Metal–Organic Frameworks

DOI: 10.1002/ange.201302682

A Water Stable Metal–Organic Framework with Optimal Features for CO_2 Capture**

Qingyuan Yang, Sébastien Vaesen, Florence Ragon, Andrew D. Wiersum, Dong Wu, Ana Lago, Thomas Devic, Charlotte Martineau, Francis Taulelle, Philip L. Llewellyn, Hervé Jobic, Chongli Zhong, Christian Serre, Guy De Weireld,* and Guillaume Maurin**

The escalating level of atmospheric CO_2 is a subject of widespread public concern associated to global warming and climate change. Flue gas emitted from power plants running on carbon-based fossil fuels is a primary source for this worsening climatic issue.[1] To decrease its impact on the environment, the anthropogenic CO_2 emission from post-combustion flue gas must be minimized, however the great challenge in doing this is achieving a selective adsorption of CO_2 over N_2. Pressure swing adsorption (PSA) technology is considered as an energetically efficient way for the industrial scale capture.[2] For these physisorption-based processes, it is indispensable to have porous adsorbents with good adsorption performance. In this context, porous crystalline materials, as exemplified by zeolite 13X (also known as NaX), are very attractive.[3] During the past decades, a novel class of hybrid nanoporous solids, metal–organic frameworks (MOFs) have rapidly developed into one of the most fruitful research areas in chemistry, materials science, and multiple branches of engineering.[4] The chemical features of such materials allow their structural properties to be finely tuned over an extremely broad range. Indeed, a number of recent studies have claimed that MOFs could serve as an ideal platform for the removal of CO_2 from a series of gases (e.g. natural gas, syngas, biogas)[5] and in particular from flue gas.

To date, the performances of most of the promising MOFs for CO_2 capture have been assessed primarily on the criteria of: 1) a thermodynamically high selectivity of CO_2 over other gases, however, this approach is often questionable as this parameter has been roughly estimated from simple macroscopic thermodynamic models, such as the ideal adsorbed solution theory (IAST) or from the slopes of the adsorption isotherms,[6] and 2) a large CO_2 uptake, however, this is not necessarily of prime importance to efficiently purify gases under practical conditions.[7] This assessment strategy led the community to design many targeted MOFs combining extra-large surface areas and the presence of specific adsorption sites that can strongly interact with CO_2.[8] In contrast, little attention has been paid to the regeneration of such adsorbents, and it is well established that an additional heating of the column of a PSA process for the removal of the adsorbed species induces a significant extra-cost.[9] Further, while the thermal behavior of the envisaged MOFs is well-documented, their stabilities under humidity have been poorly explored.[10,11] This is clearly a limiting factor for a potential application of such materials for CO_2 recovery as certain amounts of water vapor are usually present in gas-separation processes, which can contribute to dramatically alter the performance of the adsorbents. The questions of cost/production scale of the best MOFs have also been mostly avoided so far for such related applications. Typically, the MOF-type SIFSIX-2-Cu-i[11b] material which has been very recently reported as an ideal candidate for the capture of CO_2

[*] Prof. Q. Yang, D. Wu, Prof. C. Zhong
State Key Laboratory of Organic-Inorganic Composites, Beijing University of Chemical Technology, Beijing, 100029 (China)
Dr. S. Vaesen, Prof. G. De Weireld
Thermodynamics Department, Faculté Polytechnique
Université de UMONS
Place du Parc 20, 7000 Mons (Belgium)
E-mail: guy.deweireld@umons.ac.be
Dr. A. D. Wiersum, Dr. P. L. Llewellyn
Laboratoire MADIREL, Aix-Marseille Univ. - CNRS, UMR 7246
Centre de Saint Jérôme, 13397 Marseille (France)
F. Ragon, Dr. A. Lago, Dr. T. Devic, Dr. C. Martineau, Dr. F. Taulelle, Dr. C. Serre
Institut Lavoisier, UMR CNRS 8180-Université de Versailles St Quentin en Yvelines
45 avenue des Etats-Unis, 78035 Versailles (France)
E-mail: serre@chimie.uvsq.fr
Dr. H. Jobic
Institut de Recherches sur la Catalyse et l'Environnement de Lyon, Université de Lyon, CNRS
2. Av. A. Einstein, 69626 Villeurbanne (France)
Prof. G. Maurin
Institut Charles Gerhardt Montpellier
UMR CNRS 5253, UM2, ENSCM
Place E. Bataillon, 34095 Montpellier cedex 05 (France)
E-mail: guillaume.maurin@um2.fr

[**] This research was funded by the European Community's Seventh Framework Programme (FP7/2007-2013) under grant agreement No. 228862, the Natural Science Foundation of China (21136001, 21276009), and the Beijing Nova Program (No. 2008B15). We thank Dr. M. M. Koza for his help during the measurements on the IN6 spectrometer at the Institut Laue Langevin, Grenoble, France.

Supporting information for this article (the synthetic procedure for the preparation of the UiO-66(Zr)-$(COOH)_2$, together with details on its computational assisted structure determination, thermal and humidity resistance. Thermodynamic co-adsorption and QENS measurements as well as regeneration are also described) is available on the WWW under http://dx.doi.org/10.1002/anie.201302682.

from flue gas is only synthesized at the laboratory scale (ca. 100 mg). Finally, the recycling and environmental issues of such novel materials have been not prioritized in the choice of the metal precursors and the synthesis route.

All these factors put together still call for the development of novel porous hybrid solids as to our knowledge, there is still not a MOF combining outstanding separation performance (such as IRMOFs,[12a] Cu-BTC[12b] or DMOFs,[12c] CPO-27/MOF-74,[12d] SIFSIX,[11b,12e] MIL-53[4a]) with a high chemical resistance and easy "green" synthesis and scalability associated to the absence of toxicity or environmental concerns (e.g. MOFs containing toxic metals such as MIL-100(Cr)[12f] or CPO-27(Ni)[12d]).

Alternatively, tetravalent-based carboxylate MOFs have been revealed to be very promising materials with excellent chemical and mechanical resistance[13] associated with a very low toxicity. Some of them show interesting, although not exceptional CO_2 capture abilities.[14a] To meet the above considerations, we report herein a new Zr^{IV} water-stable MOF of the UiO-66 type incorporating benzene-1,2,4,5-tetracarboxylate (H_2BTEC) ligands. Its preparation (see Supporting Information for details) specially emphasizes:

1) the introduction of organic functionalities decorating the pores: polar free carboxylic groups that are prone to strongly interact with CO_2 molecules.[13e,14]
2) the nature of the solvent: whereas Zr carboxylates-based MOFs are prepared in *N*,*N*′-dimethylformamide (DMF) solution, only water was used, both for the synthesis and activation procedures. This approach is not only environmentally friendly, but also beneficial in terms of cost and regeneration issues.
3) the scale: a simple round bottom flask, room-pressure procedure, allowing readily scale up of the synthesis was developed. As a proof of principle, the material was prepared at the 40 g scale, without any loss of performance, together with a significant space time yield (STY) of approximately 96 $kg\,m^{-3}\,day^{-1}$.

The Lebail refinement of the experimental X-ray powder diffraction (XRPD) pattern (Figure S1 in the Supporting Information) was performed using the software WinPlotR included in the FullProf suite 2011 ($\lambda_{Cu} \approx 1.5406$ Å) to extract the unit cell parameter (20.736 Å) and possible space group (F23). The resulting cell dimension/symmetry are consistent with the UiO-66 type topology framework; the crystal structure was then further constructed through the combined use of this experimental information and computational strategy based on density functional theory (DFT) calculations (see Supporting Information).

This new MOF labeled as UiO-66(Zr)-$(COOH)_2$ or $Zr_6O_4(OH)_4(O_2C\text{-}C_6H_2\text{-}CO_2\text{-}(CO_2H)_2)_6 \cdot x\,H_2O$ ($x \approx 16$), shows tetrahedral (Figure 1a) and octahedral (Figure 1b) cages whose dimensions are, as expected, smaller than the UiO-66(Zr)[15] analogue (see Supporting Information), leading to a decrease of the theoretical accessible surface area (from 1018 to 428 $m^2\,g^{-1}$) and pore volume (from 0.45 vs. 0.26 $cm^3\,g^{-1}$) as summarized in Table S1. In light of our recent findings,[16] this model was further validated by a very good agreement obtained between the NMR ^{13}C isotropic chemical shifts and the DFT calculated ones (Figure 2b, and Supporting Information). Nitrogen sorption analysis on the synthesized sample also confirmed a good accordance between the BET surface area and the theoretical accessible surface area (428 vs. 415 $m^2\,g^{-1}$) while the pore volume is slightly lower (0.21 vs. 0.26 $cm^3\,g^{-1}$, see Supporting Information).

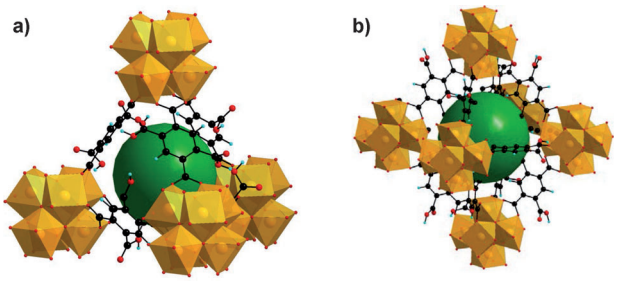

Figure 1. The UiO-66(Zr)-$(COOH)_2$ crystalline structure: a) tetrahedral cage, b) octahedral cage. The large green spheres represent the void regions inside the cages (Zr polyhedra; C black; O red, and H cyan).

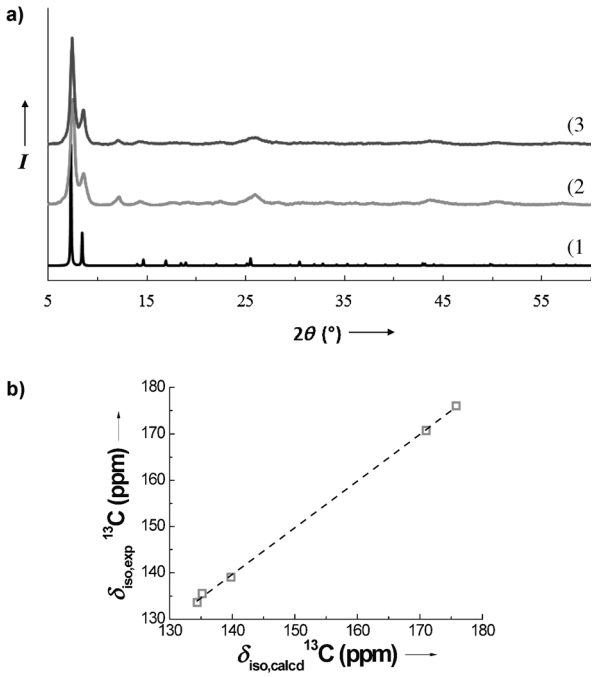

Figure 2. a) PXRD pattern of UiO-66(Zr)-$(COOH)_2$: 1) theoretical; 2) as-synthesized; 3) after treatment in H_2O at 373 K for 16 h ($\lambda_{Cu} \approx 1.5406$ Å). b) Correlation between NMR-measured and DFT-calculated ^{13}C isotropic chemical shifts.

It is noteworthy that UiO-66(Zr)-$(COOH)_2$ is water stable as shown by XRPD of the sample dispersed 16 h at 373 K in water (Figure 2a). This moisture stability was confirmed through repetitive water adsorption isotherms at 303 K (Figure 3) which show the same uptakes for each relative pressure. This result is a clear-cut advantage over most of the MOFs envisaged so far for CO_2 capture.[5a,10,17]

Based on the UiO-66(Zr)-$(COOH)_2$ structure model, preliminary Monte Carlo simulations were realized for each single CO_2 and N_2 adsorbate (see Supporting Information) to

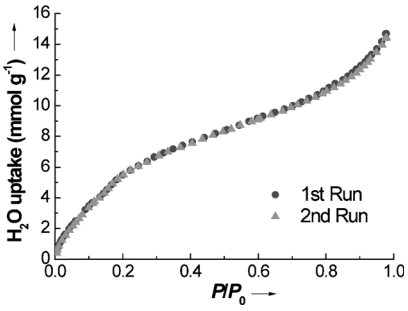

Figure 3. Water adsorption isotherms in UiO-66(Zr)-$(COOH)_2$ at 303 K. P/P_0 is the relative pressure of water with $P_0 = 4.247$ kPa.

first confirm that such a porosity can accommodate CO_2 and whether or not CO_2 interacts more preferentially than N_2 with the pore walls of the MOF. A detailed analysis of the configurations so obtained indicated that CO_2 molecules are primarily distributed in the regions close to the μ_3-OH group of the $Zr_6O_4(OH)_4$ oxo-cluster node and the -COOH organic functions, while N_2 does not lead to specific interactions with the pore walls. Such a scenario illustrated in Figure 4 holds

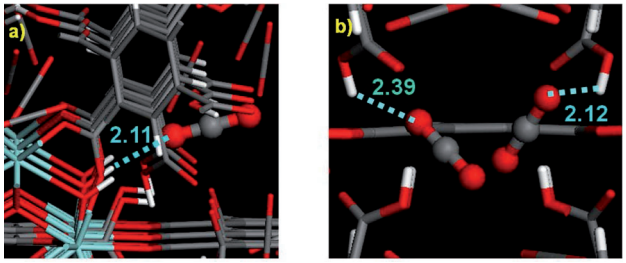

Figure 4. Local views of the snapshots extracted from the GCMC simulations at 1.0 bar and 303 K, emphasizing the interactions between the CO_2 molecule and: a) μ_3-OH group of the inorganic node, b) the -COOH organic functions. Some framework atoms are deleted for clarity. The distances are reported in Å. (Zr sky blue; O red; C gray, and H white; ball and stick representation for the interacting CO_2 while stick representation for non-interacting CO_2 molecules).

also true for the gas mixture. These observations clearly emphasize that despite the relatively high degree of confinement of its cages, this solid allows an optimal role of the grafting functions by authorizing a direct interaction between the -COOH groups and the gas we aim to selectively adsorb.

In light of such favorable features, a step further consisted of carefully characterizing the adsorption performances of this novel porous solid. Based on our previous conclusions from the study of a series of MOFs, such as the MIL-100(Cr),[18] for which we have established that the complexity of the host–guest interactions sometimes render the use of macroscopic co-adsorption models including IAST inaccurate, special attention has been paid to realize direct co-adsorption measurements using a large amount of sample at the laboratory level (ca. 20 g) to minimize experimental deviations. Such real co-adsorption data, only scarcely reported in the literature, were collected by using an advanced home-made device which combines a volumetric apparatus and gas chromatograph analysis. The measurements were realized at 303 K for a gas mixture CO_2:N_2 = 15:85 at 1.0 bar, that is, the typical industrial concentration and pressure conditions for the separation of flue gas emitted from power plants. A CO_2/N_2 selectivity of 56 was thus obtained. This excellent performance was further supported by Grand Canonical Monte Carlo simulations (GCMC; see Supporting Information) based on our structure model and a validated set of potential parameters that led to a predicted selectivity of CO_2 over N_2 of approximately 90, which is again higher than the experimental value under the same conditions. While this comparison confirms the great promises of this novel MOF, it also suggests that there is still a need to optimize some parameters of the synthesis. In particular, the formation of anhydride species cannot be fully excluded as referred to a recent work reported on the MIL-53(Al)-COOH.[19] that could be at the origin of a slightly lower experimental pore volume compared to the simulated value.

This selectivity value surpasses the performances reported for other MOFs under similar conditions that have been determined by real CO_2/N_2 co-adsorption (CID-3 (selectivity: 39))[20a] or breakthrough measurements (MOF-74(Ni) (38)[20b]), while it is only slightly below the top experimental record reported recently for SIFSIX-2-Cu-i (72)[11b] whose water stability is expected to be significantly lower than our sample as this Cu-based MOF is constructed from hexafluorosilicate anions that shall be easily hydrolysable.[21]

This great promise even holds true when this data is compared with the performances of the majority of MOFs that have been evaluated solely using simple macroscopic models, such as IAST, or estimated from the simple consideration of the initial slopes of the pure CO_2 and N_2 adsorption isotherms. Indeed, our novel material outperforms a series of MOFs, such as ZIF-78 (selectivity: 50),[6a] PCN-80 (19),[6c] Zn_2(BTetB)(py-CF_3)$_2$ (37),[22] Ca(SDB) (50),[23a] Cu-BTC (20),[23b] and ZIF-8 (8),[23c] while its selective ability remains lower than those of some other MOFs, such as Bio-MOF-11 (75)[6b] and Cu-TDPAT (79),[6d] for which however the performances need to be confirmed by real co-adsorption measurements. Finally, the selectivity so-obtained is much higher than those previously reported for the conventional zeolite 13X (ca. 20 corresponding to the ideal selectivity)[3a] and the activated carbon Norit R1 Extra (13).[23d]

To assess the regeneration of UiO-66(Zr)-$(COOH)_2$, microcalorimetry experiments were performed using a manometric dosing apparatus linked to the sample cell housed in a Tian-Calvet type microcalorimetrer (see Supporting Information). It is generally desirable for the strongly adsorbed species to have a relatively low adsorption enthalpy for minimizing the amount of heat required for regeneration. The measurements evidenced that the zero-coverage adsorption enthalpies at 303 K are -34.8 and -17.8 kJ mol^{-1} for the single gases CO_2 and N_2, respectively, which agree well with the GCMC simulated values of -36.4 and -19.7 kJ mol^{-1}. The energetic value for CO_2 is very similar to those reported for SIFSIX-2-Cu-i (CO_2: -31.9 kJ mol^{-1}), while it remains lower than those reported for most of the MOFs, that is, MOF-74(Ni) (-41.0 kJ mol^{-1}),[24] Bio-MOF-11 (-45.0 kJ mol^{-1}),[6b] Cu-TDPAT (-42.2 kJ mol^{-1}),[6d] as well as zeolite 13X

($-45.0\ kJ\,mol^{-1}$), suggesting a regeneration of this material under relatively mild conditions. Complementary experiments (see Supporting Information) have shown that a full regeneration is obtained at only 70 °C (see Supporting Information) which is much lower than the temperature required for zeolite 13X (160 °C).

Further, the working capacity defined as the difference between the CO_2 amount taken up at the adsorption (high) pressure and the amount remaining in the bed at the desorption (low) pressure of the process, is a much more significant factor regarding separation applications than the absolute uptake most commonly reported for MOFs.[6b,8b] For post-combustion CO_2 capture from flue gas by a PSA process, the working capacity is usually calculated between the adsorptions at 0.1 and 1 bar.[2] According to this definition, despite its relatively low pore volume, the experimental CO_2 working capacity reaches here approximately $42\ cm^3(STP)\,cm^{-3}$, which is slightly higher than that reported for the zeolite 13X ($34\ cm^3(STP)\,cm^{-3}$) used commercially.[3a]

Further as our new material shows a relatively bulky environment of the cages due to the presence of the two carboxylic functions, at first sight it would be intuitionally thought that the separation process could have some kinetic limitations. Therefore, the kinetic behaviors of both confined gases have been investigated by quasi-elastic neutron scattering (QENS) measurements. This experimental technique is a valuable tool to follow the diffusivity (D_t) of various guest molecules in MOF type materials.[15b,25] The in situ QENS measurements were performed at 230 K on a deuterated sample loaded with 12 and 3 molecules per unit cell for CO_2 and N_2 respectively, using the time-of-flight spectrometer IN6 at the Institut Laue-Langevin (see the Supporting Information). As both species are totally coherent scatterers, the collective mobilities, that is, the transport diffusivities are extracted from these QENS data. It was found that in this low loading range, the D_t values for CO_2 and N_2 are 1.0×10^{-10} and $4.0\times10^{-9}\ m^2s^{-1}$ respectively. Noteworthy, despite the bulky nature of our sample, the resulting diffusivities for both species are finally very similar to the values reported for the conventional faujasite 13X for the same temperature range (CO_2:$1.5\times10^{-10}\ m^2s^{-1}$ and N_2:$2\times10^{-9}\ m^2s^{-1}$).[26] Indeed, it can be considered that kinetics will not be a drawback for the use of such a novel material in physisorption-based processes.

In summary, we have demonstrated that a new Zr-based MOF, containing two carboxylic functions grafted on the organic linkers, shows great promises for CO_2/N_2 gas mixture separation with not only a very good selectivity, relatively high working capacity, a regeneration expected to occur under mild conditions, and no kinetic limitations, but also a water stability and a relatively high-scale production involving an environmental friendly and cheap scalable synthesis. All these considerations suggest that this material can serve as a bona-fide alternative to conventional porous solids involved in the physisorption-based processes for selective capture of CO_2 from post-combustion gas mixture.

Received: April 1, 2013
Published online: June 20, 2013

Keywords: CO_2 separation · flue gas · green synthesis · metal–organic frameworks · zirconium

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