

Journal of Materials Chemistry A

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.



Journal Name

ARTICLE

MIL-91(Ti), a small pore Metal-Organic Framework which fulfils several criteria: an upscaled green synthesis, excellent water stability, high CO₂ selectivity and fast CO₂ transport

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Virginie Benoit^a, Renjith S. Pillai^b, Angelica Orsi^c, Périne Normand^d, Hervé Jobic^e, Farid Nouar^f, Pierre Billemond^d, Emily Bloch^a, Sandrine Bourrelly^a, Thomas Devic^f, Paul A. Wright^c, Guy De Weireld^d, Christian Serre^f, Guillaume Maurin^{b,†}, Philip L. Llewellyn^{a,†}

A multidisciplinary approach combining advanced experimental and modelling tools was undertaken to characterize the promises of a small-pore type Ti-based Metal-Organic Framework, MIL-91(Ti) for CO₂ capture. This material was prepared using two synthesis strategies, i.e. under hydrothermal conditions and under reflux, and its single component adsorption behaviour with respect to CO₂, CH₄ and N₂ was first revealed by gravimetry measurements. This hydrophilic and highly water stable MOF is characterized by a relatively high CO₂ adsorption enthalpy. Molecular simulations combined with in situ Powder X-ray diffraction evidenced that this is due to the combined interaction of this probe with N-H and P-O groups in the phosphonate linker. High CO₂ selectivities in the presence of either N₂ or CH₄ were also predicted and confirmed by co-adsorption measurements. The possibility to prepare this sample under reflux represents an environmentally friendly route which can easily be upscaled. This green synthesis route, excellent water stability, high selectivities and relatively fast transport kinetics of CO₂ are significant points rendering this sample of utmost interest for CO₂ capture.

Introduction

Metal-Organic Frameworks (MOFs) are porous coordination polymers which combine the diverse architectures of coordination chemistry with porous properties relevant to materials science, leading to novel solids targeted for societally relevant applications.^{1,2} These crystalline hybrid materials, where inorganic nodes are linked through polytopic organic moieties to give porous frameworks, show promise for applications such as catalysis, biomedicine, adsorption and separation, among others.³⁻⁷ In spite of their attractive properties, some of these materials have received criticism in light of their poor chemical stability,⁸⁻⁹ the extensive use of organic solvents during their synthesis and the high cost of certain reactants required for scale up of their synthesis to a commercial level.¹⁰ Whilst such points would limit the use of

any material for many applications, these disadvantages do not apply universally to MOFs. Indeed, the wide spectrum of possible inorganic and organic building blocks permits the design of water-stable MOFs and 'green' synthesis routes can be devised.¹¹⁻¹³ Amongst the water-stable MOFs reported so far, there is the potential to find promising candidates for a targeted application. For instance, it has been reported that small pore MOFs¹⁴⁻²³ with openings of 3.0-4.0 Å, could be of interest for diverse gas separations. More particularly, most of these promising MOFs can be used for CO₂ capture from binary gas mixtures with molecules of larger kinetic diameters such as N₂ (flue gas treatment) and/or CH₄ (natural gas or biogas purification) via molecular sieving.

The small pore bis-phosphonate MIL-91(Al),²⁴ one of the relatively few porous phosphonate MOF reported so far,²⁴⁻²⁹ was shown to interact strongly with CO₂ due to the presence of accessible phosphonate P-OH groups and the high degree of confinement afforded by its narrow pores.¹⁸ However, it displays an S-shaped CO₂ adsorption isotherm below 1 bar, as a result of guest-induced rearrangement of the MOF framework. Previous work has suggested that such a structural flexibility is not ideal in mixture separation.^{30,31} By analogy with the flexible MIL-53(Al, Cr, Fe)/MIL-47(V) systems,³⁰⁻³² a possible way to modulate the structural behaviour of a MOF solid upon adsorption is to change the metal centre. Hence, here we focus on the Ti-version of MIL-91 (Figure 1). This differs structurally from the Al analogue by the absence of bridging hydroxyl groups between adjacent metal centres (Ti_{IV}-O-Ti_{IV} vs Al_{III}-OH-Al_{III}). A combination of advanced experimental

^a Aix-Marseille University, CNRS, MADIREL UMR 7246, 13397 Marseille, France.

^b UMR-5253, Université Montpellier, CNRS, ENSCM, Place E. Bataillon, 34095 Montpellier cedex 05, France.

^c Eastchem School of Chemistry, University of St. Andrews, Purdie Building, North Haugh, St Andrews, Fife KY16 9ST, United Kingdom.

^d Service de Thermodynamique, Faculté Polytechnique, Université de Mons, Place du Parc 20, 7000 Mons, Belgium

^e Institut de Recherches sur la Catalyse et l'Environnement de Lyon, CNRS, Université de Lyon, 2. Av. A. Einstein, 69626 Villeurbanne, France.

^f Institut Lavoisier, UMR CNRS 8180, Université de Versailles St Quentin en Yvelines, Université Paris-Saclay, 45 avenue des Etats-Unis, Versailles, 78035, France.

† Corresponding authors.

Electronic Supplementary Information (ESI) available: These include the experimental details and complementary figures and tables. See DOI: 10.1039/x0xx00000x

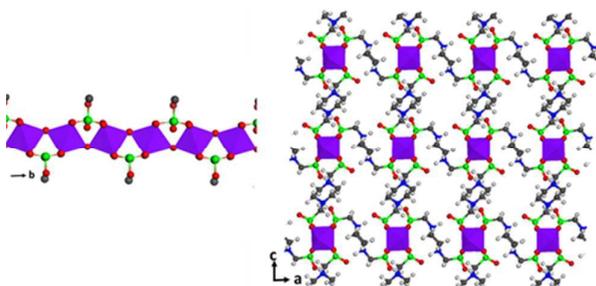


Fig 1. Structure of MIL-91(Ti) ($\text{TiO}(\text{O}_3\text{PCH}_2\text{NHC}_4\text{H}_8\text{NHCH}_2\text{PO}_3$), showing the chain of corner-sharing TiO_6 octahedra along the b-axis (left) and the view down the b axis (right). The atoms are represented as follows: Ti, violet; P, green; C, grey; O, red; N, blue; H, white.

and modelling tools reveals that this solid exhibits a standard Type I CO_2 adsorption isotherm, with no S-shape, while maintaining a significantly higher affinity for CO_2 compared to other gases (N_2 , CH_4). This results in MIL-91 being highly favourable in comparison with other MOFs in terms of CO_2 uptake and separation ability.

We also report a new preparative aqueous HF free reflux route to this water-stable MOF,²⁴ suitable for its easy and green upscaled preparation. Co-adsorption measurements which have been only very rarely reported for small pore solids due to slow adsorption kinetics and large error bars as a result of the very small amounts adsorbed were further performed on this material. They confirm the predicted promise of MIL-91(Ti) for CO_2/CH_4 and CO_2/N_2 separation. Moreover, this solid shows adsorption performance indicators ranking above most of the MOFs reported so far. Finally, Quasi-elastic Neutron Scattering (QENS) experiments evidence that although this solid has quite small pore channels, the diffusivity of CO_2 is relatively high, a requirement for its further application in physisorption-based processes for CO_2 recovery.

MIL-91(Ti) prepared by hydrothermal synthesis

Textural characterization and water stability

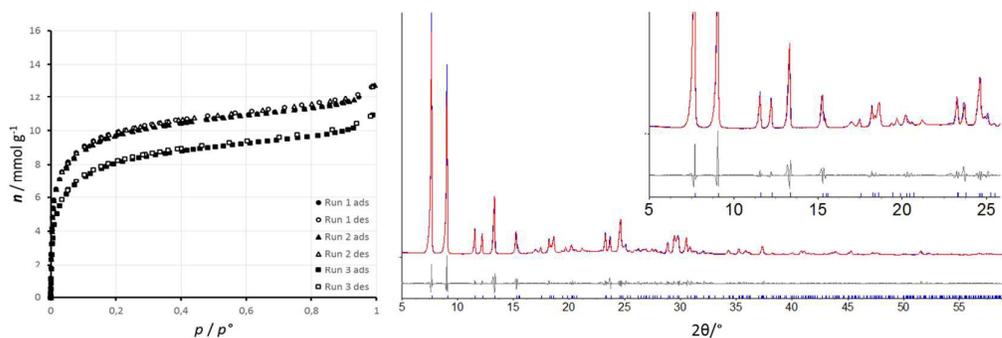


Fig 2. Water adsorption cycles at 25°C (left) and pattern matching (right) for MIL-91(Ti) synthesised under hydrothermal conditions after water adsorption/desorption cycling at 25°C for 3 weeks. Capillary data was collected on a Bruker D8 Advance diffractometer ($\lambda_{\text{Cu}} \sim 1.5406 \text{ \AA}$), pattern matching was performed using Topas software.³³ $a = 19.448(8) \text{ \AA}$, $b = 7.044(4) \text{ \AA}$, $c = 11.465(6) \text{ \AA}$, $\beta = 93.20(3)^\circ$, $V = 1568(1) \text{ \AA}^3$; $r_{\text{wp}} = 9.25$. It should be noted that impurities (probably a polymorph phase) are present within the material before and after water treatments (2θ values of about 17° and 21.2°). A pattern matching of the material before the treatment was also performed (not shown here), the following cell parameters were obtained: $a = 19.414(9) \text{ \AA}$, $b = 7.040(4) \text{ \AA}$, $c = 11.449(7) \text{ \AA}$, $\beta = 92.98(4)^\circ$, $V = 1562(1) \text{ \AA}^3$; $r_{\text{wp}} = 9.25$.

The synthesis for MIL-91(Ti) reported previously²⁴ employs hydrothermal conditions and hydrofluoric acid (HF) as a mineralizing agent. This leads to a material with zeolite-like textural properties in terms of pore size and pore volume, a hydrophilic character although stable to humidity. The free pore size of MIL-91(Ti) can be estimated at around $0.35 \times 0.40 \text{ nm}^2$ from crystallographic data which can be considered in the small range for many porous materials. Further, the porosity of this material, measured using nitrogen physisorption at 77 K, shows a BET area of $\sim 380 \text{ m}^2 \text{ g}^{-1}$ and a pore volume of $0.141 \text{ cm}^3 \text{ g}^{-1}$ (at $p/p^\circ = 0.1$, Table S1, Fig. S7) in good agreement with the theoretically accessible N_2 -surface area ($\sim 403 \text{ m}^2 \text{ g}^{-1}$) and pore volume ($0.160 \text{ cm}^3 \text{ g}^{-1}$) calculated from the crystal structure of MIL-91(Ti) (Table S2). The increase in uptake in the N_2 isotherm at high p/p° can be attributed to intra-particle adsorption.

The water adsorption isotherm obtained at 25°C after outgassing to 150°C is of Type I, (Figure 2). A second water adsorption cycle recorded after identical outgassing led to an overlapping isotherm suggesting that no structural degradation occurs during water adsorption-desorption. However, placing the sample under secondary vacuum for 1 hour between cycles is not sufficient to completely liberate the porosity, as a 16% decrease in uptake was observed (Fig. S8). In a separate series of experiments after outgassing to 80°C under nitrogen flow, the sample showed reversible behaviour for three water cycles, which indicates this MOF's stability under these conditions and within the 3 week experimental period (Fig. S8). The water stability was finally confirmed by Powder X-ray diffraction (PXRD), which evidenced a very similar pattern for the sample dispersed in boiling water for 24 hours compared to that of the pristine solid. This valuable latter feature is not shown by most of the MOFs proposed so far for CO_2 capture.^{34,35}

Single gas adsorption and comparison with molecular simulations

The adsorption isotherms of MIL-91(Ti) were initially evaluated using gravimetry and the adsorption enthalpies were measured using calorimetry at 303 K, with CO_2 , CH_4 and N_2 .

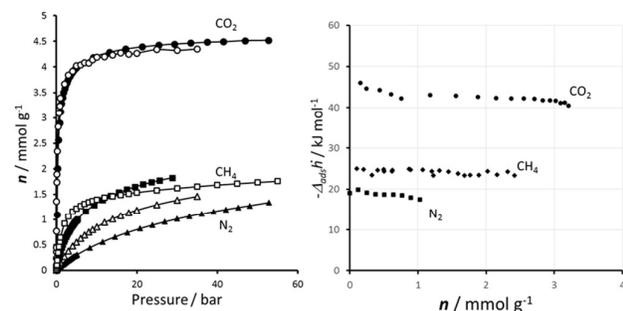


Fig 3. Comparison of the adsorption isotherms (left) obtained by gravimetry (filled symbols) and by GCMC simulations (open symbols) at 303 K for CO₂ (circles), CH₄ (squares), N₂ (triangles) for MIL-91(Ti). The corresponding adsorption enthalpies as a function of the coverage collected by microcalorimetry (right).

The corresponding data are reported in Figure 3.

The amounts adsorbed for both CH₄ and N₂ are relatively low with saturation capacities of ~ 1.5 mmol g⁻¹ and ~1.0 mmol g⁻¹ at 40 bar, respectively, while their enthalpies are slightly larger than those obtained from many other MOFs (see the comparison on table S3). This can be explained by the more confined pore space exhibited by this structure. Grand Canonical Monte Carlo (GCMC) simulations confirmed (i) the low amounts adsorbed of both gases and (ii) their relatively high adsorption enthalpies at zero coverage, i.e. around ~ -19.6 kJ mol⁻¹ (exp. -19.5 kJ mol⁻¹) and ~ -24.6 kJ mol⁻¹ (exp. -23.8 kJ mol⁻¹) for N₂ and CH₄ respectively (Figure 3). Analysis of the adsorption mechanism for these two guest molecules indicated the absence of specific adsorption sites for these probes at the MOF surfaces, as both N₂ and CH₄ are mainly distributed in the centre of the pores (Fig. S19, S20).

For CO₂, the adsorption uptakes at 1 bar (~3.0 mmol g⁻¹) and 10 bar (~4.5 mmol g⁻¹) are rather high compared to other small pore MOFs previously proposed for separation purposes, such as MIL-53(Al)-NH₂ (1.6 mmol g⁻¹ at 283 K and 1 bar³⁶), Sc₂BDC₃-NO₂ (1.1 mmol g⁻¹ at 303 K and 1 bar²⁰), UiO-66(Zr)-2CO₂H (1.0 mmol g⁻¹ at 303 K and 1 bar¹²) and SIFSIX-3-Zn (2.3 mmol g⁻¹ at 308 K and 1 bar²¹). Interestingly, the adsorption enthalpies for CO₂, ranging from -47 kJ mol⁻¹ to -43 kJ mol⁻¹, are amongst the highest reported to date for MOFs and in particular these values are larger than those observed for MOFs without open metal sites (Table S3). Furthermore, this isotherm is completely reversible and repeatable after primary vacuum treatment at 303 K, indicating that a simple regeneration process for this porous solid is possible.

Furthermore, in contrast to its Al-analogue,¹⁸ the CO₂ adsorption isotherm for MIL-91(Ti) does not show any inflection point below 1 bar, but exhibits a standard Langmuir-type shape, also applicable to the other gases, CH₄ and N₂. In situ Synchrotron PXRD data collected on the sample during CO₂ loading (Fig. S12) and Density Functional Theory (DFT) calculations (see SI) performed on the structure in the presence of CO₂ both suggest that a volume change of only ~2% occurs (Table S9) with respect to the pristine structure (predicted and experimental unit cell volumes of 1576.05 Å³ and 1574.73 Å³, respectively, vs 1516.86 Å³ for the unloaded

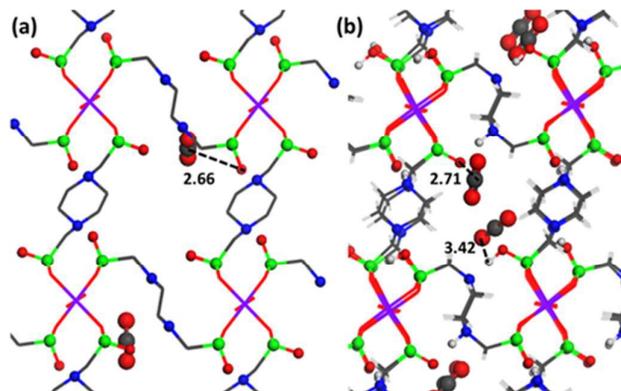


Fig. 4. (a) Crystal structure obtained from the in situ Synchrotron XRPD data collected at P_{CO2} = 35 bar and 230 K. (b) Local views of the snapshots extracted from the GCMC simulations of MIL-91(Ti) at 1 bar and 303 K. The interacting distances are reported in Å and the atoms are represented with the same colour code as in Fig. 1.

solid). However, the fact that there is no particular signature in the isotherm (inflection point) or change in the enthalpy curve suggests that this structure change on CO₂ adsorption may be gradual.

The CO₂ adsorption data are well reproduced by the GCMC simulations performed on the DFT-optimized CO₂ loaded structure. Both in situ PXRD and GCMC data reveal that CO₂ molecules preferentially interact in a dual manner with the phosphonate linkers, the CO₂ molecules being aligned in such a way that carbon atoms of C=O groups (CCO₂) interact with O atoms present in the environment of the P=O group and the N atom (PO...H...N), giving rise to CCO₂ - OPO...H...N distances of about 2.7 Å (Figure 4). Such a confined geometry gives rise to a very high, predicted CO₂ adsorption enthalpy at low coverage (i.e. -44.0 kJ mol⁻¹), which is consistent with the microcalorimetry measurements (Figure 3).

From the combination of experimental and modelling single component adsorption data it was possible to make a preliminary comparison, using the energies of adsorption, to deliver a first evaluation of MIL-91(Ti) for gas separation. The high adsorption enthalpy differences between CO₂ and other gases, i.e. Δ(ΔH(CO₂)-ΔH(CH₄)) ~ -20.0 (simulated: 19.4) kJ mol⁻¹ and Δ(ΔH(CO₂)-ΔH(N₂)) ~ -25 (simulated: -24.4) kJ mol⁻¹, suggested that MIL-91(Ti) is of interest both for the selective adsorption of CO₂ over CH₄ and/or N₂ (see Table S3). However further comparisons and mixture adsorption data were required to validate this initial approach, as shown below.

Green synthesis of MIL-91(Ti) under reflux conditions

Synthesis and comparison between samples

To confirm the promise of MIL-91(Ti) for CO₂ capture, a relatively large amount of sample was required to perform co-adsorption experiments. To upscale the synthesis of this material, a method is required which does not necessitate hydrothermal conditions or the use of HF. Hence, a reflux route in water was developed (see SI for full details) where

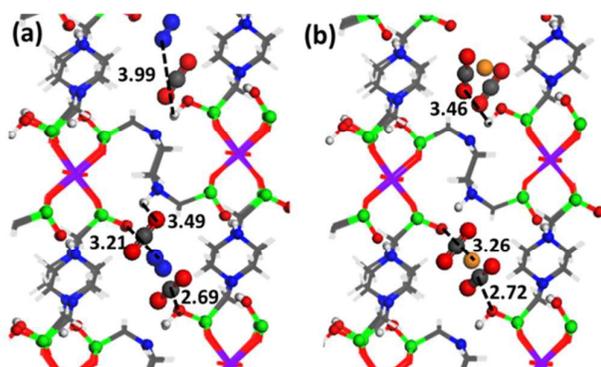


Fig. 5. Snapshots obtained during GCMC simulated arrangements of CO₂ and N₂ molecules (left) and CO₂ and CH₄ molecules (right) from binary mixture simulations on MIL-91(Ti)-CO₂. (CO₂/N₂ system at a molar composition of 0.05/0.95 and the CO₂/CH₄ system at a molar composition of 0.5/0.5, both in the gas phase at 303 K).

N,N'-piperazinebis(methylenephosphonic acid) is dissolved, with the aid of NaOH, in water under reflux before the addition of titanium oxyacetylacetonate and prior to a further reflux for 68 hours. The initial characterization data of this material (PXRD, TGA, SEM) is provided in the supporting information. The BET area of the obtained solid was 360 m² g⁻¹ and the pore volume 0.138 cm³ g⁻¹. Both values are similar to those obtained for the hydrothermally synthesized sample (380 m² g⁻¹ and 0.141 cm³ g⁻¹), which validates this new synthetic route.

The water isotherms (Fig. S8) shows that this solid has attractive water stability with a fully reversible water adsorption / desorption cycling under nitrogen flow. This is further confirmed by structure analysis where comparable PXRD patterns are obtained with the pristine sample and the one recorded after the 3 weeks of water adsorption/desorption cycling (Fig. S9). Further comparison between the samples was made using single gas adsorption at 303 K (Fig. S10). It was shown that the uptakes and adsorption enthalpies for CH₄ and N₂ were similar for the two samples. A small deviation is observed for the CO₂ adsorption with a slightly higher enthalpy for the sample prepared under hydrothermal conditions. This is equally translated in a steeper uptake at lower pressures and a sharper knee in the isotherm. However, the overall uptakes are similar at pressures above 10 bar for both samples.

Adsorption of gas mixtures: modelling and real co-adsorption measurements

GCMC simulations, which concur with experimental data from single gas adsorptions, are a convenient initial means to predict the behaviour of this MOF with respect to binary gas mixtures. Hence, an evaluation of the potential applications of MIL-91(Ti) can then be deduced. With both post-combustion and natural gas upgrading scenarios in mind, GCMC simulations were carried out with mixtures of CO₂/N₂ (gas phase composition: 0.05/0.95; 0.1/0.9 and 0.15/0.85) and CO₂/CH₄ (gas phase composition: 0.5/0.5) at 303 K and 313 K (Details in SI). The predicted selectivities varied from 80 to 100

Table 1 CO₂ / N₂ experimental selectivities measured at 303 K

Total pressure	% CO ₂	Measured selectivity	Average measured selectivity
1 bar	0.108	65	86
	0.099	89	
	0.102	106	
	0.173	67	
3 bars	0.168	53	60
	0.103	89	73
	0.117	61	
	0.118	69	
	0.176	60	51
	0.169	49	
0.168	45		

Table 2 CO₂ / CH₄ experimental selectivities measured at 303 K

Total pressure	% CO ₂	Measured selectivity
1 bar	50	18
5 bars	50	15
13 bars	50	13

at 1 bar, for CO₂/N₂ with 0.05/0.95; 0.1/0.9 and 0.15/0.85 molar concentrations and in the temperature range 303 – 313 K (Fig. S25).

For CO₂/CH₄, the simulated data for an equimolar concentration resulted in values from 16 to 20 for the same temperature range (Fig. S26). These separation performances are amongst the highest reported so far for water stable MOFs (Tables S5 & S6). Analysis of the co-adsorption mechanism revealed that the behaviour of CO₂ is similar to the single gas component scenario (Figure 5), i.e. the CO₂ molecules are mainly distributed in the vicinity of the PO...H...N sites, with mean distances between CCO₂ and OPO...H...N for CO₂/N₂ and CO₂/CH₄ systems of 2.69 and 2.72 Å, respectively (Figure 5). Both N₂ and CH₄ are distributed in the centre of the pore with characteristic host/guest distances exceeding 3.2 Å (N₂ - PO...H...N : Fig. S23; CH₄ - PO...H...N : Fig. S24).

This clearly emphasizes that for both mixtures, the separations are mainly driven by a preferential CO₂ adsorption around P-OH and NH groups combined with the high degree of confinement of this solid due to its restricted pore size conjugated with a small pore volume, which favours the adsorption of molecules with smaller kinetic diameters.

To investigate this MOF further, co-adsorption measurements were performed on several grams of the sample, prepared under reflux conditions. The results are given in Tables 1 and 2. Each mixture point was repeated several times and an average separation value was obtained. The co-adsorption selectivity of ~90 was observed at 1 bar and 303 K for the case of CO₂/N₂ = 10/90, which then decreased to 60 at 1 bar and 303 K for the mixture CO₂/N₂ = 15/85. For the co-adsorption of the equimolar mixture of CO₂/CH₄, MIL-91(Ti) shows a selectivity of around 18 at 1 bar and 303K. All of this experimental data concurs with the predicted data from GCMC simulations.

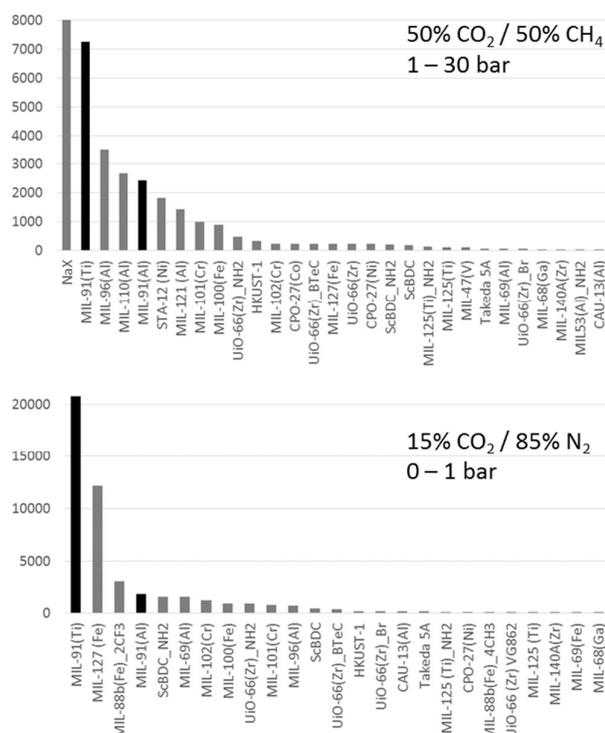


Fig. 6. API values for CO₂/CH₄ (upper) and CO₂/N₂ (lower) for several MOFs. Both MIL-91(Ti) and MIL-91(Al) are given in black. Data for an activated carbon (Takeda 5A) and a zeolite (13X) are also given for comparison.

Adsorption performances of MIL-91(Ti) vs other MOFs

The above discussion indicates how MIL-91(Ti) competes well with other porous materials as a CO₂ adsorbent. Indeed, the relatively high adsorption enthalpies and selectivities suggest that this material could be of interest for the recovery of CO₂ from N₂ or CH₄. A third factor to consider is the working capacity, i.e. the adsorption/desorption between an upper and lower working pressure as defined by a given pressure swing adsorption (PSA) process. Making a comparison between MOFs is not simple as most materials are still only available in powder form. Furthermore, one would wish to compare the uptakes per volume of material as this is what is required for process design. However, the real density of many MOFs is not always given. Thus, to make a comparison, the uptakes of available MOF powders were deduced and the individual crystallographic densities were obtained to calculate uptakes per unit volume. A comparison between MOF samples is provided in Table S4 for the two separations under investigation. For the CO₂/N₂ separation at 1 bar, MIL-91(Ti) has however a working capacity which is not amongst the highest; being at around a third of that obtained with HKUST-1 for example (Table S4). One shall nevertheless bear in mind the poor water stability of the copper MOF ruling its use for the recovery of CO₂ from flues.

Noteworthy, for the recovery of CO₂ from methane, considered at 30 bar, the working capacity of MIL-91(Ti) is amongst the highest of the MOFs considered.

These varying results thus open the question of how to make a fair but global comparison between samples, which, inter alia, resulted in the development of the concept of the adsorption performance indicator (API)³⁷. The API considers the volumetric working capacity (WC), adsorption enthalpies ($\Delta_{ads} \dot{h}$) and selectivities ($\alpha_{1/2}$), as indicated below.

$$API = \frac{(\alpha_{1/2} - 1)^A \cdot WC_1^B}{\Delta_{ads} \dot{h}^C}$$

Each parameter can be emphasised using power laws, defined by the process under consideration. In the present comparison, gas sweetening is considered and thus the selectivity towards was emphasized (A=2). In this exercise, single gas data previously obtained in house on fully activated samples are used as the conditions of collection are identical (T = 30°C) and the enthalpies have been measured directly. For MIL-91(Ti) the measured selectivities were applied, but for other MOF species the calculated IAST values were considered. Note that in this reported exercise there was fairly good agreement between experimental and IAST calculated selectivities that make the comparison with the other MOFs consistent. The API values for the two separations, CO₂/CH₄ and CO₂/N₂, obtained for MIL-91(Ti) were compared with around 20 other MOFs (Figure 6).

For CO₂/CH₄ separation, the zeolite 13X shows the highest API value, which is due to its very high selectivity. However, for the analysed MOFs (i.e. where data was obtainable), MIL-91(Ti) is highly ranked, which again reflects the medium to high selectivity and relatively high working capacity. For CO₂/N₂ separation, MIL-91(Ti) is again deduced to be the most interesting material considered by our group thus far, which is also attributed to its relatively high measured selectivity. Nevertheless, one should temper this conclusion with the fact that other MOFs from other groups may also be of interest (for example, those in refs 21-23).

Kinetics of CO₂ and N₂ in MIL-91(Ti)

Nevertheless, for such a small pore material with relatively large interactions, the question arises as to whether the adsorption could have some kinetic limitations. Therefore, the dynamics of CO₂ and N₂ were probed using QENS measurements (see SI for details). This approach has previously proven to be successful when applied to deduce the transport diffusivity (D_t) of two species (CO₂ and N₂) in a diverse range of MOFs.³⁸⁻⁴² It was found that in the low loading range (0.7 N₂ molecule/u.c. and 1.2 CO₂ molecule/u.c.), the D_t values for CO₂ and N₂ are respectively, 8.5×10^{-10} m²/s at 300 K and 1.4×10^{-9} m²/s at 220 K. These values for MIL-91(Ti) are as high as those previously shown for UiO-66(Zr)-2CO₂H¹² (CO₂ : 1.0×10^{-10} m²/s and N₂ : 4.0×10^{-9} m²/s) and also in the reference zeolite 13X for the same region of temperature (CO₂ : 1.5×10^{-10} m²/s and N₂ : 2×10^{-9} m²/s) measured at 230 K.⁴³⁻⁴⁴ These values confirm that kinetics should not be a hindrance to the use of MIL-91(Ti) in physisorption-based processes.

Conclusions

In summary, the titanium form of MIL-91 is a promising candidate for CO₂ recovery while its “green” reflux synthesis conditions pave the way for its upscale production. This hydrophilic metal bisphosphonate material seems to be one of the relatively few MOFs that are stable towards humidity. The nature of the small pores and the chemistry of this porous framework results in significant CO₂ uptakes at low pressures, along with strong interactions towards this greenhouse gas. However the strength of this interaction and the small pore nature of this material does not hinder the transport kinetics of CO₂ in the pore system as measured by QENS. Co-adsorption measurements confirmed the performances predicted from molecular simulations, with selectivities for CO₂/CH₄ and CO₂/N₂ above 18 and 90, respectively, at 1 bar and 298 K. This makes MIL-91(Ti) attractive for the selective capture of CO₂ from both CH₄ and N₂. Evaluation of the APIs for a wide range of MOFs at our disposition further suggests that MIL-91(Ti) compares well with respect to many other materials. In addition to these separations, one can consider that good results could be obtained with hydrogen purification from CO₂ as H₂ generally does not adsorb on porous materials at ambient temperatures.

Indeed this study shows that MIL-91(Ti) seems to tick boxes concerning up-scalable environmentally favourable synthesis, water stability, high CO₂ selectivity and rapid kinetics promoting this MOF as one of the very few of real interest for CO₂ capture.

Acknowledgements

The research leading to these results has received funding from the European Community Seventh Framework Program (FP7/2007-2013) [grant agreement number 608490] (project M⁴CO₂) and from the ANR ‘CHESDENS’ (ANR-13-SEED-0001-01). The authors would like to thank the ESRF (SNBL & Prof. Y. Filinchuk) for X-ray beamtime and ILL (IN6 & Dr. M. M. Koza) for neutron beamtime. G.M. thanks the Institut Universitaire de France for their support.

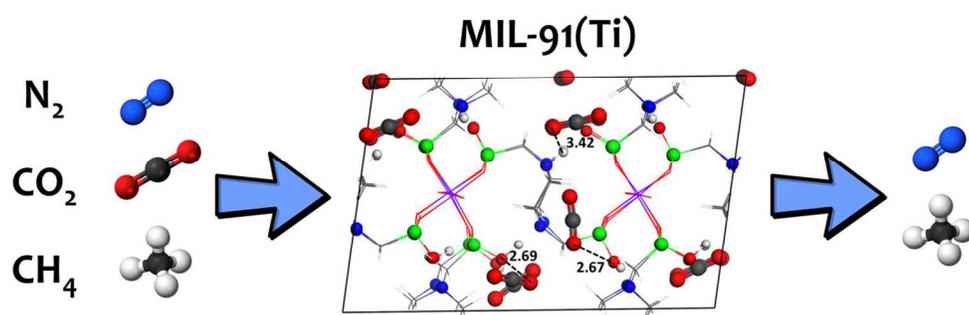
Notes and references

† The experimental and computational details can all be found in the supporting information.

- H.-C. Zhou, J. R. Long and O. M. Yaghi, *Chem. Rev.*, 2012, **112**, 673.
- H.-C. Zhou and S. Kitagawa, *Chem. Soc. Rev.*, 2014, **43**, 5415.
- M. Zhao, S. Ou and C. D. Wu, *Acc. Chem. Res.*, 2014, **47**(4), 1199.
- M. W. Zhang, Z. Y. Gu, M. Bosch, Z. Perry and H.-C. Zhou, *Coord. Chem. Rev.*, 2015, **293**, 327.
- P. Horcajada, R. Gref, T. Baati, P. K. Allan, G. Maurin, P. Couvreur, G. Férey, R.E. Morris and C. Serre, *Chem. Rev.*, 2012, **112**(2), 1232.
- B. Seoane, J. Coronas, I. Gascon, M. E. Benavides, O. Karvan, J. Caro, F. Kapteijn and J. Gascon, *Chem. Soc. Rev.*, 2015, **44**(8), 2421.

- E. Barea, C. Montoro and J. A. R., Navarro, *Chem. Soc. Rev.*, 2014, **43**(16), 5419.
- J. J. Low, A. I. Benin, P. Jakubczak, J. F. Abrahamian, S. A. Faheem and R. R. Willis, *J. Amer. Chem. Soc.*, 2009, **131**(43), 15834.
- P. Guo, D. Dutta, A. G. Wong-Foy, D. W. Gidley and A. J. Matzger, *J. Amer. Chem. Soc.*, 2015, **137**(7), 2651.
- J. Liu, P. K. Thallapally, B. P. McGrail, D. R. Brown and J. Liu, *Chem. Soc. Rev.*, 2012, **41**(6), 2308.
- A. G. Marquez, P. Horcajada, D. Grosso, G. Férey, C. Serre, C. Sanchez and C. Boissiere, *Chem. Comm.*, 2013, **49**(37), 3848.
- Q. Yang, S. Vaesen, F. Ragon, A. D. Wiersum, D. Wu, A. Lago, T. Devic, C. Martineau, F. Taulelle, P. L. Llewellyn, H. Jobic, C. L. Zhong, C. Serre, G. De Weireld and G. Maurin, *Angew. Chem. Int. Ed.*, 2013, **52**(39), 10316.
- H. Reinsch, B. Bueken; F. Vermoortele, I. Stassen, A. Lieb, K.-P. Lillerud and D. De Vos, *CrystEngComm*, 2015, **17**(22), 4070.
- K. S. Park, Z. Ni, A. P. Cote, J. Y. Choi, R. D. Huang, F. J. Uribe-Romo, H. K. Chae, M. O’Keeffe and O. M. Yaghi, *P. Natl. Acad. Sci. USA*, 2006, **103**, 10186.
- S. R. Miller, P. A. Wright, C. Serre, T. Loiseau, J. Marrot and G. Férey, *Chem Comm.*, 2005, 3850.
- S. R. Miller, P. A. Wright, T. Devic, C. Serre, G. Férey, P. L. Llewellyn, R. Denoyel, L. Gaberova and Y. Filinchuk, *Langmuir*, 2009, **25**(6), 3618.
- J. P. S. Mowat, S. R. Miller, J. M. Griffin, V. R. Seymour, S. E. Ashbrook, S. P. Thompson, D. Fairen-Jimenez, A. M. Banu, T. Duren and P. A. Wright, *Inorg. Chem.*, 2011, **50**, 10844.
- P. L. Llewellyn, M. Garcia-Rates, L. Gaberova, S. R. Miller, T. Devic, J.-C. Lavalley, S. Bourrelly, E. Bloch, Y. Filinchuk, P. A. Wright, C. Serre, A. Vimont and G. Maurin, *J. Phys. Chem. C*, 2015, **119**, 4208.
- D. Damasceno Borges, M. Prakash, N.A. Ramsahye, P.L. Llewellyn, S. Surblé, P. Horcajada, C. Serre and G. Maurin, *Mol. Sim.*, 2015, **41**(16-17), 1357.
- R. S. Pillai, V. Benoit, A. Orsi, P. L. Llewellyn, P. A. Wright and G. Maurin, *J. Phys. Chem C*, 2015, **119**(41), 23592.
- P. Nugent, Y. Belmabkhout, S. D. Burd, A. J. Cairns, R. Luebke, K. Forrest, T. Pham, S. Ma, B. Space, L. Wojtas, M. Eddaoudi and M. J. Zaworotko, *Nature*, 2013, **495**, 80.
- D. X. Xue, Y. Belmabkhout, I. Shekhat, H. Jiang, K. Adil, A.J. Cairns and M. Eddaoudi, *J. Am. Chem. Soc.*, 2015, **137**, 5034.
- A. H. Assen, Y. Belmabkhout, K. Adil, P. M. Bhatt, D. X. Xue, H. Jiang and M. Eddaoudi, *Angew. Chem. Int. Ed.*, 2015, DOI: 10.1002/anie.201506345
- C. Serre, J. A. Groves, P. Lightfoot, A. M. Z. Slawin, P.A. Wright, N. Stock, T. Bein, M. Haouas, F. Taulelle and G. Férey, *Chem. Mater.*, 2006, **18**, 1451.
- S. R. Miller, G. M. Pearce, P. A. Wright, F. Bonino, S. Chavan, S. Bordiga, I. Margiolaki, N. Guillou, G. Férey, S. Bourrelly and P. L., Llewellyn, *J. Amer. Chem. Soc.*, 2008, **130**, 15967.
- S. Begun, *Chem. Eur. J.*, 2014, **20**, 8862.
- F.P. Zhai, Q. S. Zheng, Z. X. Chen, Y. Ling, X. F. Liu, L. H. Weng and Y. M. Zhou, *CrysEngComm.*, 2013, **15**, 2040.
- P. Ramaswamy, N. E. Wong and G. K. H. Shimizu, *Chem. Soc. Rev.*, 2014, **43**, 5913.
- M. Taddei, F. Costantino, F. Marmottini, A. Comotti, P. Sozzani and R. Vivani, *Chem. Comm.*, 2014, **50**, 14831.
- V. Finsy, L. Ma, L. Alaerts, D.E. De Vos, G.V. Baron and J.F.M. Denayer, *Micro. Meso. Mater.*, 2009, **120**(3), 221.
- L. Hamon, P. L. Llewellyn, T. Devic, A. Ghoufi, G. Clet, V. Guillerm, G. D. Pirngruber, G. Maurin, C. Serre, G. Driver, W. van Beek, E. Jolimaître, A. Vimont, M. Daturi and G. Férey, *J. Amer. Chem. Soc.*, 2009, **131**(47), 17490.
- P. L. Llewellyn, S. Bourrelly, C. Vagner, N. Heymans, H. Leclerc, A. Ghoufi, P. Bazin, A. Vimont, M. Daturi, T. Devic, C.

- Serre, G. De Weireld and G. Maurin, *J. Phys. Chem. C.*, 2013, **117**(2), 962.
- 33 TOPAS V4.2: General Profile and Structure Analysis Software for Powder Diffraction Data, Bruker AXS Ltd, 2004.
- 34 N.C. Burtch, H. Jasuja and K.S. Walton, *Chem. Rev.*, 2014, **114**, 10575.
- 35 J. Canivet, A. Fateeva, Y.M. Guo, B. Coasne and D. Farrusseng, *Chem. Soc. Rev.*, 2014, **43**, 5594.
- 36 E. Stavitski, E. A. Pidko, S. Couck, T. Remy, E. J. M. Hensen, B. M. Weckhuysen, J. Denayer, J. Gascon and F. Kapteijn, *Langmuir*, 2011, **27**, 3970.
- 37 A. D. Wiersum, J.-S. Chang, C. Serre and P. L. Llewellyn, *Langmuir*, 2013, **29**(10), 3301.
- 38 F. Salles, H. Jobic, T. Devic, V. Guillerm, C. Serre, M. M. Koza, G. Férey and G. Maurin, *J. Phys. Chem. C*, 2013, **117**, 11275.
- 39 Q. Y. Yang, A. D. Wiersum, H. Jobic, V. Guillerm, C. Serre, P. L. Llewellyn and G. Maurin, *J. Phys. Chem. C*, 2011, **115**, 13768.
- 40 Q. Yang, H. Jobic, F. Salles, D. Kolokolov, V. Guillerm, C. Serre and G. Maurin, *Chem. Eur. J.*, 2011, **17**, 8882.
- 41 F. Salles, H. Jobic, A. Ghoufi, P. L. Llewellyn, C. Serre, S. Bourrelly, G. Férey and G. Maurin, *Angew. Chem. Int. Ed.*, 2009, **48**, 8335.
- 42 D. Wu, G. Maurin, Q. Yang, C. Serre, H. Jobic, C. Zhong and J. Mater. Chem. A, 2014, **2**, 1657.
- 43 D. Plant, H. Jobic, P. L. Llewellyn and G. Maurin, *Eur. Phys. J. Special Topics*, 2007, **141**, 127.
- 44 N.-K. Bär, P. L. Mc Daniel, C. G. Coe, G. Seiffert and J. Kärger, *Zeolites*, 1997, **18**, 71.



481x161mm (72 x 72 DPI)