineffective in the presence of water vapor due to their relatively low tolerance to water.

Metal organic frameworks (MOFs), a tunable class of porous solid-state materials, are regarded to offer prospective solutions to various challenges pertaining to gas storage and gas separation.^{20–29} Evidently, the modular and hybrid character of MOFs permit the fine-tuning of their affinity for CO_2 via the introduction of appropriate prefunctionalized ligands and/or the grafting of judiciously selected amine moieties on the open metal sites and subsequently explore their potential for the CCS.^{22,25–28} Nevertheless, only a limited number of functionalized MOFs affording the CO_2 chemisorption showed promise for DAC and low-concentration CO_2 capture from confined spaces (<0.5%).^{22,26} Outwardly, it was intuited that chemisorption-based sorbents are the foremost option for traces CO_2 capture,⁸ and atypically put forward that physical adsorbents are prone to be ineffective for carbon capture at the low CO_2

concentration of 400 ppm due to their plausibly weak interactions with the adsorbed CO_2 molecules. Contradictorily to this uncorroborated assumption, we recently published a series of CO_2 -selective MOF adsorbents, namely, $\text{MSiF}_6(\text{pyrazine})_2 \cdot 2\text{H}_2\text{O}$ (referred to as SIFSIX-3-M where M = Ni, Cu, and Zn), showing excellent CO_2 selectivity and uptake at relatively low CO_2 concentrations using solely the physisorption mechanism^{17,30,31} and in some instances outclassing some of the amine grafted chemical sorbents.²² Nevertheless, extended exposure of SIFSIX-3-M adsorbents to water vapor resulted in a lessening over time of their associated CO_2 capture capabilities, suggesting their limited prospective deployment to mainly dry conditions.

RESULTS AND DISCUSSION

To extend the scope of this class of materials, we focused our efforts in better understanding the structure–property relationship of these materials and as a result conceivably adjusted/altered their molecular composition to enhance their water stability while maintaining or enhancing their carbon capture capabilities. The ability to construct the looked-for hydrolytically stable MOF with the desired CO_2 adsorption properties will permit its potential use for carbon capture under practical humid conditions and the subsequent elimination of the costly predrying step.

Accordingly, we conducted a structural analysis of the SIFSIX-3-M adsorbents with the aim to pinpoint the key structural features responsible for the noted unique CO_2 capture properties. The key objective is to be able to derive a reasonable structure–property relationship that will assist and guide us in fine-tuning the resultant adsorbent structure to withstand the water vapor and concurrently enhance its intrinsic CO_2 uptake and selectivity at traces CO_2 .

Appropriately, close examination of the SIFSIX-3-M adsorbents and their respective CO_2 adsorption properties revealed the impact of the periodically aligned fluorine moieties in the contracted square-shaped channels, and that the F...F distance, dictating the channel size, is directly correlated to the strength of the CO_2 interactions with the host framework. Namely, the comparison of SIFSIX-3-Zn ($Q_{\text{st}} = 45 \text{ kJ mol}^{-1}$, F...F dist. = 6.784(1) Å), SIFSIX-3-Ni ($Q_{\text{st}} = 47 \text{ kJ mol}^{-1}$, F...F dist. = 6.694(1) Å), and SIFSIX-3-Cu ($Q_{\text{st}} = 54 \text{ kJ mol}^{-1}$, F...F dist. = 6.483(1) Å) revealed that CO_2 is more strongly adsorbed at lower concentrations when the size of the square-shaped channel is further contracted, as a result of the shortened distance between the pendant fluorine moieties from diagonally

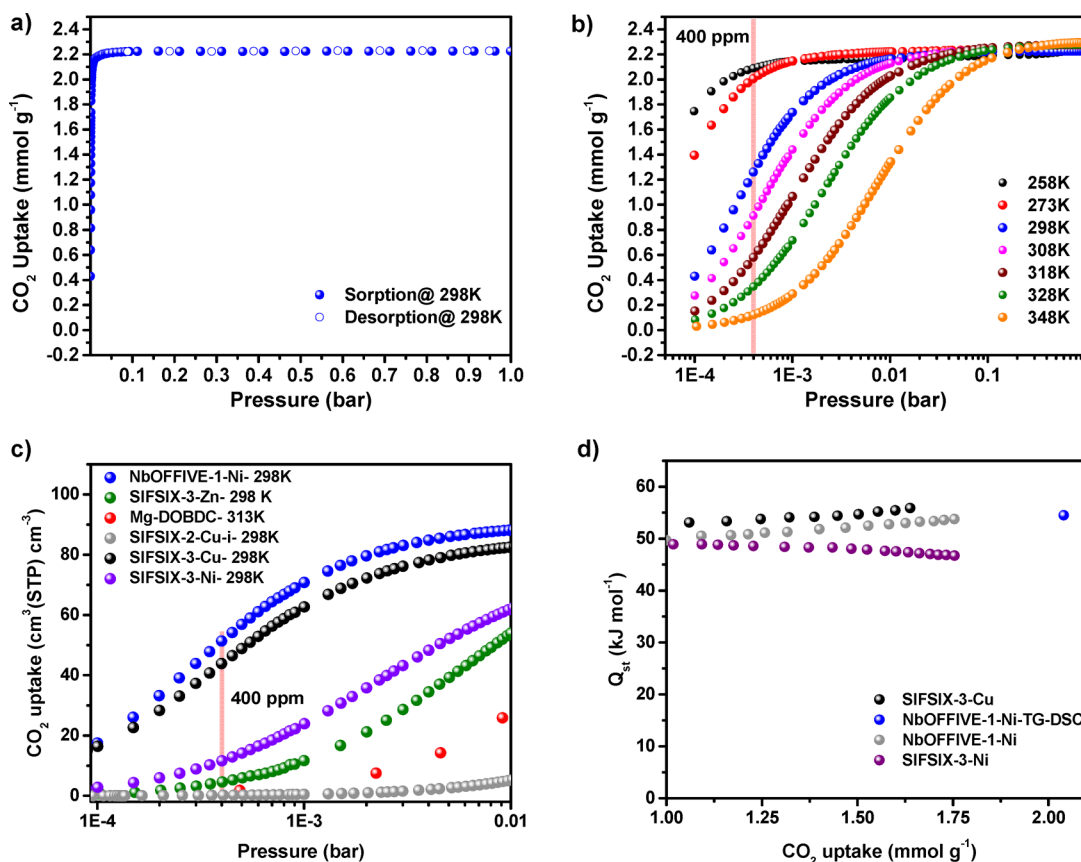


Figure 2. (a) CO₂ adsorption isotherm for NbOFFIVE-1-Ni up to 1 bar and 298 K. (b) CO₂ adsorption isotherms for NbOFFIVE-1-Ni at different temperatures. (c) Comparison of the CO₂ uptake at low pressures between NbOFFIVE-1-Ni and the SIFSIX family as well as the Mg-MOF-74, one of the best MOF for low-pressure CO₂ adsorption. (d) CO₂ heat of adsorption for NbOFFIVE-1-Ni as compared to that of SIFSIX-3-Ni and SIFSIX-3-Cu, determined using multiple CO₂ adsorption isotherms as well as TG-DSC measurements.

adjacent (SiF₆)²⁻ pillars.^{17,30,31} Considerately, in addition to contracted square-shaped channels with a periodically aligned proximal fluorine moieties enabling the MOF pore system characteristics, two other parameters were considered for the design and construction of the looked-for hydrolytically stable MOF for carbon capture. Specifically, we elected (i) to employ Ni(II) as the octahedrally coordinated metal node since the SIFSIX-3-Ni offers a shorter M–F bond distance ($d_{M-F} = 1.99(5)$ Å)³² than SIFSIX-3-Cu ($d_{M-F} = 2.12(1)$ Å)¹⁷ and thus is prone to express the requisite water vapor tolerance and (ii) to substitute the (SiF₆)²⁻ pillar with an appropriate fluorinated inorganic pillar, offering a relatively stronger coordination bonds and the adequate nucleophilicity that can preclude the observed phase change in the SIFSIX-3-Cu associated with the water molecule introduction within the Cu(II) coordination sphere.³¹

Accordingly, (NbOF₅)²⁻ was explored as a potential pillar to replace the original inorganic pillar, (SiF₆)²⁻ due its associated distinct attributes: (i) The larger size of Nb⁵⁺ imparts a longer Nb–F bond length (1.899(1) Å) than the Si–F bond (1.681(1) Å), signifying the plausible reduction in the distance between the pendant proximal fluorine moieties within the channel. (ii) The greater nucleophile behavior of (NbOF₅)²⁻ is anticipated to enhance the water stability of the resultant MOF (Figure 1).

Solvothermal reaction in a hydrofluoric acid aqueous solution containing a mixture of Ni(NO₃)₂·6H₂O, Nb₂O₅ and pyrazine afforded violet square-shaped crystals of NiNbOF₅(pyrazine)₂·

2H₂O (1) which we referred to as NbOFFIVE-1-Ni. Single-crystal X-ray diffraction (SCXRD) study on a suitable single crystal of NbOFFIVE-1-Ni at 296 K revealed that the resultant compound crystallized in a tetragonal space group *I4/mcm* with unit cell parameters $a = b = 9.942(4)$ Å and $c = 15.764(6)$ Å (Table S1). The purity of the material was confirmed by a full pattern matching using the Le Bail³³ method implemented in FULLPROF software³⁴ (Figure S1). As anticipated, NbOFFIVE-1-Ni can be regarded as a 3-periodic *pcu*-MOF based on the 2-periodic square grid, Ni-(pyrazine)₂, bridged by the (NbOF₅)²⁻ pillars via the axial oxygen and fluorine centers. Each Ni(II) is octahedrally coordinated to four nitrogen centers, from four distinct pyrazine ligands, and one oxygen and one fluorine from the (NbOF₅)²⁻ pillar. It is noteworthy that the assignment of one coordinating oxygen atom and one coordinating fluorine atom to the two apical positions in the pillar has been observed and validated in similar materials with supporting techniques.^{35–37} As expected, NbOFFIVE-1-Ni encloses a relatively contracted square-shaped channels with a slightly smaller diameter of 3.210(8) Å (derived from the distance between the pendant fluorine centers, F...F, and by taking account van der Waals radii) than those of the SIFSIX-3-Ni and SIFSIX-3-Cu adsorbents (3.694(1) and 3.483(1) Å, respectively). It is noteworthy that the Ni...Ni distance (7.030(3) Å) in the 2-periodic square grid, Ni-(pyrazine)₂, is preserved and is the same in both NbOFFIVE-1-Ni and SIFSIX-3-Ni adsorbents.

High thermal stability of the material was evaluated by TGA (Figure S5) and variable-temperature powder X-ray diffraction (VT-PXRD) performed in the range of 25–400 °C, establishing that the material retained its crystallinity over the explored temperature range (Figure S3). Markedly, the hydrolytic stability of the material was confirmed by performing in situ variable-humidity PXRD (Figure S4) and multiple water adsorption isotherms (Figure S6a) on **NbOFFIVE-1-Ni**. The exceptional water stability was further confirmed by the conformity of the resultant CO₂ isotherms before and after immersion of material in liquid water for 6 months (Figure S8). Moreover, **NbOFFIVE-1-Ni** showed excellent tolerance to hydrogen sulfide, a feature that is rarely proven for MOFs, as evidenced by the preservation of the material PXRD pattern after exposure to H₂S (Figure S2) and by performing H₂S adsorption isotherms (Figure S6b). It is of note that N₂ adsorption studies performed at 77 K on the activated material indicated as expected that **NbOFFIVE-1-Ni** does not adsorb N₂ at this cryogenic temperature. Conversely, **NbOFFIVE-1-Ni** adsorbs CO₂; accordingly, this probe was employed to evaluate the porosity properties of this adsorbent. Specifically, the apparent surface area and the pore volume were derived from the CO₂ adsorption isotherm at 273 K (Figure 2b) and estimated to be 280 m²/g and 0.095 cm³/g, respectively. Distinctly, **NbOFFIVE-1-Ni** provided the expected high affinity for CO₂ at low concentrations as evidenced by the steepness in the CO₂ adsorption isotherm and the attainment of the plateau at relatively very low CO₂ pressures (Figures 2a and S7).

Detailed analysis of the CO₂ adsorption isotherms associated with **NbOFFIVE-1-Ni** and their comparison with a closely related material, **SIFSIX-3-Ni**, revealed an enhancement in the CO₂ heat of the adsorption (Figure 2d) and most importantly a noticeable increase in the CO₂ volumetric uptake at 400 ppm of nearly 340%. This remarkable CO₂ uptake improvement, synonymous to enhanced CO₂–framework interactions, is directly correlated to the closer proximity of the pendant fluorine centers decorating the square-shaped channels, as in the case of **NbOFFIVE-1-Ni** with an F...F distance of 3.210(8) Å as compared to the 3.694(1) Å distance in the case of the **SIFSIX-3-Ni**.

Significantly, **NbOFFIVE-1-Ni** adsorbent offers an even higher CO₂ volumetric uptake at 400 ppm than the best material so far for carbon capture at traces CO₂ using physisorption mechanism, namely, **SIFSIX-3-Cu** (Figure 2c). Precisely, **NbOFFIVE-1-Ni** adsorbs a 51.4 cm³/cm³ (1.3 mmol/g) of CO₂ at 400 ppm and 298 K as compared to 44.6 cm³/cm³ for the **SIFSIX-3-Cu**, equivalent to a 15% increase relative to the best reported physical adsorbent to the best of our knowledge. In view of this, **NbOFFIVE-1-Ni** can be regarded as the best physical adsorbent material for carbon capture at very low concentration of CO₂ (traces) with the highest CO₂ gravimetric and volumetric uptakes, driven mainly by physisorption mechanism. Excellent stability and the relatively mild condition for regeneration of the material also contribute to its prominence over other materials. The preeminent carbon capture potential of **NbOFFIVE-1-Ni** at 400 ppm of CO₂ is even magnified at higher temperatures where **NbOFFIVE-1-Ni** adsorbed the equivalence of an additional 63% more CO₂ at 400 ppm and 328 K than the **SIFSIX-3-Cu** adsorbent. The volumetric uptake for well-known MOFs such as Mg-MOF-74 is comparatively very small at 400 ppm (~1.7 cm³/cm³). In terms of gravimetric uptake, both **NbOFFIVE-1-Ni** and **SIFSIX-3-Cu** have similar CO₂ capacities and adsorb an

equivalent of 43 cm³ STP/g at 1300 ppm and 298 K. This gravimetric uptake amounts to a notable 300% increase relative to that of SAPO-34 (Sr²⁺), the reference physical adsorbent for the CO₂ removal in long-duration crewed space exploration missions. Recently, a copper silicate (SGU-29) was reported to show a CO₂ volumetric uptake of 26 and 40 cm³/cm³ at CO₂ concentrations of 400 and 1000 ppm (single-gas adsorption), respectively.³⁸ Noticeably, the CO₂ volumetric and gravimetric uptakes of this purely inorganic CO₂ adsorbent are much lower than those of **NbOFFIVE-1-Ni** at very low CO₂ pressures.

To gain better insight on the structure–property relationship leading to the unusually strong physisorption of CO₂ and the subsequent improvement in the CO₂ adsorption capabilities of **NbOFFIVE-1-Ni**, we succeeded in solving the crystal structure of **NbOFFIVE-1-Ni** in the presence CO₂ and most importantly localized the adsorbed CO₂ molecules. We collected SCXRD data on a degassed crystal of **NbOFFIVE-1-Ni** under 1 bar dry CO₂ atmosphere at 298 K. The structure containing CO₂ molecules was solved in the same space group as the as-synthesized compound hosting water molecules, namely, a tetragonal space group *I4/mcm* with unit cell parameters $a = b = 9.903(1)$ Å and $c = 15.720(2)$ Å and formulated as NiNbOF₅(pyrazine)₂·0.84(CO₂) (2) (Table S2).

The interpretation of the Fourier difference data allows us to clearly localize the CO₂ molecules within the square-shaped channels of **NbOFFIVE-1-Ni**·0.84(CO₂) structure. Interestingly, the CO₂ molecule occupy a high energetically favorable position, where the electropositive carbon of the CO₂ is surrounded by four electronegative fluorine centers from four distinct (NbOF₅)²⁻ pillars (F...C_{CO2} distance = 3.050(8) Å) and the electronegative oxygen atoms of the CO₂ are surrounded by pyrazine hydrogens (C–H...O distance = 2.99 Å, angle = 117°) as depicted in Figure 3. It is worth to mention that the F...C_{CO2} distance (ca. 3.050 (8) Å) in the case of **NbOFFIVE-1-Ni**·0.84(CO₂) is less than the sum of the C and F van der Waals radii, supporting the CO₂ molecules strong interactions with the host framework. These interactions are relatively stronger than those observed in the case of the **SIFSIX-3-Ni** structure derived from the PXRD data, where the distance F...C_{CO2} is found to be equal to 3.302 Å,³² a distance clearly larger than the C and F van der Waals radii and confirming the relatively weaker CO₂–framework interactions than in the case of the CO₂ adsorbed in **NbOFFIVE-1-Ni** adsorbent.

It can be inferred from the crystal structure that the presence at close proximity of relatively strong and concurrent complementary interactions created an ideal and energetically favorable “sweet spot” for the adsorption of CO₂ and proffered unique CO₂ capture features to **NbOFFIVE-1-Ni** adsorbent. The presence of highly favorable CO₂–framework interactions in the case of **NbOFFIVE-1-Ni** is also evidenced by the steady and marked high CO₂ heat of adsorption (Figures 2d and S12). The CO₂ heat of adsorption for **NbOFFIVE-1-Ni** was determined using CO₂ adsorption isotherms at variable temperature (Figures 2b and S7) and further supported by the direct TG-DSC measurement (Figures 2d and S12).

To assert the potential of **NbOFFIVE-1-Ni** as a proper physical adsorbent for carbon capture at dilute CO₂ concentrations, we performed mixed-gas experiments under conditions akin to real-world carbon capture in confined spaces or from ambient air. A series of cyclic CO₂ (1%)/N₂ (99%) column breakthrough experiments at 298 K were performed in the presence and absence of water vapor (both dry and humid

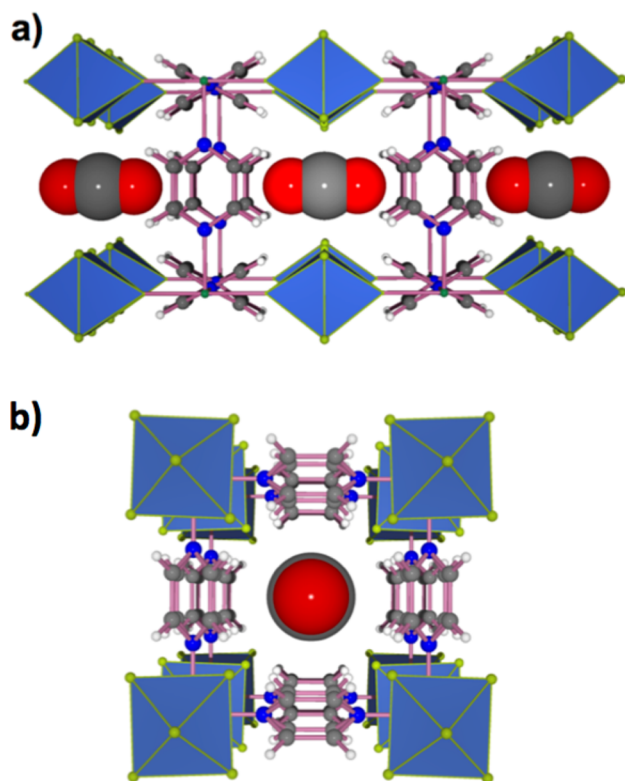


Figure 3. Direct visualization of CO₂ molecules inside the crystal structure of NbOFFIVE-1-Ni highlighting the highly favorable arrangement of the CO₂ molecules within the contracted square-shaped channels along [010] and [001].

conditions; Figure 4). The breakthrough time under dry conditions for a 1% CO₂ in the gas stream with the flow rate of

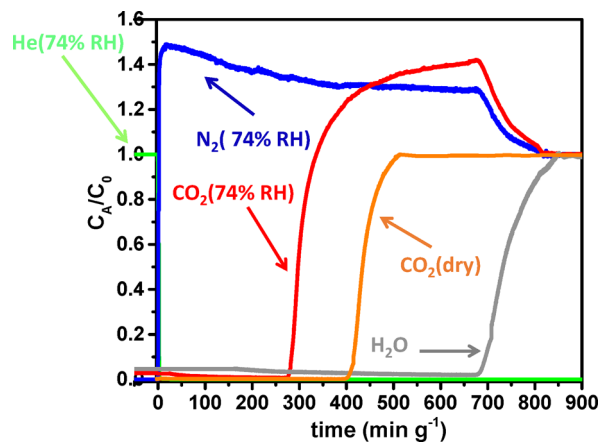


Figure 4. Column breakthrough tests for NbOFFIVE-1-Ni with the mixed-gas CO₂/N₂ (1%/99%) at 1 bar and 298 K under both dry and humid conditions (10 cm³/min flow rate).

10 cc/min revealed a remarkable retention of 415 min/g that is equivalent to the adsorbed CO₂ equaling 8.2 wt %.

Certainly, the presence of humidity (75% RH) did not significantly alter the CO₂ breakthrough time (283 min/g, uptake of 5.6 wt %). In addition, the CO₂ uptakes in dry and humid streams were conserved as proven by the reproducible data from multiple cycle breakthrough experiments, where prior to each new cycle the adsorbent was fully reactivated at 378 K (Figure S10, S11). Interestingly, the water vapor was retained in

the column for 680 min/g, which is equivalent to a water uptake of 13.8 wt %. We note that the noticeable adsorbed water uptake did not jeopardize the carbon capture capabilities of NbOFFIVE-1-Ni which suggests a rare simultaneous adsorption of water and CO₂ in contrast to most MOFs and zeolites. Appropriately, column breakthrough experiments for very dilute CO₂ concentrations (i.e., 1000 ppm of CO₂) with a flow rate of 20 cm³/min showed that CO₂ is retained in the column for 1880 min/g with an equivalent uptake of 7.4 wt % (Figure S9).

Finally, to position the carbon capture performance of NbOFFIVE-1-Ni vis-à-vis the existing technologies and in comparison with key benchmark materials (both chemical and physical adsorbents) deployed in real-world applications or regarded to offer great promise we compiled and assessed each material CO₂ removal capacity at around 1000 ppm of CO₂ for 1 day against the given material's associated CO₂ heat of adsorption. For practical reasons, we assumed that all sorbents are fully recyclable with the exception of the lithium hydroxide (LiOH), a nonrecyclable sorbent.³⁹ For comparison purposes, we arbitrarily fixed and adopted the full adsorption–desorption cycle to 60 min (24 cycles a day) and the evaluation was based on the requirements for the CO₂ scrubbing in confined spaces, specifically 1 kg of CO₂ captured per day per person.

Interestingly, as depicted in Figure 5, NbOFFIVE-1-Ni exhibits the best compromise between the carbon capture

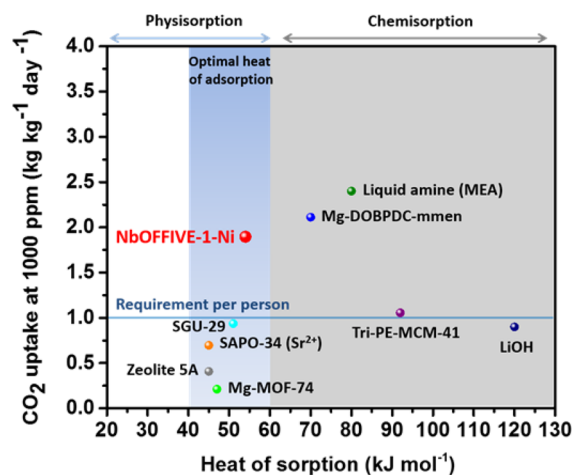


Figure 5. Heat of adsorption–CO₂ uptake (at 1000 ppm for 1 day) trade-off for NbOFFIVE-1-Ni as compared to benchmark and newly developed materials. With the exception of LiOH, the CO₂ uptake for 1 day for all the materials was calculated assuming a 60 min adsorption–desorption cycle.

capacity and the required heat for regeneration. Precisely, at 1000 ppm of CO₂, NbOFFIVE-1-Ni offers the highest CO₂ capacity in 1 day (24 cycles) associated with the optimal heat of adsorption (dictating the required energy for regeneration) than all the evaluated sorbents such as LiOH, liquid amine, amine-supported solids, zeolites 5A (Ca²⁺), SAPO-34 (Sr²⁺), and the recently reported copper silicate (SGU-29). The CO₂ uptake at 1000 ppm (kg.kg⁻¹.day⁻¹) was calculated from mixed-gas breakthrough experiment for NbOFFIVE-1-Ni adsorbent and from the reported adsorption isotherms or reported data for other materials. CO₂ uptake obtained from dynamic conditions such as breakthrough adsorption column is always slightly lower than CO₂ uptake obtained from adsorption isotherms (equilibrium condition). These values, associated

with one cycle, were multiplied by 24 (1 h cycle) in order to obtain a given material daily performance and derive a relative comparison between evaluated materials per 1 day.

Evidently, although this is a simplified analysis assuming 24 cycles per day and not taking into account the rate of CO₂ adsorption/desorption and many other constraints relevant to real processes particularly for amine supported materials and chemical sorbents,^{14,40} it portrays and places **NbOFFIVE-1-Ni** as a prospective physical adsorbent for an effective and energy-efficient CO₂ capture in confined spaces and from atmospheric air. Work is in progress to assess the related economics and technicalities associated with the potential deployment of **NbOFFIVE-1-Ni** adsorbent in practical carbon capture applications from atmosphere and in confined spaces using rapid thermal swing adsorption.

CONCLUSIONS

The close examination of the structural features of the **SIFSIX** adsorbent family permitted the election of a bulkier and a relatively nucleophilic inorganic pillar, namely, (NbOF₅)²⁻ instead of the original (SiF₆)²⁻ pillar, and the successful practice of reticular chemistry for the construction a hydrolytically stable **pcu**-MOF, **NbOFFIVE-1-Ni**, with contracted square channels decorated with proximal fluorine moieties and ideal for carbon capture at very dilute CO₂ concentrations. To the best of our knowledge, the reported **NbOFFIVE-1-Ni** stands as the best physical adsorbent material for CO₂ capture from atmospheric and confined spaces, driven mainly by physical adsorption. Specifically, in terms of the CO₂ adsorption energetics and uptake, **NbOFFIVE-1-Ni** has the highest uptake for CO₂ at 400 ppm with associated relatively optimal energy for regeneration. From the perspective of the carbon capture in a confined-space/air-removal viewpoint, **NbOFFIVE-1-Ni** offers a 300% higher CO₂ gravimetric and volumetric uptakes than those of SAPO-34 (Sr²⁺), the reference physical adsorbent for the CO₂ removal in a long-duration crewed space exploration missions, with equivalent CO₂ adsorption energetics.

Direct observation and localization of the adsorbed CO₂ molecules within the adsorbent channels using single-crystal X-ray diffraction data give valuable insights on the nature of the CO₂-framework interactions governing the high affinity of **NbOFFIVE-1-Ni** for CO₂ even at very dilute concentrations. This unique structural insight will certainly pave the way to design and construction of new and practical physical adsorbents with a similar CO₂ affinity and a further improved CO₂ uptake. Practically, unlike many other MOFs, **NbOFFIVE-1-Ni** offers great potential to be easily synthesized in large quantities (g to kg) in a cost-effective manner, thus placing this physical adsorbent on the right track for large-scale deployment and plausible commercialization. Work is in progress to scale-up and test this MOF at a pilot scale.

EXPERIMENTAL SECTION

Materials and Methods. Elemental analyses for C, H, and N were carried out on a ThermoFinnigan Apparatus. Thermal gravimetric analyses (TGA) were performed under N₂ flow (25 mL/min) with a heating rate of 5 °C/min using a TA Q500 apparatus. Enthalpy of adsorption for CO₂ and H₂O was measured using a SENSYS evo TG-DSC from Setaram Instrumentation that can carry out simultaneous high-resolution DSC and TGA experiments. In a typical experiment, the sample was activated in situ at 105 °C under continuous dry N₂ flow at the rate of 15 mL/min. For the sorption experiment, baseline

was obtained under dry N₂ flow at the rate of 15 mL/min at 25 °C. CO₂ or humid N₂ was connected at auxiliary gas port, and gas was changed from N₂ to CO₂/humid N₂ exactly after 1 h. TGA and DSC signals were monitored for few hours to obtain uptake and heat of sorption, respectively. The powder X-ray diffraction patterns and the variable-humidity powder X-ray diffraction patterns (VH-PXRD) were collected over the 2θ range 4–40° on a high-resolution PANalytical X'Pert MPD-PRO diffractometer with Cu Kα₁ radiation (λ = 1.5406 Å, 45 kV/40 mA). Variable-temperature powder X-ray diffraction (VT-PXRD) pattern measurements were collected on a PANalytical X'Pert MPD-PRO X-ray diffractometer equipped with an Anton-Parr CHC+ variable temperature stage. Measurements were performed at 45 kV, 40 mA for Cu Kα (λ = 1.5418 Å) with a scan speed of 1.0°/min and a step size of 0.02° in 2θ. Samples were placed under vacuum during analysis, and the sample was held at the designated temperatures for at least 15 min between each scan.

Synthesis of NbOFFIVE-1-Ni. All reagents were used as received from commercial suppliers without further purification: Ni(NO₃)₂·6H₂O (Acros), Nb₂O₅ (Aldrich), pyrazine (Aldrich), and HF (Aldrich). Pyrazine (384.40 mg, 4.80 mmol), Ni(NO₃)₂·6H₂O (174.50 mg, 0.60 mmol), Nb₂O₅ (79.70 mg, 0.30 mmol), and HF (aqueous, 48%, 0.26 mL, 7.15 mmol) were mixed in a 20 mL Teflon liner. The mixture was diluted with 3 mL of deionized water, and then the autoclave was sealed and heated to 130 °C for 24 h. After cooling down the reaction mixture to room temperature, the resultant violet square-shaped crystals, suitable for single crystal X-ray structure determination, were collected by filtration, washed with ethanol and dried in air. Elemental anal. C₈H₁₂O₂N₄F₅NiNb: N, 11.88 (theo: 12.21), C, 20.58 (theo: 20.54), H, 2.54 (theo: 2.64), O, 11.42 (theo: 10.46). NiNbOF₅(pyr)₂·(H₂O)₂ (called **NbOFFIVE-1-Ni**) was activated at 105 °C for 12 h under high vacuum (3 mTorr) before each adsorption experiment.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b05345.

PXRD, TGA, TG-DSC, and sorption data (PDF)
Single-crystal X-ray diffraction data for **1** (CIF)
Single-crystal X-ray diffraction data for **2** (CIF)

AUTHOR INFORMATION

Corresponding Author

*mohamed.eddaoudi@kaust.edu.sa

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

Research reported in this publication was supported by King Abdullah University of Science and Technology (KAUST) under CCF/1/1972-02-01, CCF/1/1972-6-01, and CCF/1/1972-8-01.

REFERENCES

- (1) *Materials for Separation Technology: Energy and Emission Reduction Opportunities*; prepared for Industrial Technologies Program, U.S. Department of Energy: Washington, DC, 2005. DOI: 10.2172/1218755.
- (2) Al-Maythaly, B. A.; Shekhah, O.; Swaidan, R.; Belmabkhout, Y.; Pinnau, I.; Eddaoudi, M. *J. Am. Chem. Soc.* **2015**, *137*, 1754.
- (3) Belmabkhout, Y.; Guillerm, V.; Eddaoudi, M. *Chem. Eng. J.* **2016**, *296*, 386.
- (4) Choi, S.; Drese, J. H.; Eisenberger, P. M.; Jones, C. W. *Environ. Sci. Technol.* **2011**, *45*, 2420.
- (5) Eisaman, M. D.; Alvarado, L.; Larner, D.; Wang, P.; Garg, B.; Littau, K. A. *Energy Environ. Sci.* **2011**, *4*, 1319.

- (6) Goepfert, A.; Czaun, M.; Surya Prakash, G. K.; Olah, G. A. *Energy Environ. Sci.* **2012**, *5*, 7833.
- (7) Keith, D. W. *Science* **2009**, *325*, 1654.
- (8) Lackner, K. S.; Brennan, S.; Matter, J. M.; Park, A.-H. A.; Wright, A.; van der Zwaan, B. *Proc. Natl. Acad. Sci. U. S. A.* **2012**, *109*, 13156.
- (9) Mahmoudkhani, M.; Heidel, K. R.; Ferreira, J. C.; Keith, D. W.; Cherry, R. S. *Energy Procedia* **2009**, *1*, 1535.
- (10) Sayari, A.; Belmabkhout, Y.; Serna-Guerrero, R. *Chem. Eng. J.* **2011**, *171*, 760.
- (11) Stolaroff, J. K.; Keith, D. W.; Lowry, G. V. *Environ. Sci. Technol.* **2008**, *42*, 2728.
- (12) Carey, R.; Gomezplata, A.; Sarich, A. *Ocean Eng.* **1983**, *10*, 227.
- (13) Dallbauman, L. A.; Finn, J. E. In *Adsorption and Its Applications in Industry and Environmental Protection: Applications in Environmental Protection, Part B*; Dąbrowski, A., Ed.; Elsevier: New York, 1999; Vol. 120, pp 455–471.
- (14) Belmabkhout, Y.; Serna-Guerrero, R.; Sayari, A. *Chem. Eng. Sci.* **2010**, *65*, 3695.
- (15) Xue, D.-X.; Cairns, A. J.; Belmabkhout, Y.; Wojtas, L.; Liu, Y.; Alkordi, M. H.; Eddaoudi, M. *J. Am. Chem. Soc.* **2013**, *135*, 7660.
- (16) Sayari, A.; Belmabkhout, Y.; Da'na, E. *Langmuir* **2012**, *28*, 4241.
- (17) Shekhah, O.; Belmabkhout, Y.; Chen, Z.; Guillerm, V.; Cairns, A.; Adil, K.; Eddaoudi, M. *Nat. Commun.* **2014**, *5*, 4228.
- (18) García-Ricard, O. J.; Arévalo-Hidalgo, A. G.; Yu, M.; Almodóvar-Arbelo, N. E.; Varghese, M.; Mulloth, L.; Luna, B.; Hernández-Maldonado, A. *J. Sep. Sci. Technol.* **2014**, *49*, 490.
- (19) Mulloth, L. M.; Finn, J. E. *Carbon dioxide adsorption on a 5A zeolite designed for CO₂ removal in spacecraft cabins*, NASA Ames Research Center; report NASA/TM-1998-208752 prepared for NASA Ames Research Center: Moffett Field, CA, 1998.
- (20) Eddaoudi, M.; Kim, J.; Rosi, N.; Vodak, D.; Wachter, J.; O'Keeffe, M.; Yaghi, O. M. *Science* **2002**, *295*, 469.
- (21) Ferey, G.; Serre, C. *Chem. Soc. Rev.* **2009**, *38*, 1380.
- (22) Fracaroli, A. M.; Furukawa, H.; Suzuki, M.; Dodd, M.; Okajima, S.; Gándara, F.; Reimer, J. A.; Yaghi, O. M. *J. Am. Chem. Soc.* **2014**, *136*, 8863.
- (23) Guillerm, V.; Weseliński, Ł. J.; Belmabkhout, Y.; Cairns, A. J.; D'Elia, V.; Wojtas, L.; Adil, K.; Eddaoudi, M. *Nat. Chem.* **2014**, *6*, 673.
- (24) Horike, S.; Shimomura, S.; Kitagawa, S. *Nat. Chem.* **2009**, *1*, 695.
- (25) Li, J.-R.; Ma, Y.; McCarthy, M. C.; Sculley, J.; Yu, J.; Jeong, H.-K.; Balbuena, P. B.; Zhou, H.-C. *Coord. Chem. Rev.* **2011**, *255*, 1791.
- (26) McDonald, T. M.; Lee, W. R.; Mason, J. A.; Wiers, B. M.; Hong, C. S.; Long, J. R. *J. Am. Chem. Soc.* **2012**, *134*, 7056.
- (27) McDonald, T. M.; Mason, J. A.; Kong, X.; Bloch, E. D.; Gygi, D.; Dani, A.; Crocella, V.; Giordanino, F.; Odoh, S. O.; Drisdell, W. S.; Vlaisavljevich, B.; Dzubak, A. L.; Poloni, R.; Schnell, S. K.; Planas, N.; Lee, K.; Pascal, T.; Wan, L. F.; Prendergast, D.; Neaton, J. B.; Smit, B.; Kortright, J. B.; Gagliardi, L.; Bordiga, S.; Reimer, J. A.; Long, J. R. *Nature* **2015**, *519*, 303.
- (28) Xiang, S.; He, Y.; Zhang, Z.; Wu, H.; Zhou, W.; Krishna, R.; Chen, B. *Nat. Commun.* **2012**, *3*, 954.
- (29) Zhang, M.; Chen, Y.-P.; Bosch, M.; Gentle, T.; Wang, K.; Feng, D.; Wang, Z. U.; Zhou, H.-C. *Angew. Chem., Int. Ed.* **2014**, *53*, 815.
- (30) Nugent, P.; Belmabkhout, Y.; Burd, S. D.; Cairns, A. J.; Luebke, R.; Forrest, K.; Pham, T.; Ma, S.; Space, B.; Wojtas, L.; Eddaoudi, M.; Zaworotko, M. J. *Nature* **2013**, *495*, 80.
- (31) Shekhah, O.; Belmabkhout, Y.; Adil, K.; Bhatt, P. M.; Cairns, A. J.; Eddaoudi, M. *Chem. Commun.* **2015**, *51*, 13595.
- (32) Elsaïdi, S. K.; Mohamed, M. H.; Schaefer, H. T.; Kumar, A.; Lusi, M.; Pham, T.; Forrest, K. A.; Space, B.; Xu, W.; Halder, G. J.; Liu, J.; Zaworotko, M. J.; Thallapally, P. K. *Chem. Commun.* **2015**, *51*, 15530.
- (33) Le Bail, A.; Duroy, H.; Fourquet, J. L. *Mater. Res. Bull.* **1988**, *23*, 447.
- (34) Rodriguez-Carvajal, J. FULLPROF: A Program for Rietveld Refinement and Pattern Matching Analysis. *Abstracts of the Satellite Meeting on Powder Diffraction of the XV Congress of the IUCr, Toulouse, France, 1990*; p 127.
- (35) Gautier, R.; Donakowski, M. D.; Poeppelmeier, K. R. *J. Solid State Chem.* **2012**, *195*, 132.
- (36) Izumi, H. K.; Kirsch, J. E.; Stern, C. L.; Poeppelmeier, K. R. *Inorg. Chem.* **2005**, *44*, 884.
- (37) Maggard, P. A.; Kopf, A. L.; Stern, C. L.; Poeppelmeier, K. R. *CrystEngComm* **2004**, *6*, 451.
- (38) Datta, S. J.; Khumnoon, C.; Lee, Z. H.; Moon, W. K.; Docao, S.; Nguyen, T. H.; Hwang, I. C.; Moon, D.; Oleynikov, P.; Terasaki, O.; Yoon, K. B. *Science* **2015**, *350*, 302.
- (39) Norfleet, W.; Horn, W. *Carbon Dioxide Scrubbing Capabilities of Two New Non-Powdered Technologies*; MSMRL Report No. TR1228 prepared for Naval Submarine Medical Research Laboratory: Groton, CT, 2003.
- (40) Belmabkhout, Y.; Serna-Guerrero, R.; Sayari, A. *Adsorption* **2011**, *17*, 395.