Selective CO₂ Adsorption by a Triazacyclononane-Bridged Microporous Metal–Organic Framework

Guillaume Ortiz, Stéphane Brandès, Yoann Rousselin, and Roger Guilard^{*[a]}

Abstract: Metal–organic frameworks constructed by self-assembly of metal ions and organic linkers have recently been of great interest in the preparation of porous hybrid materials with a wide variety of functions. Despite much research in this area and the large choice of building blocks used to fine-tune pore size and structure, it remains a challenge to synthesise frameworks composed of polyamines to tailor the porosity and adsorption properties for CO_2 . Herein, we describe a rigid and microporous three-dimensional metal-organic framework with the formula $[Zn_2(L)(H_2O)]Cl$ (L= 1,4,7-tris(4-carboxybenzyl)-1,4,7-triazacyclononane) synthesised in a one-pot solvothermal reaction between zinc ions and a flexible cyclic polyaminocar-

Keywords: adsorption • gas separation • metal-organic frameworks • microporous materials • carbon dioxide boxylate. We have demonstrated, for the first time, that a porous rigid framework can be obtained by starting from a flexible amine building block. Sorption measurements revealed that the material exhibited a high surface area ($1350 \text{ m}^2 \text{g}^{-1}$) and was the best compromise between capacity and selectivity for CO₂ over CO, CH₄, N₂ and O₂; as such it is a promising new selective adsorbent for CO₂ capture.

Introduction

The ability to design an adsorbent with fine-tuning of the pore size, pore shape and chemical functionality would provide a significant advance in areas such as gas separation and catalysis. Metal-organic frameworks (MOFs) are an attractive alternative to the use of zeolites for gas adsorption processes because of the large number of possible structures that can be effectively elaborated.^[1-4] In the last decade, many crystalline porous coordination polymers have led to a new class of porous materials with the potential for a range of applications,^[2,5-10] and they have also provided flexible platforms for developing well-designed gas molecule adsorbents,^[1,4,11,12] in particular, for CO₂ capture with high selectivity.^[13-24] To enhance the adsorption capacity, microporous materials with open metal sites, such as Cu₃(BTC)₂^[25] (BTC = 1,3,5-benzenetricarboxylate) and $M_2(DOTP)$ (CPO-27M; M=Ni, Mg, DOTP=2,5-dioxyterephtalate),^[26,27] were studied and their high capacity for CO₂ adsorption was shown thanks to strong electrostatic interactions with the exposed metallic ions.^[26,27] The Lewis acid character of the coordinatively unsaturated metal ions was taken advantage of by using zeolites and Cu₃(BTC)₂ for the separation of gas mixtures with high selectivity,^[28,29] and the CPO-27M mate-

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9 avenue Alain Savary, 21078 Dijon Cedex (France) Fax: (+33)380-39-61-17 E-mail: Roger.Guilard@u-bourgogne.fr rials were shown to be among the best sorbents for CO₂ separation close to 1 atm.^[27,30,31] By taking into account the Lewis acid properties of CO₂ itself, strong interactions through chemisorption processes can occur with primary and secondary alkyl amines, both in solution^[32] and in the solid state.[33-35] The choice of the nitrogen-functionalised organic linker is of critical importance for the required application and it is still a challenge to develop new porous MOFs, containing polyamine linkers that are able to interact with CO₂.^[36-39] Our contribution was to use an N-functionalised triazamacrocycle as a spacer ligand to build a new MOF with the aza ligand integrated into the framework of the adsorbent. These materials, including cyclic polyaminocarboxylates, were aimed at enhancing CO₂ capture by strong interactions (coulombic, van der Waals) with the amine or the Lewis acid metals of the framework and also to increase the selectivity for CO₂ towards CO, CH₄, O₂ and N₂ thanks to the polarity of the surface. Herein, a microporous coordination polymer incorporating the cyclic amine 1,4,7-triazacyclononane (TACN) was synthesised and characterised by single-crystal and powder X-ray diffraction, porosity and gas adsorption measurements. The high adsorption capacity and selectivity for CO₂ versus N₂, O₂, CH₄ and CO was clearly demonstrated.

Results and Discussion

Synthesis and X-ray structure of $[1(H_2O)]Cl$: We have designed and synthesised a new MOF composed of a tris-carboxybenzyl TACN (L) ligand, which possesses a high porosity. The crude cyclic triamine was first isolated in its penta-

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protonated form (LH_5^{2+}) and used as such (Scheme 1). In contrast to the frameworks constructed by the reaction of metallo-tetraazacycloalkane with pillared ligands,^[40] this ma-





terial was prepared by self-assembly of the zinc–TACN complex without adding an exogenous ligand. Reaction of an excess of $Zn(NO_3)_2$ ·6H₂O with LH₅²⁺ in a mixture of DMF, EtOH and Et₃N at 353 K for 24 h under autogeneous pressure afforded crystals of $[Zn_2(L)(H_2O)]Cl$ ·DMF (=[**1**-(H₂O)]Cl·DMF), which was colourless and had a trigonal prismatic-like morphology with curved edges (Figure S1 in

the Supporting Information). Depending on the scale of the synthesis, the crystals had sizes between 10 and 30 μ m. Energy-dispersive X-ray spectroscopy (EDS) and elemental analyses supported a twofold excess of zinc relative to TACN and revealed the presence of a chloride anion in approximately half the amount of the zinc (Table S1 in the Supporting information).

Single crystals of $[1(H_2O)]Cl$ were analysed by X-ray diffraction and the coordination polyhedra of the dinuclear cluster and its porous framework are depicted in Figure 1. The complex crystallises in a cubic system (space group: $I\bar{4}3d$) with a unit cell parameter a =25.8644(10) Å and unit cell volume of 17302.4(12) Å³. Unexpectedly, two zinc ions are coordinated to three nitrogen atoms of TACN and six oxygen atoms of the carboxylate functions. Zn1 is hexacoordinated with O_h symmetry; it is chelated to the three nitrogen atoms of the macrocycle and bound with three carboxylate oxygen atoms from another pendant

arm ligand. Zn1 is located 1.436(1) Å from the mean plane formed by the three nitrogen atoms. A tetracoordinated Zn2 metal is located above Zn1 and presents T_d symmetry. The tetrahedron was formed by three carboxylate oxygen atoms and one water molecule in the apical position. The Zn2–O3(H₂O) distance (2.183(10) Å, Table S2 in the Supporting Information) is comparable to the distance found for a complex with T_d geometry (Zn–O (aqua) = 2.092(61) Å).^[41] The two zinc ions are bridged by three carboxylate groups and are arranged in close proximity to each other (Zn1-Zn2: 3.517(1) Å). The Zn1-N1 bond lengths of 2.201(5) Å are similar to the average Zn-N tertiary amine bond length of 2.147(68).^[41] The most noteworthy feature of the structure is the trigonal distortion of the octahedron. The N1-Zn1-N1 angles of 81.1(2)° are constrained by the ring size of the macrocycle. As a consequence of this distortion, the O1-Zn1-O1 bite angle is higher (96.51(19)°) than that expected for a regular octahedron. The structure owes its robustness to this dinuclear zinc cluster despite the absence of hydrogen bonding.

The diameters of the channels are between 6.9 and 8.7 Å and interconnected through circular and rectangular windows, which can be seen along a, b or c crystallographic



Figure 1. a) ORTEP^[60] view of the dinuclear zinc cluster in $[1(H_2O)]Cl$. Hydrogen atoms are omitted for clarity. The thermal ellipsoids are drawn at probability level of 50%. b) Packing view of $[1(H_2O)]Cl$ along the crystallographic *ab* plane. c) 3D pore channel along the crystallographic *ab* plane. Green spaces represent the inside of the channel. d) View of the channels along the crystallographic *ab* plane showing the coordination polyhedra (tetrahedron and octahedron). H atoms were omitted for clarity.

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axes (Figure 1 d). The space-filling model shows clearly that pore accessibility is not restricted (Figure 1 b). The simulation of a Connolly void surface with a 1.4 Å probe size shows that channels are connected by narrower necks (Figure 1 c). The solvent molecules and chloride counterion are disordered within the pores and their contributions to the X-ray diffraction patterns were estimated by using Platon/ Squeeze.^[42] The electroneutrality of the structure is fulfilled when considering one negative charge (chloride) in the pores in accordance with the EDS analysis. By using Platon/ Solv,^[42] the accessible voids in the desolvated structures were estimated to be 47.5% of the total volume.

Gas adsorption and structural properties: Prior to gas adsorption measurements, the thermal stability of [1-(H₂O)]Cl·DMF was studied by thermogravimetric analysis (TGA) and X-ray powder diffraction at different steps of the synthesis. TGA analysis performed on the as-synthesised samples showed the loss of solvent molecules (DMF guest) from 373 to 543 K and a further mass decrease occurred up to 903 K as a result of ligand calcination (Figure S2 in the Supporting Information). Soaking [1(H₂O)]Cl·DMF in chloroform at reflux led to a total exchange of the guest molecules, as revealed by FTIR spectroscopy of the material and ¹H NMR spectroscopy of the decomposed framework in a mixture of [D₆]DMSO/DCl (Figures S3 and S4 in the Supporting Information). Evacuation at 393 K led to removal of the solvent and water molecules in the porous matrix, as shown by the TGA trace because no abrupt weight loss occurred before 623 K. TGA curves indicated that after evacuation of the sample to 393 K for 12 h and re-exposition to humid air for few minutes, a weight loss of 2% assigned to water release was observed below 423 K. This loss was due to the re-binding of water on the zinc ion during exposition to air and was in perfect agreement with the expected theoretical value. This result demonstrates that evacuation of the material leads to a framework with open zinc sites. Accordingly, the CHCl₃-exchanged material was activated at 393 K under reduced pressure before adsorption measurements in order to remove traces of guest molecules in the pores and to create unsaturated metal sites.

Powder X-ray diffraction (PXRD) provided a measure of the phase purity and the stability of the framework. The PXRD patterns of the as-synthesised crystals were found to be identical to those simulated from single-crystal structures of [1(H₂O)]Cl·DMF, thus indicating the similarity of the bulk sample with the single crystal even after exchange with CHCl₃ (Figure 2). After drying of the DMF-exchanged solid at temperatures up to 463 K under vacuum, a weak phase change or collapse had barely begun, and the XRD patterns matched the simulated ones. Moreover, variable-temperature PXRD experiments showed that the material kept its crystallinity up to 433 K with no shift of the diffraction peaks (Figure S5 in the Supporting Information). This indicates that no shrinkage occurs and the porous framework is still robust after removal of free guest molecules in the channels. It also demonstrates the rigidity of the framework,



Figure 2. PXRD patterns (Cu_{Kal}) showing the stability of the framework: a) simulated from the X-ray single-crystal diffraction data of [1(H₂O)]Cl; b) experimental patterns for as-synthesised [1(H₂O)]Cl·DMF degassed at 353 K under 10⁻³ torr; c) after degassing at 463 K under 10⁻³ torr, and d) experimental patterns after chloroform exchange and degassing at 353 K under 10⁻³ torr.

in contrast to that described previously with tetraazacycloalkanes.^[40] To the best of our knowledge, rigid frameworks obtained from flexible building blocks have not been described in the literature.

In addition, PXRD analyses of the dehydrated [1]Cl have displayed a partial collapse of the framework in humid air over a few weeks (Figure S11 in the Supporting Information). However, the material is stable for several weeks in a pre-dried inert gas containing less than 10 ppm of water. Another important point is related to the stability of the assynthesised material. PXRD analyses have shown that before elimination of DMF by thermal activation or after chloroform exchange, the material is stable for months. The persistence of the porous framework after solvent removal was confirmed by the N₂ adsorption data. The N₂ isotherm [1]Cl at 77 K (Figure 3) exhibits a type I profile characteristic of the presence of micropores and the desorption profile shows no hysteresis. The BET and apparent Langmuir sur-



Figure 3. N₂ adsorption–desorption isotherm of [1]Cl at 77 K after activation under 10^{-5} torr at 393 K. The inset displays the pore size distribution using the Horvath–Kawazoe method (Saito Foley) calculation. STP= standard temperature and pressure.

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face areas were estimated to be 1199 and 1350 m²g⁻¹, respectively. The small discrepancies between the two values lies in the pore-filling mechanism, which is not valid for the BET assumption, but a fairly good agreement was obtained by using a proper pressure range.^[43,44] The micropore volume was estimated by using the Dubinin-Radushkevich equation to give $0.45 \text{ cm}^3 \text{g}^{-1}$; a value very close to the experimental one ($0.48 \text{ cm}^3 \text{g}^{-1}$). These data are totally consistent with the accessible porosity calculated geometrically from the crystal structure $(0.46 \text{ cm}^3 \text{g}^{-1})$. The excellent agreement between adsorption and crystallographic data rules out any collapse of the crystalline structure and demonstrates the high stability of the porous framework after solvent removal. It is noteworthy than when DMF is removed by heating without chloroform exchange, a lower porosity was obtained, whatever the activation temperature (Figure S6 in the Supporting Information). The onset pressure was analysed by using the Horvath-Kawazoe method and the pore diameter was shown to be 8.2 Å, in accordance with the crystallographic results (mean pore size 7.8 Å). The adsorption-desorption of CO₂ at 195 K (Figure S7 in the Supporting Information) displayed a capacity close to $251 \text{ cm}^3 \text{g}^{-1}$ at 1 atm and the Langmuir surface area estimated from the CO_2 isotherm was 1245 m²g⁻¹, very close to that for N₂ at 77 K. The isotherm shows a large hysteresis that is generally assigned to guest-directed framework rearrangement leading to a gate-opening structure^[40,45] due its flexibility. It is unlikely that this mechanism operates in the case described herein because [1]Cl keeps its crystallinity up to 433 K without structural change. The hindrance of some counteranions at the pore entrance can lead to partial pore blocking. Hence, the hampered diffusion of the gas molecules is likely to be the cause of such hysteresis. We also speculate that such behaviour is a result of the CO₂-anion interactions because no hysteresis was observed with N2 at 77 K.

The permanent porosity for [1]Cl allowed us to examine its potential application as a selective sorbent. The CO₂, CO, CH₄, O₂ and N₂ adsorption isotherms at 298 K are illustrated in Figure 4 and the selective adsorption of CO₂ is clearly evidenced. The material uptake of CO₂ is 88 cm³g⁻¹ at 1 atm, which corresponds to 3.92 mmolg⁻¹ or 17.8 wt%. A perfect adjustment of the adsorption branch for CO₂ was obtained by using a dual-site Langmuir-type isotherm model and a single Langmuir isotherm for the other gases (see Eqs. (1) and (2) in the Experimental Section and Table S3 in the Supporting Information).^[46-49]

The heat of CO_2 adsorption was determined with the Clausius–Clapeyron analysis by recording isotherms at 273, 288 and 298 K (Figures S8 and S9 in the Supporting Information). As expected, the Henry constant increases as the temperature decreases and the enthalpy at zero coverage is -26 kJ mol^{-1} , corresponding clearly to a physisorption process. This value is significantly lower than for $Cu_3(BTC)_2$ (-35 kJ mol^{-1}),^[28] MIL-53 (-35 kJ mol^{-1})^[15] and MIL-101 (-44 kJ mol^{-1}).^[19] Nevertheless, there is no direct correlation between the enthalpy of adsorption and CO_2 capacity close to 1 atm because lower adsorption capacities of CO_2 were



Figure 4. Adsorption–desorption isotherms for [1]Cl at 298 K with CO_2 (ads: \blacksquare , des: \square), CH_4 (\odot), CO (\bullet), N_2 (\bullet), and O_2 (\blacktriangle). The thin solid lines are related to the calculated dual-site Langmuir isotherm model for CO_2 and single-site Langmuir-type isotherms for the other gases. Dashed and dotted lines indicate the two contributions for the calculated CO_2 isotherm.

observed for MIL-53 and MIL-101 than that for [1]Cl at low pressure (≤ 1 atm). In the higher coverage region, the heat of adsorption slightly decreases to -23 kJ mol⁻¹, which shows that the interaction energies are almost homogeneously distributed on the surface and relatively weak interactions of CO₂ with the metal sites occur even after water molecule decoordination. The quasi-independence of the heat of adsorption with the coverage clearly indicates that zinc is slightly accessible to CO₂. The relatively low value of the enthalpy also indicates that the free anions in the pores do not participate in the adsorption process. In fact, material with a higher heat of adsorption is unlikely to be satisfactory in practical applications because of the large energy required to desorb CO₂ from the porous solid.

The ability for selective CO_2/CO and CO_2/CH_4 separation was further examined for post- and pre-combustion capture technologies. Indeed, the adsorption selectivity for CO_2 over CO, CH₄, O₂ and N₂ is important for applications of the material as a CO₂ sorbent.^[32,50] [1]Cl did not show any significant uptake of N₂, O₂ or CO at 298 K.

The selectivity for CO₂ towards other gases was calculated from the Henry constants [see Eq. (4) in the Experimental Section] and values were 21.1, 4.2, 26.0 and 22.6 over CO, CH₄, O₂ and N₂, respectively. The selectivity over CH₄ is quite similar to that described for ZIF materials.^[22] To the best of our knowledge, the selectivity over CO^[18,22,25] is one of the highest ever obtained for microporous materials and is significantly higher than for the ZIF family^[18,22,51] or Cu₃-(BTC)₂.^[52] Moreover, although the CPO-27-Ni described by Dietzel et al. ranks among the best adsorbent for CO₂,^[26,27] a low selectivity over CO was observed because of its coordination to the nickel ions.^[53]

Since the diameter and pore entrance are close to 8 Å, the selectivity for CO_2 cannot be attributed to small pores restricting the adsorption of gases thanks to a molecular sieving process, giving rise to a diffusion barrier. In other words, the diffusion barrier is not the limiting factor. Ac-

cordingly, a size exclusion effect could not be evoked because the pore size was significantly higher than the kinetic diameter of CO₂. On the other hand, [1]Cl has shown a higher adsorption capacity for CH₄, but it is still lower than that for CO₂. The gas-solid interaction of the MOF materials results from coulombic and van der Waals interactions between gas molecules and the microporous surface. Because the material is composed of dinuclear zinc clusters and chloride anions, which are supposed to be non-coordinating and remain free in the pores, a large adsorption of gas molecules with large quadrupole moments, such as CO₂ $(1.34 \times 10^{-39} \text{ Cm}^2)$, is expected thanks to strong electrostatic interactions between the field gradient induced by Zn²⁺ and Cl⁻. Hence, the lower CO and CH₄ adsorption is due to their smaller quadrupole moment and lower polarisability than that of CO_2 .

Multicycle adsorption realised in dynamic conditions by gravimetric measurements also showed the reversibility of the CO₂ adsorption process at 298 K (Figure S10 in the Supporting Information), while no loss of activity was observed through six cycles, indicating that the material is able to withstand repeated cycles of CO₂ stream. The material was then recovered totally free of CO₂ by switching the gas stream to Ar. The weight change under a CO₂ flow was 15.5% in an 80% CO₂/Ar mixture over repeated cycles and this value agreed with the static measurements described above. Moreover, the adsorption kinetic is high because the half-saturation capacity is reached in only 30 s under dynamic conditions. This result thus shows that the material is a suitable adsorbent candidate in a vacuum swing adsorption (VSA) or pressure swing adsorption (PSA) process for CO₂ removal like amine-containing silica adsorbents.^[54]

Conclusion

We have synthesised a new porous MOF $[1(H_2O)]Cl$ composed of a cyclic triamine and zinc ions. The material displayed a high surface area and a high adsorption capacity close to 1 atm. The crystallinity and the ordered channels were retained after solvent removal from the porous structure. The originality of the material lies in the high rigidity of the framework despite the flexibility of the cyclic polyaminocarboxylate building block. The polarisation of the surface led to a high adsorption capacity of CO₂ up to 88 cm³g⁻¹ at 1 atm with a high selectivity over CO, CH₄, N₂ and O₂. The combination of these two properties makes such a microporous material very competitive as a CO₂-selective sorbent for capture applications.

Experimental Section

Synthesis of L'=1,4,7-tris(4-cyanobenzyl)-1,4,7-triazacyclononane (see Scheme S1 in the Supporting Information): A solution of α -bromo-*p*-tolunitrile (12.32 g, 62.8 mmol) in CH₃CN (100 mL) was added to a suspension of trihydrochloride 1,4,7-triazacyclononane (5 g, 20.9 mmol) and

K₂CO₃ (25.9 g, 188.1 mmol) in CH₃CN (200 mL). After heating at reflux for 24 h, the salts were removed by filtration and the yellow solution was evaporated to dryness. Water (40 mL) was added and the yellow powder was extracted with CH₂Cl₂ (3×50 mL). The combined extracts were dried (MgSO₄) and evaporated to give a yellow oil, which precipitated in Et₂O/pentane 2/1. The crude product was filtered and dried in vacuo (8.7 g, 18.3 mmol, yield 87.8%). ¹H NMR (300 MHz, CDCl₃, 300 K): δ = 7.57 (d, ³*J*=8.1 Hz, 6H; Ar), 7.41 (d, ³*J*=8.2 Hz, 6H; Ar), 3.64 (s, 6H; NCH₂Ph), 2.75 ppm (s, 12H; NCH₂CH₂N); ¹¹3C[¹H] NMR (75 MHz, CDCl₃, 300 K): δ = 145.8 (*C*_{At}CH₂), 132.2 (CH_{At}), 129.4 (CH_{At}), 119.1 (CN), 110.7 (*C*_{At}CN), 62.7 (CH₂-Ph), 55.5 ppm (NCH₂CH₂N); FTIR (ATR): \tilde{v} = 2229 cm⁻¹ (CN); MS (*m*/*z*): 474.98 [*M*+H]⁺; elemental analysis calcd (%) for C₃₀H₃₀N₆-0.23 H₂O: C 75.26, H 6.41, N 17.55; found: C 75.29, H 6.31, N 17.39.

Synthesis of LH5²⁺=1,4,7-tris(4-carboxybenzyl)-1,4,7-triazacyclononane-2HCl-2H₂O: A suspension of L' (8.5 g, 17.9 mmol) was heated at reflux in HCl (12 M, 80 mL) for 48 h. The crude white solid was filtered and washed with water (3×100 mL). The product was stirred for 24 h in a solution of NaOH (4M). Concentrated HCl was added to the cooled solution until pH 1 was reached. The white solid formed was filtered, washed with water $(3 \times 40 \text{ mL})$ and the crude product was dried in vacuo (70.3%), 8.1 g, 12.6 mmol). ¹H NMR (600 MHz, D₂O, NaOD, dioxane as an internal reference, 300 K): $\delta = 7.91$ (d, ${}^{3}J = 7.9$ Hz, 6H; Ar), 7.15 (d, ${}^{3}J =$ 7.9 Hz, 6H; Ar), 3.66 (s, 6H; CH₂Ph), 2.75 ppm (s, 12H; NCH₂CH₂N); ¹³C¹H} NMR (150 MHz, D₂O, NaOD, dioxane as an internal reference, 300 K): $\delta = 174.9$ (CO₂H), 138.6 ($C_{Ar}CO_2H$), 137.2 ($C_{Ar}CH_2$), 130.6 (CH_{Ar}); 130.1 (CH_{Ar}), 59.4 (CH₂Ph), 49.5 ppm (NCH₂CH₂N); FTIR (ATR): $\tilde{\nu} = 1706$ (C=O), 2996 cm⁻¹ (CH); TGA: 5.5% weight lost for water (loss of two water molecules); MS (m/z): 531.9 [M+H]⁺; elemental analysis calcd (%) for C₃₀H₃₃N₃O₆·2HCl·2H₂O: C 56.25, H 6.14, N 6.56; found: C 56.35, H 6.10, N 6.51.

Synthesis of [1(H₂O)]Cl ([Zn₂(L)(H₂O)]Cl): The material was prepared by using the solvothermal method. A solution of the protonated ligand LH5²⁺ (1 g, 1.56 mmol) in DMF (60 mL) and a solution of Zn-(NO₃)₂·6H₂O (4.2 g, 14 mmol) in DMF (45 mL) was added. A solution of triethylamine (0.158 g, 1.56 mmol) in EtOH (12 mL) was added and the colourless solution was sealed in a 150 mL glass autoclave and heated at 353 K for 24 h. Trigonal prismatic shaped crystals were thus obtained. DMF was removed and fresh DMF (50 mL) was added to the crystals and they were left overnight. After removal of DMF, the crystals were heated at reflux in CHCl₃ (50 mL) for 6 h without stirring. The yield was 96% after drying in vacuum for 14 h at 293 K. The absence of residual solvent was shown by ¹H NMR spectroscopic analysis after material decomposition in [D₆]DMSO/DCl (see Figure S4 in the Supporting Information) or by FTIR analysis. FTIR (ATR): $\tilde{\nu} = 1610 \text{ cm}^{-1}$ (C=O for CO2⁻); elemental analysis calcd (%), after drying in vacuum for 6 h at 393 K under 10⁻⁵ torr, for C₃₀H₃₂N₃O₇Zn₂Cl·3H₂O: C 46.99, H 4.99, N 5.48; found: C 46.92, H 4.09, N 5.95; FTIR (ATR) before chloroform exchange: $\tilde{\nu} = 1655$ (C=O free DMF), 1614 cm⁻¹ (C=O for CO₂⁻); elemental analysis calcd (%), before chloroform exchange, for $C_{30}H_{32}N_3O_7Zn_2Cl{\cdot}0.8\,DMF{\cdot}1.9\,H_2O{\cdot}$ C 48.31, H 5.18, N 6.61; found: C 48.21, H 4.71, N 6.77.

Single-crystal X-ray crystallography: Single crystals were grown by using the previous procedure in the absence of triethylamine and without DMF exchange. Diffraction data were collected on a Nonius Kappa Apex II CCD diffractometer equipped with a nitrogen jet stream low-temperature system (Oxford Cryosystems). The X-ray source was graphite-monochromated Mo_{Ka} radiation ($\lambda = 0.71073$ Å) from a sealed tube. The lattice parameters were obtained by least-squares fit to the optimised setting angles of the entire set of collected reflections. No significant temperature drift was observed during the data collections. Data were reduced by using Denzo^[55] software and the structure was solved by direct methods using the SIR97^[56] program. Refinements were carried out by full-matrix least-squares on F^2 using the SHELXL97^[57,58] program on the complete set of reflections. Anisotropic thermal parameters were used for non-hydrogen atoms. All hydrogen atoms, on carbon atoms, were placed at calculated positions using a riding model with C-H=0.95 Å (aromatic), 0.99 Å (methylene) with $U_{iso}(H) = 1.2U_{eq}(CH_2)$, $U_{iso}(H) = 1.2U_{eq}(CH)$.

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In [1(H₂O)]Cl material, the hydrogen atoms of the coordinated water molecule have not been located and were not included in the formulae. The distance between C1 and C2 was restrained by using DFIX restraints.^[57] The components of the anisotropic displacement parameters, of O3 and Zn2, in the direction of the bond are restrained by using DELU restraint^[57] to be equal within an effective standard deviation to maintain a reasonable model. The unit cell includes a large region of disordered solvent and counterion (Cl⁻) molecules and cannot be modelled as discrete atomic sites. We employed Platon/Squeze^[59] to calculate the diffraction contribution of these molecules and, thereby, to produce a set of solvent-free diffraction intensities. CCDC-786902 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Gas sorption measurements: Gas adsorption isotherms on evacuated nanoporous materials were performed by using the volumetric method recording the adsorption isotherms on a Micromeritics ASAP 2010 or 2020 analyser. Samples were previously degassed by heating at 393 K in vacuo (10⁻⁵ torr) for at least 6 h. The equilibrium of the solid-gas reaction was determined for several relative pressures $(P/P_0, P_0 = \text{saturated})$ vapour pressure) to record the adsorption isotherm at a controlled temperature in a large range of P/P_0 (10⁻⁶ to 1). The specific surface area were determined by physisorption of N2 in the channels at 77 K by using the BET and the apparent Langmuir equations assuming a monolayer coverage of N₂ and a cross-sectional area of 16.2 $Å^2$ per molecule. To avoid large discrepancies between the two values due to the invalid BET assumption for microporous solids over the usual range $0.05 < P/P_0 <$ 0.25, care was taken to choose a suitable pressure range for which the BET analysis could be applied. As required by the groups of Snurr^[43] and Rouquerol,^[44] the pressure range selected should give increasing values of V(P_0-P) with P/P_0. Hence, a pressure range $5 \times 10^{-4} < P/P_0 < 0.025$ was used for BET analysis, which gave a fairly good agreement with the Langmuir isotherm estimation. The pore volume was determined directly from the isotherms or by extrapolation of the Dubinin-Radushkevich equation across the linear region of the low-pressure data points, assuming the sorbate is a liquid and the sorption involves a pore-filling process. The pore diameter was calculated from the adsorption isotherm by using the Horvath-Kawazoe method based on a cylindrical-shaped pore geometry (Saito-Foley). The reactivity of the materials towards CO2, CH4, CO, O2 and N2 was analysed by recording the adsorption isotherms at 298 K by using the same analytical apparatus. The CO₂ adsorption isotherm was analysed by using a model based on two Langmuir isotherms [Eq. (1)] to consider different energy interactions with the surface and then to perfectly fit the experimental isotherms. The equilibrium constants for the gas-binding affinity and the adsorption capacity are thus calculated from the experimental data by using a nonlinear regression least-squares method. Therefore, two sets of K_i and V_i are calculated for each contribution. The experimental data corresponding to the CO, CH₄, O2 and N2 adsorption isotherms were analysed by using single Langmuir isotherms [Eq. (2)]:

$$V_{\rm CO_2} = \frac{V_1 K_1 P}{I + K_1 P} + \frac{V_2 K_2 P}{I + K_2 P} \tag{1}$$

$$V_{\mathrm{T,i}} = \frac{V_{\mathrm{i}}K_{\mathrm{i}}P}{I + K_{\mathrm{i}}P} \tag{2}$$

in which V_{Ti} is the total volume adsorbed for gas i (CO, CH₄, O₂, N₂), V_i is the adsorbed volume, P is the applied pressure and K_i is the affinity. The gas-solid interaction strength was determined by the isosteric heat of adsorption, which was calculated by recording CO₂ adsorption isotherms at temperatures of 273, 288 and 298 K. The heats of adsorption were then calculated by applying the Clausius–Clapeyron equation [Eq. (3)], in which ΔH is the heat of adsorption, P is the pressure, R is the gas constant and T is the temperature:

$$\frac{\partial \ln P}{\partial (1/T)} = -\frac{\Delta H}{R} \tag{3}$$

Fitting of the adsorption branch for CO₂, CO, CH₄, N₂ and O₂ based on the Langmuir isotherm models allowed us to calculate the Henry constants for CO₂, $H^{CO_2} = K_1 V_1 + K_2 V_2$, and for the other gases, $H_i = K_i V_i$.

The Henry law selectivity (=upper limit selectivity) for CO_2 over gas i is then expressed by Equation (4):

$$S_{\rm CO_2} = \frac{H_{\rm CO_2}}{H_{\rm i}} \tag{4}$$

It is noteworthy that selectivity was also calculated by using the Toth isotherm model and similar values were obtained.

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