

Room temperature synthesis of $[\text{Cu}(\text{SiF}_6)(\text{isna})_4]_n$ hydrate: a versatile supramolecular porous framework for flue-gas and biogas separation

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ABSTRACT

A new, simple, and environmentally friendly synthesis using water as the main solvent is described to produce $[\text{Cu}(\text{SiF}_6)(\text{isna})_4]_n$ -hydrate (**1**, isna: isonicotinamide), a 1D coordination polymer previously obtained unintentionally. The 1D coordination chains in **1** interact through intermolecular forces generating a 3D supramolecular porous framework with channels occupied by water molecules. The present work proves that the activation of this compound can be carried out under relatively mild conditions (333 K and vacuum during 48 h), effectively removing the water inside the channels while preserving the structural integrity and porosity of the material. Water molecules can be further readsorbed when material is exposed to a medium of saturated humidity without causing any significant damage to the crystalline structure, thus denoting significant chemical stability. The adsorption properties of **1** are determined by the presence of narrow bottlenecks of ca. 3.0 Å width, which are present along the porous framework and hinder the uptake of N₂ and Ar at 77 K. Nevertheless, the material is capable of reversibly adsorbing CO₂, as well as water and methanol vapors, at low pressure. High-pressure adsorption isotherms reveal significant CO₂/N₂ and CO₂/CH₄ selectivity, thus placing compound **1** as a promising material for both flue-gas and biogas separations.

1. Introduction

The divalent cation hexafluorosilicate ($[\text{SiF}_6]^{2-}$) has often been used as a bridging ligand in a wide range of MOFs that show interesting adsorption properties, including selective gas uptake [1–5]. To produce 3D MOFs, the $[\text{SiF}_6]^{2-}$ dianion has been combined with transition metal cations of charge 2+, along with neutral ditopic ligands, such as bipyridines of different sizes, e.g., 4,4'-bipyridine or 1,4-bis(4-pyridyl) benzene. In these structures, the neutral ditopic ligand coordinates metal centers, frequently yielding cationic square lattice layers, which are pillared by bridging $[\text{SiF}_6]^{2-}$ anions, thus generating 3D porous architectures [6,7]. In this research, the attention is focused on a related coordination polymer (CP), the $[\text{Cu}(\text{SiF}_6)(\text{isna})_4]_n$ -hydrate (**1**, isna: isonicotinamide), which was serendipitously synthesized and described in 2015 [8]. In the reported protocol, the $[\text{SiF}_6]^{2-}$ anion was not intentionally added to the reaction medium, but formed *in situ* by the reaction between HF, generated from the hydrolysis of CuF₂, and the glass of the vessel. The coordination of Cu(II) in **1** includes four pyridinic nitrogen

atoms from four equivalent monotopic isna ligands defining a plane around the metal center, and two fluoride atoms at relative trans positions from two equivalent bridging hexafluorosilicate ligands (Fig. 1a). As a result, the CP **1** extends in 1D. The isna ligand in CPs not only coordinates metal cations through the pyridine group, but also typically establishes hydrogen-bonding interactions through the amide groups, thereby determining the supramolecular structure of the solid crystalline material [9–11]. Commonly, spatially adjacent isonicotinamide molecules form two self-complementary interactions by head-to-head amide–amide contacts consisting in two N–H...O hydrogen bonds [12–14]. However, in compound **1** a less common amide–fluoride interaction with N–H...F–Si contacts are the key intermolecular bonds that govern the 3D supramolecular arrangement [15,16]. Therefore, the parallel chains in **1** are interconnected through relatively weak hydrogen bonds instead of the coordinating bonds found in 3D MOFs. The 3D supramolecular arrangement of **1** defines channels parallel to the chain axis that are filled with water molecules (Fig. 1b–c). In this system, the appropriate selection of the isna:Cu(II) ratio, together with the

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coordinating ability of the anion, directs the formation of molecular compounds instead of the target 1D CP. For instance, $[\text{Cu}(\text{SiF}_6)(\text{isna})_2(\text{H}_2\text{O})_3] \cdot \text{H}_2\text{O}$ was obtained when decreasing the isna:Cu(II) ratio [17]. In that material, the $[\text{SiF}_6]^{2-}$ dianion acts as a monodentate ligand and water has an active role coordinating the metal center (three aqua ligands per copper atom). Additionally, when using an anion with lower coordinating ability than $[\text{SiF}_6]^{2-}$, such as tetrafluoroborate or perchlorate, $[\text{Cu}(\text{isna})_4(\text{H}_2\text{O})_2](\text{BF}_4)_2$ [17] or $[\text{Cu}(\text{isna})_4(\text{H}_2\text{O})_2](\text{ClO}_4)_2$ were obtained [18].

The first main objective of this work is to develop a rational, facile, reproducible, and sustainable synthetic method for **1**. Next, the potential porosity of **1** is evaluated by using different gases and vapors (N_2 , Ar, CO_2 , H_2O , CH_4 and CH_3OH) under different temperatures and pressures, giving rise to a comprehensive understanding of the adsorption behavior of this supramolecular structure. The present work demonstrates that the supramolecular arrangement of the chains linked by weak $\text{N-H} \cdots \text{F-Si}$ contacts (Fig. 1d) is sufficiently stable to preserve the 3D supramolecular architecture upon water removal, thereby generating empty channels accessible for adsorption. The water molecules of **1** located within the channels are hydrogen-bonded to each other and also to the amide groups of the isna ligands (Fig. 1b). However, they do not play a key role in maintaining the framework integrity, as they are neither required for the formation of the 1D chains nor for establishing interchain interactions. According to “in silico” measurements, upon removal of water molecules from **1**, the resulting channels consist of irregular voids with a maximum diameter of ca. 11 Å, interconnected by narrow bottlenecks of ca. 3.0 Å wide (Fig. 1e–f). The ultramicroporous windows, and associated dynamic framework flexibility or breathing, dictate the gas separation capacity of compound **1**. Taken together, the adsorption and selectivity trends obtained for CO_2/N_2 demonstrate that **1** behaves as an ultramicroporous adsorbent, with strong potential for post-combustion CO_2/N_2 gas separation. Similarly, **1** also shows promise for biogas upgrading by eliminating CO_2 from CH_4 .

2. Materials and methods

2.1. Materials

Copper(II) hydroxide ($\text{Cu}(\text{OH})_2$), isonicotinamide (isna), hexafluorosilicic acid (H_2SiF_6 , 33.5 % aqueous solution), methanol (MeOH) and polyvinyl butyral (PVB) were purchased from commercial sources and used as received. Ultrapure water (Milli-Q system, conductivity lower than $0.05 \mu\text{S cm}^{-1}$) was used.

2.2. Methods

The synthesis of $[\text{Cu}(\text{SiF}_6)(\text{isna})_4]_n$ hydrate (**1**) was performed starting from an aqueous solution of $\text{Cu}(\text{SiF}_6)$ prepared by gentle agitation of a mixture of concentrated H_2SiF_6 (4.75 mmol) and solid $\text{Cu}(\text{OH})_2$ (4.75 mmol) in 15 mL of water. Solid isna (19.0 mmol) was then added to the blue solution and the mixture was stirred for 1 h at room temperature. During this period, the isna reagent dissolved and, simultaneously, a blue crystalline solid precipitated, which was filtered and washed twice with 2 mL of cold water. The as-synthesized solid was resuspended in MeOH and stirred for 20 h. Then, the material was filtered, washed with few mL of MeOH and, finally, allowed to dry in air at room temperature. The yield of the process was around 75 %.

To obtain the polymeric monolithic composite, a weighted amount of PVB was dissolved in the minimum amount of methanol. Then, powdered compound **1** was dispersed in the viscous medium with the aid of ultrasounds. The added amount of **1** was calculated to obtain a monolith with a composition of 10 wt% of PVB. The solid composite was recovered by allowing the MeOH to evaporate at room temperature.

2.3. Characterization

Samples chemical composition was assessed by C, H, N elemental analysis (E.A., Thermo Carlo Erba Flash 2000). Powder X-ray diffraction

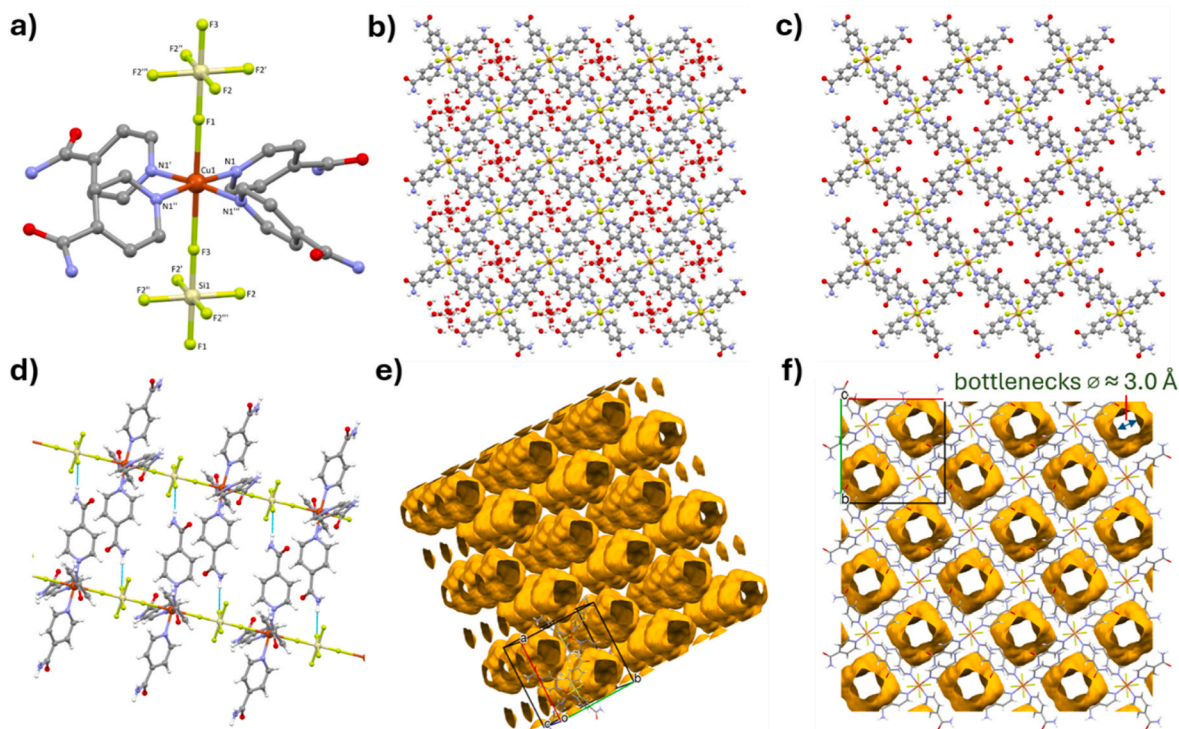


Fig. 1. Graphical representation of the crystal structure of compound **1**, $[\text{Cu}(\text{SiF}_6)(\text{isna})_4]_n$ hydrate, generated from the.cif file CCDC 688359 (VOXKEA) [8] using Mercury software: a) complex unit; b) view along c axis; c) same projection without including the water molecules to appreciate the potential channels present in the structure; d) detail of the $\text{N-H} \cdots \text{F-Si}$ contacts between neighboring chains; each chain is connected to four adjacent chains; e) and f) different views of the potential voids after water removal.

patterns (PXRD) were recorded at room temperature in a Siemens D5000 diffractometer using the Cu K α incident radiation in the 2θ range $5\text{--}30^\circ$ with steps of $0.02^\circ \text{ s}^{-1}$. Scanning electron microscopy (SEM Quanta FEI 200) pictures were taken to observe particle morphology.

N_2 , Ar, CO_2 , water, MeOH and CH_4 isotherms were measured at different pressures and temperatures. In all cases, the samples were previously activated at 333 K under high vacuum ($<10^{-4}$ bar) during 48 h. Low-pressure measurements (from high vacuum up to 1 bar) were performed in an ASAP 2020 Micromeritics. Ar and N_2 physisorption were measured at 77 K. CO_2 adsorption isotherms were collected at 273, 298 and 313 K. The isosteric heat of adsorption, Q_{st} , was evaluated as a function of loading by applying the Clausius–Clapeyron equation under isosteric conditions. Thus, for each surface occupancy n , the equilibrium pressures interpolated from the isotherms at the three temperatures were used to fit $\ln p$ as a function of $1/T$, and Q_{st} was calculated from the corresponding slope. Using an automatic volumetric adsorption analyzer (Belsorp MAX-II), the water adsorption–desorption isotherm was measured at 298 K, while MeOH was measured at 298 and 323 K. The isotherms were recorded over a relative pressure range from 0.001 to 1.0, i.e., up to the corresponding saturation vapor pressure of each adsorbate at the measurement temperature (0.0032 bar for H_2O and 0.0168 bar for MeOH at 298 K, and 0.0555 bar for MeOH at 323 K). Equilibrium at each adsorption point was assumed when the pressure variation remained below 0.1 % over a 300 s interval. High-pressure adsorption–desorption isotherms for up to 30, 85 and 75 bar for CO_2 , CH_4 and N_2 , respectively, were measured at 298 K in a high-pressure volumetric gas sorption analyzer (iSorB, Anton Paar). Selectivities for CO_2/N_2 and CO_2/CH_4 binary mixtures were calculated using the Ideal Adsorbed Solution Theory (IAST), following a previously described thermodynamic procedure [19]. To ensure that the high-pressure adsorption data used for the IAST calculations corresponded to true equilibrium conditions, the adsorption isotherms were acquired using extended equilibration times of 180 s for CO_2 and CH_4 , and 200 s for N_2 . Furthermore, a stringent equilibrium criterion was adopted. At each pressure point, five consecutive measurements were recorded after the selected equilibration period, and equilibrium was accepted only when the pressure variation between the first and the fifth measurement was below $0.25 \text{ mbar min}^{-1}$. Consequently, the effective equilibration time for each adsorption point was approximately 900 s for CO_2 and CH_4 , and 1000 s for N_2 . Although adsorption kinetics are generally expected to improve at higher temperatures, these deliberately conservative equilibration conditions were selected to ensure that the adsorption data accurately represented equilibrium values, thereby maximizing the reliability of the subsequent IAST selectivity calculations. Pure-component isotherms measured at 298 K were used as input to compute the spreading pressure (π) of each adsorbate by numerical integration of the adsorption isotherm. At a given gas-phase composition (y_i) and total pressure (P), the corresponding adsorbed-phase mole fractions (x_i) were obtained by solving the IAST equations enforcing equal spreading pressure for all components. The total adsorbed amount n_t was then computed as the mole-fraction-weighted sum of the pure-component loadings at the calculated P_i^0 , and the selectivity factor S_{ij} was obtained as $S_{ij} = (x_i/y_i)/(x_j/y_j)$. This method provides predictive mixture adsorption behavior consistent with ideal adsorbed-phase thermodynamics and enables reliable comparison with benchmark adsorbents.

3. Results and discussion

3.1. Composition and structural characterization

A facile room-temperature procedure was developed to precipitate the target product **1** as a crystalline material. The method involves adding isonicotinamide to an aqueous solution of $\text{Cu}(\text{SiF}_6)$ in a 4:1 stoichiometric ratio under stirring. The isna ligand dissolves rapidly in the aqueous solution, giving rise to a blue precipitate. In the original

report, $[\text{Cu}(\text{SiF}_6)(\text{isna})_4]_n$ hydrate was obtained with a low yield (ca. 25 wt%), likely due to the uncontrolled *in situ* formation of the $[\text{SiF}_6]^{2-}$ dianion during the reaction [8]. The simple and direct synthetic route presented here for **1** attains a significantly higher yield of ca. 75 wt%.

The PXRD diffractogram of the as-synthesized compound, only washed with cold water, agrees reasonably with the powder pattern simulated from the single crystal data reported for **1**. The small, systematic shift of the peak positions toward lower angles observed for **1** relative to the simulated pattern (Fig. 2a and b) are mainly attributed to the different temperatures used for data collection, namely 110 K for the single-crystal structure and room temperature for the powder sample, but also to variations in the amount of water retained within the channels. The C, H, N elemental analysis of the as-prepared material matches to the stoichiometry $[\text{Cu}(\text{SiF}_6)(\text{isna})_4]_n \cdot 7n\text{H}_2\text{O}$, particularly in regard of C content, rather than the reported nonahydrate specie (Table 1). This result further suggests the presence of residual materials in the inter-particle space due to fast crystal growth and aggregation [20]. In a subsequent processing step, the as-synthesized material was washed with methanol (MeOH) under stirring for 20 h. After filtering and drying the product at room temperature, the sample displayed the original PXRD pattern (Fig. 2c). The C, N, H elemental analysis of the washed sample fits better with the stoichiometry $[\text{Cu}(\text{SiF}_6)(\text{isna})_4]_n \cdot 7n\text{H}_2\text{O}$, particularly the C and N content, indicating the successful removal of impurities (Table 1). This is further supported by SEM images, which reveal that the washing step with MeOH induces significant changes in the morphological characteristics of the powder, leading to more disaggregated and defined individual particles (Fig. 3). MeOH-washed sample activation at 333 K under vacuum during a prolonged period of 48 h resulted in a weight loss of 15–17 wt%, closely matching the water content calculated for the formula $[\text{Cu}(\text{SiF}_6)(\text{isna})_4]_n \cdot 7n\text{H}_2\text{O}$ (i.e., 15.4 wt%), and lower than that estimated for the nonhydrated compound (18.9 wt%). The PXRD of the activated material exhibits only small variations in the width and relative intensity of the peaks with respect to the as-synthesized and MeOH-washed materials, without significant shifts in peak position (Fig. 2d). This result strongly suggests that the supramolecular architecture of **1** remains stable after water removal, thereby generating open pores accessible for adsorption. Interestingly, when the activated sample was kept at 303 K in a water-saturated atmosphere, the original weight was completely recovered, which is a clear evidence of the reversibility of the hydration

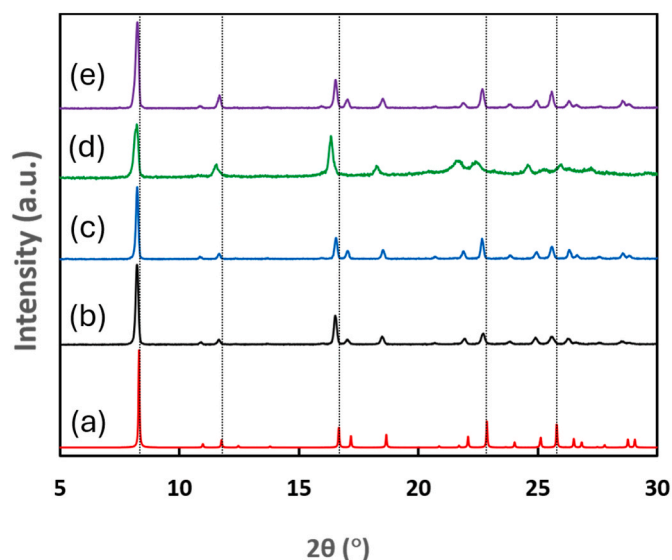
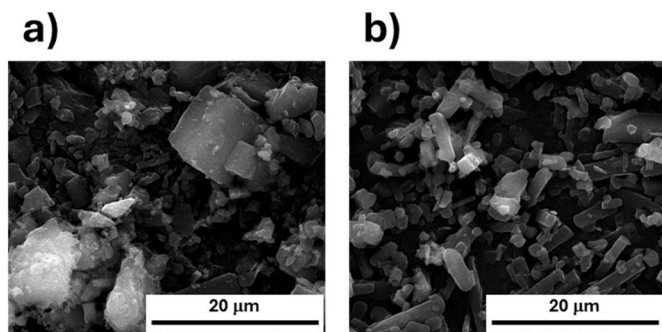


Fig. 2. PXRD diffractograms of: a) the simulated pattern generated from CCDC 688359 file, corresponding to the crystal structure of **1** determined at 110 K [8], b) as-synthesized; c) MeOH-washed; d) vacuum activated; and e) rehydrated sample.

Table 1
Elemental analysis data.

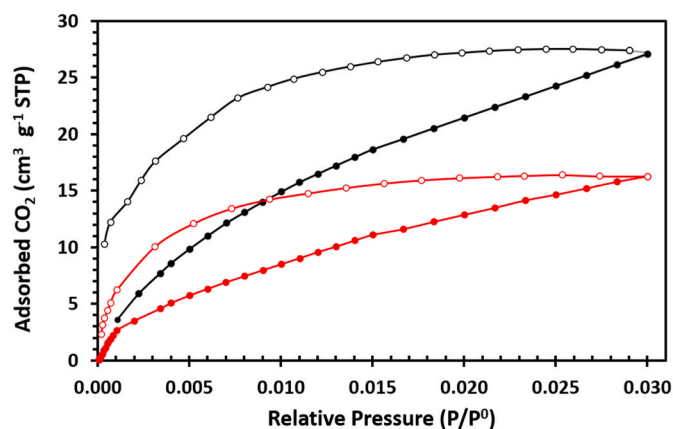
Sample	% C	% H	%N
Calculated for $[\text{Cu}(\text{SiF}_6)(\text{isna})_4]_n \cdot 9\text{nH}_2\text{O}$	33.67	4.94	13.09
Calculated for $[\text{Cu}(\text{SiF}_6)(\text{isna})_4]_n \cdot 7\text{nH}_2\text{O}$	35.14	4.67	13.66
1 as synthesized	35.50	4.58	13.32
1 after MeOH washing	35.42	4.58	13.53

**Fig. 3.** SEM micrographs of 1: a) as-synthesized; and b) MeOH-washed.

process. Furthermore, the rehydrated sample (Fig. 2e) shows the same PXRD pattern as the original hydrated sample (Fig. 2b), denoting that the full dehydration-hydration cycle proceeds without causing any structural damage to the framework. It is worth to mention that the coordination polymer may undergo subtle local structural rearrangements upon activation or gas adsorption that significantly influence their adsorption behavior, even though these changes are too small or lack sufficient long-range order to be detected by conventional PXRD. Such rearrangements may involve slight variations in linker orientation, metal–ligand bond distances, pore aperture dimensions, or framework flexibility, all of which can modify the accessibility and affinity of adsorption sites without producing measurable changes in the average crystal structure.

3.2. Low-pressure adsorption-desorption isotherms: N_2 , Ar, CO_2 , H_2O and MeOH

The adsorption capacity of the activated compound 1 was first evaluated with N_2 and Ar at 77 K. For both gases, the material showed a negligible uptake in the micropores, attributed to the presence of narrow bottlenecks ($\sigma \approx 3.0 \text{ \AA}$) along the channels (Fig. 1c and d). At the low temperature required for these measurements, the described void arrangement for 1 hinders the diffusion of N_2 and Ar molecules, with kinetic diameters of ca. 3.6 and 3.4 $\text{\AA}$, respectively [21]. To further investigate the porosity of 1, the isotherm of CO_2 was measured at 273 K up to 1 bar. The advantages of using CO_2 vs. N_2 or Ar in adsorption experiments are two-fold. First, CO_2 has a smaller kinetic diameter (ca. 3.3 $\text{\AA}$) than N_2 and Ar [22]. Second, the quadrupolar moment of CO_2 promotes specific interactions with polar functional groups in the framework [23]. In the studied system, 1 exhibited a notable CO_2 adsorption capacity, giving values of 0.6 mmol g^{-1} by applying an equilibrium time of 30 s between each adsorption point. Moreover, the CO_2 adsorption capacity increased to 1.2 mmol g^{-1} when this time was extended to 100 s (Fig. 4). These findings indicate that CO_2 diffusion through the system was not blocked under the selected measurement conditions even the kinetic diameter of CO_2 (ca. 3.3 $\text{\AA}$) was higher than the window aperture in 1 ca. (3.0 $\text{\AA}$). The relatively slow CO_2 adsorption kinetics commonly observed in porous solid adsorbents arise from a combination of diffusion limitations and adsorption equilibrium processes. The transport of CO_2 molecules from the bulk gas phase to the internal adsorption sites involves several consecutive steps, including external mass transfer, diffusion through the pore network, and

**Fig. 4.** CO_2 adsorption-desorption isotherms measured for 1 at 273 K and different values of equilibrium time: 30 s (in red) and 100 s (in black).

interaction with the active adsorption sites. In highly microporous materials, these processes are often hindered by the restricted pore apertures and the tortuous diffusion pathways, resulting in slow equilibration times. Moreover, when structural flexibility or framework breathing/gate-opening phenomena are involved, additional energy barriers associated with framework rearrangements may further delay CO_2 uptake. Consequently, achieving adsorption equilibrium frequently requires extended exposure times, particularly at low pressures where the driving force for diffusion is limited. Understanding these kinetic limitations is essential for the practical implementation of porous adsorbents in gas separation and storage. These processes require a careful balance between adsorption capacity, operating time, and energy consumption to ensure their economic viability. In practice, maximizing CO_2 uptake is not always desirable, as reaching full adsorption equilibrium often requires prohibitively long equilibration times that are incompatible with industrial operation. The significant increase in CO_2 uptake upon extending the equilibration time from 30 to 100 s suggests that CO_2 molecules initially adsorb on the external surface or at the pore mouths before undergoing a slower, rate-limiting diffusion into the ultramicropores. This diffusion limitation is consistent with a framework that requires a thermal or pressure-induced dynamic opening to access the internal pore volume. Increasing the temperature of analysis from 77 K in N_2 or Ar to 273 K in CO_2 would significantly enhance gas molecules mobility and diffusivity throughout the structure. Relative to the adsorbent framework, the increase of measurement temperature can induce CP channel expansion, associated with dynamic framework breathing [24]. Even so, CO_2 adsorption occurred slowly due to the close match between the CO_2 kinetic diameter and the pore window size. By running the analysis at different temperatures, the isosteric heats of adsorption ($Q_{\text{st}} = -\Delta H_{\text{ads},\theta}$) for 1 were calculated as a function of CO_2 uptake (Fig. 5). The estimated Q_{st} values varied from 41 to 35 kJ mol^{-1} when moving from low to high surface coverage, which can be considered moderate-to-high values if compared to conventional porous materials applied for CO_2 adsorption, such as microporous carbons, zeolites or MOFs [25]. In any case, the obtained Q_{st} values fall within the physisorption range, which indicates that sorption occurs solely through physical interactions, thereby facilitating reversible desorption and enabling material reuse [26].

The water vapor adsorption-desorption isotherm was measured at 298 K from vacuum up to saturation pressure to study the behavior of 1 with this fluid (Fig. 6). Unlike most fluorinated MOFs, typically possessing a hydrophobic nature [6], the studied CP exhibits a significant water sorption capacity of ca. 220 $\text{cm}^3 \text{g}^{-1}$ at 100 % relative humidity. The adsorbed amount matches the content of water estimated for 1 prior to activation (i.e., $[\text{Cu}(\text{SiF}_6)(\text{isna})_4]_n \cdot 7\text{nH}_2\text{O}$). The high affinity of 1 with respect to water is attributed to the orientation in the framework of the polar amide groups of the isna ligand toward the inside of the

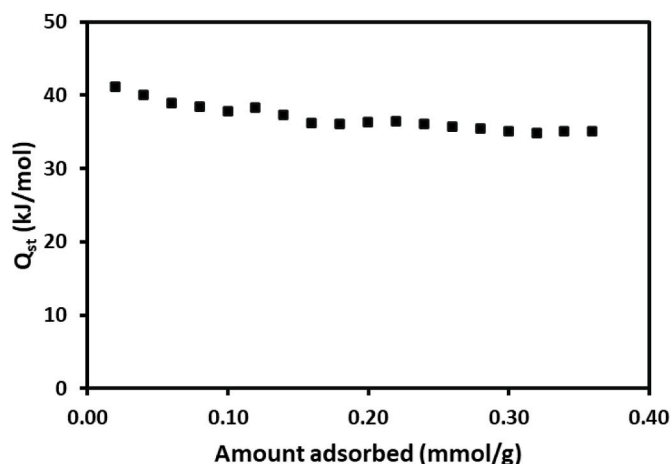


Fig. 5. CO₂ isosteric heats of adsorption (Q_{st}) calculated for **1** at different adsorbed amounts.

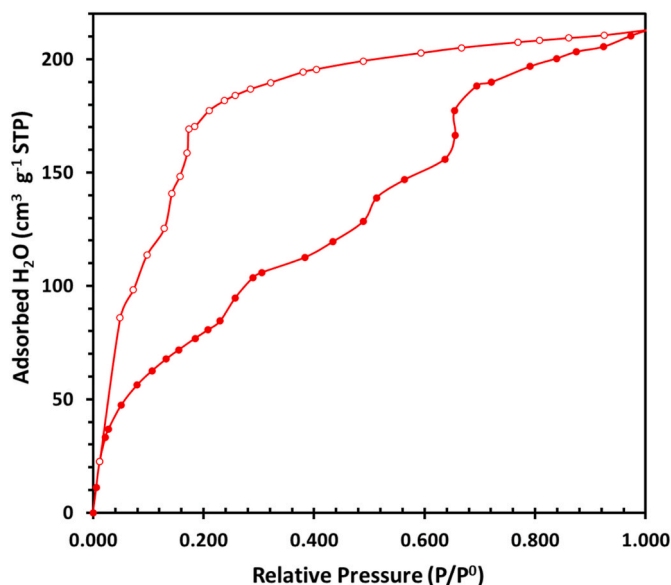


Fig. 6. H₂O adsorption-desorption isotherm measured for **1** at 298 K.

channels (Fig. 1), which confers hydrophilicity to the porous domains. The water adsorption/desorption isotherm displays a broad hysteresis. The molecular diameter of water is of ca. 2.7–2.8 Å [27], so perfectly entering the pore windows of **1**. Hence, the hysteresis must be indicative of strong intermolecular interactions among the adsorbed water molecules and the pore walls, thus requiring substantial energy input (e.g., vacuum) for desorption. The desorption branch eventually closes the hysteresis loop at very low pressures, confirming the reversibility of the hydration-dehydration process. In another experiment, it was found that a low temperature (333 K) thermal treatment of **1** in an open atmosphere is sufficient to remove a significant percentage of water (ca. 11 wt % in 4 h, 14 wt % in 24 h). Hence, this sorbent could find applications in water adsorption processes in which low-grade waste heat can be used for regeneration [28].

In solid adsorbents, the presence of water in effluents competes with CO₂ for adsorption sites, thereby reducing the CO₂ adsorption capacity and selectivity. In most cases, water can adversely affect the structural integrity and long-term performance of many porous adsorbents, leading to partial degradation or loss of adsorption efficiency. Even degradation is not a problem for compound **1**, a dehydration step to remove moisture prior to the CO₂ adsorption process can be used to avoid

competition. This is a well-established and widely implemented pre-treatment in industrial carbon capture applications [29].

Vapor MeOH adsorption-desorption isotherms for **1** were measured at 298 and 323 K from vacuum up to saturation pressure. Interestingly, the amount of adsorbed alcohol was found to increase with temperature (Fig. 7), a trend commonly only observed in chemisorption processes [30,31]. The kinetic diameter of a MeOH molecule is typically cited in the range of 3.6–3.7 Å, significantly higher than the pore aperture in **1** of ca. 3.0 Å. Hence, the adsorption of MeOH, as that of CO₂, is only possible through the thermal activation of the adsorbate diffusion barriers by a dynamic gating effect occurring in the framework [32]. As the thermal energy increases, adsorbate molecules are better able to overcome the activation energy associated with passing through the flexible pore windows, while the framework more readily undergoes the local structural fluctuations required for diffusion. Consequently, dynamic gating occurs more easily, reducing diffusion resistance and accelerating adsorption kinetics without necessarily altering the equilibrium adsorption mechanism. As the temperature increases, adsorbate diffusion through the framework accelerates, thereby facilitating the attainment of adsorption equilibrium [33]. The reversibility and purely physical nature of this process are further supported by the fact that the PXRD pattern of the sample after MeOH adsorption at 323 K showed no detectable changes in the crystal structure compared to the pristine material (data not shown), ruling out a chemisorption mechanism or permanent framework transformation. The presence of a hysteresis in the isotherm is in this case attributed to both the interactions established between the adsorbate and the adsorbent and the restricted pore apertures of **1**. When the pore mouth dimensions approach the size of the adsorbate, adsorption may trigger local structural adjustments, such as subtle linker motions or gate-opening events. These processes lead to delayed desorption, causing a hysteresis loop, that in this case extends the entire pressure range studied. Similar hysteresis behavior has been documented in MOFs exhibiting structural flexibility or pore-entrance restrictions, where adsorption-desorption transitions occur at different pressures due to entropic and enthalpic barriers associated with confined diffusion [34].

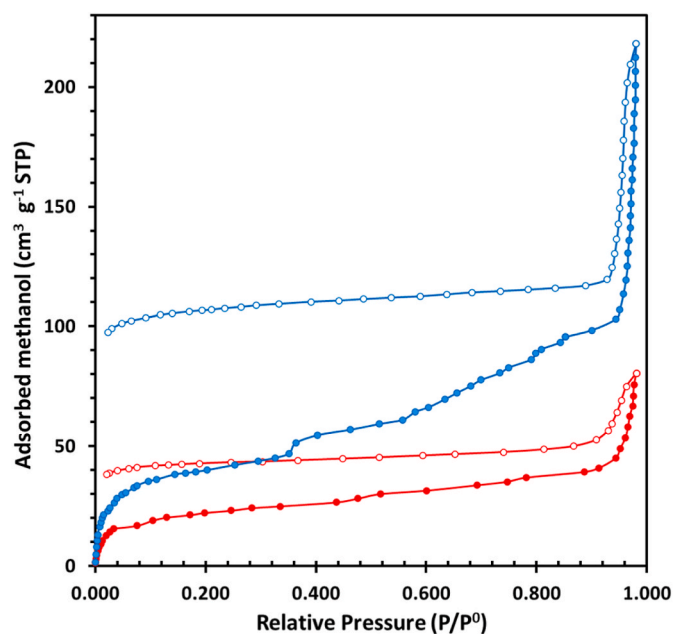


Fig. 7. Methanol adsorption-desorption isotherms measured for **1** at 298 K (in red) and 323 K (in blue).

3.3. High pressure adsorption-desorption isotherms (CO_2 , CH_4 , N_2) and selectivity

CO_2 , CH_4 and N_2 adsorption isotherms for **1** were measured at room temperature and up to the high-pressure values of 30, 85 and 75 bar, respectively (Fig. 8). The high-pressure isotherms reflect the distinct adsorption mechanisms of each gas, arising not only from differences in the kinetic diameter and adsorbate-adsorbent molecular interactions, but also from the compressibility of the adsorbed phase and the concomitant attained density.

CO_2 gas is a highly compressible fluid in which density increases largely by increasing pressure. Contrarily, CH_4 and N_2 are incompressible fluids that maintain a near-constant density with pressure. As a consequence, at similar pressure the net adsorption values measured for CO_2 were significantly larger than those of CH_4 and N_2 . Additionally, the higher polarizability of CH_4 vs. N_2 was reflected in a greater density and uptake measured for the former. The adsorbed-phase density of N_2 , with only a small quadrupole moment, remained the lowest in the entire range of studied pressure, which together with nearly free diffusion of this gas at room temperature, resulted in low uptakes. As mentioned, the kinetic diameters of CO_2 , CH_4 and N_2 significantly exceed the estimated pore aperture of **1** of ca. 3–4 Å. However, the experimental observations indicate that these molecules are able to access the pores of **1**, with the adsorbed amount increasing as pressure rises. This behavior may be consistent with a pressure-assisted opening or widening of the pore apertures. In addition, the three measured adsorption/desorption isotherms displayed noticeable hysteresis and distinct adsorption-desorption pathways, which could be associated with framework flexibility or diffusion barriers at the pore entrances. Accordingly, the gate-opening effect could be regarded as a well-supported hypothesis based on the available experimental evidence, although further direct verification is necessary to elucidate the mechanism.

To predict CO_2/N_2 and CO_2/CH_4 multicomponent gas adsorption in **1** the IAST model [19,35,36] was used based solely on experimental single-component adsorption isotherms. Estimated selectivity data for the binary systems as a function of pressure is shown in Fig. 9. The separation performance of compound **1** for these mixtures reveals a consistent trend in which CO_2 is overwhelmingly favored over both N_2 and CH_4 across the examined pressure range (Fig. 9). Aside from the distinct diffusivities of the gases at molecular-sized pore entrances and the greater densification that the compressible CO_2 can achieve inside the narrow pores, the most determinant factor for this selectivity behavior is the pore diameter of **1**, which seems to hamper the adsorption of molecules with kinetic diameters exceeding ca. 3.3–3.4 Å [37]. The sub-nanometric pore aperture of the supramolecular framework in **1** strongly restricts N_2 (Fig. 9a) and CH_4 (Fig. 9b) diffusion, while permitting CO_2 to enter more readily due to its higher framework affinity and compressibility. In the range of pressures studied, the CO_2/CH_4 selectivity remained significantly above unity, though

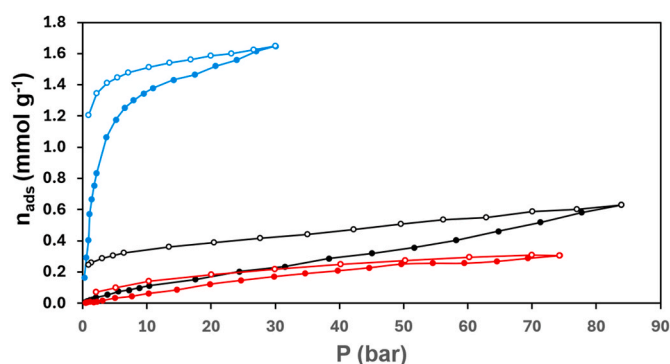


Fig. 8. High pressure adsorption-desorption isotherms measured for **1** at 298 K for CO_2 (in blue), CH_4 (in black) and N_2 (in red).

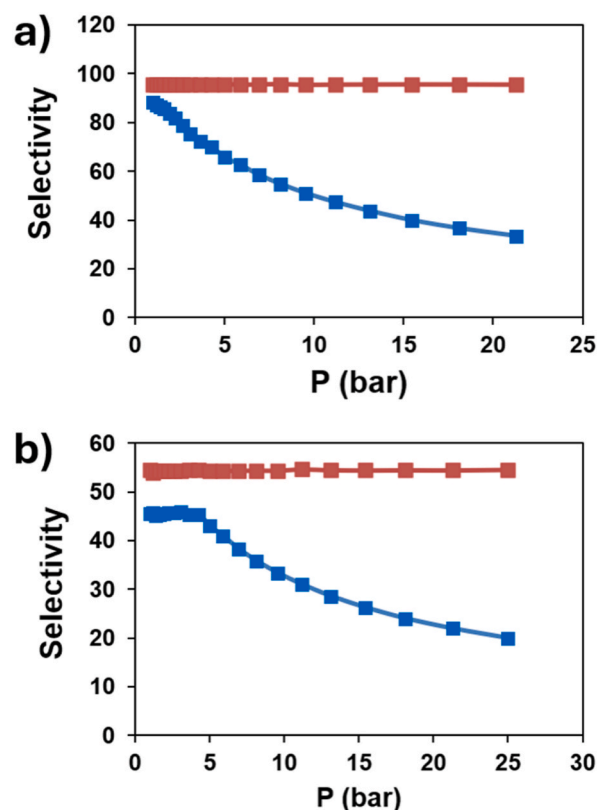


Fig. 9. IAST selectivity data calculated for **1** at 298 K [19]: a) CO_2/N_2 selectivity and b) CO_2/CH_4 selectivity. In both graphs, the blue line indicates the minimum selectivity attainable with pure CO_2 , while the red line corresponds to the maximum selectivity attainable with either pure N_2 in a) or with pure CH_4 in b). Any mixture would have a selectivity between those limits.

generally with values lower than for CO_2/N_2 . This outcome is consistent with the two mentioned key factors of higher polarizability for CH_4 with respect to N_2 resulting in more favorably interactions with the host framework, as well as the significantly upper adsorbed-phase densities attained for CH_4 . Another important aspect of the selectivity curves in Fig. 9 is the narrowing gap between their maximum and minimum theoretical limits as pressure increases. The selectivity attained for CO_2 in the mixtures was particularly high at low pressures, decreasing gradually as the pressure increased. This trend is parallel to what has been widely documented for microporous adsorbents, including microporous polymer networks [38]. This behavior reflects the tendency of gas mixtures to approach a regime in which differences in spreading pressure become less pronounced at high loading, an effect predicted by IAST [39].

The CO_2/N_2 and CO_2/CH_4 IAST selectivity data calculated for **1** fall within the broad but well-established performance envelope compiled for microporous MOFs used in flue gas (CO_2/N_2) and biogas (CO_2/CH_4) separations [40]. For microporous MOFs, published CO_2/N_2 selectivity values covers an exceptionally wide range, from moderate IAST selectivity values around 20–50, up to extremely high selectivity (>2000) in ultramicroporous frameworks. It is worth mentioning that the majority of MOFs reported to be used for practical post-combustion CO_2 capture tend to cluster in the region of 20–300. These are materials in which large-scale production is taking into account, as well as long-term use of the adsorbent through water stability and regeneration by applying low energy processes. From this perspective, the CO_2/N_2 selectivity of **1**, although not approaching the top values, fits comfortably within the technologically relevant window and is comparable to widely studied benchmark materials such as UTSA 90 (22 at 295 K) and PCN 88 (23 at 273 K), or many sulfone and azo functionalized Zn/Co frameworks

whose selectivity typically fall between 40 and 150. A similar picture emerges for CO₂/CH₄ separation. The IAST CO₂/CH₄ selectivity values for technological materials are in the 5–20 range, reaching values of several hundred for frameworks with highly confining capacity or highly polar pore environments, or even several thousand for ultramicroporous and strongly charged MOF frameworks. Within this landscape, the CO₂/CH₄ selectivity of **1** again aligns with the mid-selectivity regime common among chemically robust water-stable MOFs optimized for biogas upgrading, with values in the range 8–40. Comparing to the extensive data set compiled in IAST CO₂/N₂ and CO₂/CH₄ selectivity data, the mentioned advantages convincingly place **1** well within the performance spectrum of state-of-the-art CPs for both flue-gas and biogas separations.

3.4. Textural properties as a polymeric monolithic composite

The design of a proper adsorbent for gas separation usually involves the use of pellets or monoliths instead of powder, since it facilitates the use of the material in real applications. For this, the use of composites involving polymers is the most used approach. Nevertheless, the assembly of porous compounds into practical polymer composites can compromise the textural characteristics of the porous component by significantly reducing the porosity. The rigorous choice of the polymer binder can minimize these negative effects. In this work, PVB was chosen as the polymer to make the composite with **1**, since it has been previously used to enhance the processability and mechanical properties of various MOFs, while largely preserving their adsorption capacity [41–43]. Using this polymer, a composite with 10 wt% PVB was successfully prepared in MeOH in the form of a monolith. The CO₂ adsorption at low pressure of the so obtained monolith (Fig. S1) closely matches that of the pristine powder of **1**. For instance, at 1 bar (P/P₀ = 0.028), both the pristine powder and the monolith exhibit similar CO₂ uptake values of 27–28 cm³ g^{−1}.

4. Conclusions

A simple, direct and room-temperature synthetic route for the precipitation of [Cu(SiF₆)(isn_a)₄]_n hydrate was developed, using only water and methanol for synthesis and washing, respectively. Characterization of **1** indicates that the water present in the channels can be removed without any significant alteration in the crystalline structure, thereby displaying narrow micropores within the structure. Overall, the porosity of **1**, evaluated through gas adsorption–desorption analyses using N₂, Ar, CO₂, H₂O and MeOH, suggests a flexible adsorption behavior that is compatible with thermally and pressure-assisted access to the pore system. Although these results are consistent with a possible gate-opening mechanism, further structural or *in situ* studies would be required to unambiguously confirm this interpretation. Moreover, the separation of CO₂ from binary CO₂/N₂ or CO₂/CH₄ mixtures at high pressure and room temperature was also feasible by using **1**. The CP exhibits IAST selectivity values ranging from ca. 100 to 30 for CO₂/N₂ and from ca. 55 to 20 for CO₂/CH₄ at 298 K, which are consistent with technically viable porous compounds proposed in the literature. The performance of **1** is regarded as competitive and well balanced, because this CP does not suffer from the experimental limitations of water sensitivity and synthetic complexity. Actually, **1** demonstrates remarkable stability under humid conditions, including fully reversible water-vapor adsorption at 298 K and resistance to degradation even at 100 % relative humidity, as well as easy regenerability. Finally, compound **1** can be combined with PVB to form a practical composite material for gas separation without compromising its adsorption capacity (Fig. S1).

CRedit authorship contribution statement

Albert Rosado: Conceptualization, Investigation, Writing – original

draft. **Alejandro Borrás:** Formal analysis, Methodology. **Fabián Suárez-García:** Conceptualization, Funding acquisition, Investigation, Resources, Supervision, Writing – original draft. **Alberto Castro-Muñiz:** Formal analysis, Methodology. **Concepción Domingo:** Funding acquisition, Project administration, Resources, Supervision, Writing – review & editing. **José A. Ayllón:** Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Supervision, Writing – original draft, Writing – review & editing.

Declaration of competing interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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Data availability

Data will be made available on request.

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