

# RSC Advances



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. This *Accepted Manuscript* will be replaced by the edited, formatted and paginated article as soon as this 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

## The elasticity of MOFs under mechanical pressure

Ke. Yang<sup>ab\*</sup>, Guanglin Zhou<sup>a</sup>, Quan Xu<sup>a</sup>,

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

DOI: 10.1039/x0xx00000x

www.rsc.org/

Nowadays there is fast growing interest for characterization of mechanical behaviors of different classes of MOFs materials under moderate and high applied pressure to search the stable one to resist to different mechanical constraints in both processing and complex applications. This review article presents the performance and properties of rigid and flexible Metal–Organic Frameworks (MOFs) under mechanical pressure without or with different pressure-transmitting media. With the current reports, we could find a wide range of the bulk modulus of MOFs, which are mainly lower than the traditional porous material zeolite. Among all the MOF materials discussed in this article, the HKUST-1 (Cu-BTC) has the biggest bulk modulus. And as a outlook we discussed the possibilities of MOFs in the applications as the mechanical energy absorption/storage materials.

### Introduction

As a very important series of porous crystal materials, Metal organic frameworks (MOFs) have a large diversity and are controllable in their pore size, shape, topology and chemical environment via the selection of different metal centre and organic linkers. As MOFs have the combine properties of polymers and inorganic materials, they are very different with the traditional polymers and inorganic porous materials such as zeolite. The new structure design and synthesis, properties and

applications researches are very hot field in the recent decades. In order to fully achieve their utilization functionalities in the different fields such as, gas storage/ separation, catalysis, sensors, electronic devices and many others, besides high chemical and thermal stabilities, MOFs must be also stable enough to resist to different mechanical constraints in both processing (also called shaping) and various practical applications condition. There is nowadays fast growing



Ke Yang

Ke Yang received his Ph.D. degree from the Institute Charles Gerhardt Montpellier, Université de Montpellier in 2014. He joined the faculty of Institute of New Energy, China University of Petroleum (Beijing) in 2015 as a lecturer. His research interest focuses on the MOFs materials synthesis, physical properties and application on energy storage and gas adsorption.



Guanglin Zhou

Guanglin Zhou received his Ph.D. degree from the College of Chemical Engineering, China University of Petroleum (Beijing) in 2009 with Jinsen Gao. He is an Associate Professor in Institute of New Energy, China University of Petroleum (Beijing). His research interest focuses on technology of petrochemical and coal chemical, the industrial application of catalyst and adsorber.

<sup>a</sup> State Key Laboratory of Heavy Oil Processing, Institute of New Energy, China University of Petroleum (Beijing), Beijing, 102249, China.  
E-mail: [yangke1015@126.com](mailto:yangke1015@126.com)

<sup>b</sup> Institut Charles Gerhardt Montpellier UMR 5253 CNRS UM ENSCM, Université de Montpellier, CC 15005, Place Eugène Bataillon, F-34095 Montpellier cedex 05, France

Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

This journal is © The Royal Society of Chemistry 20xx

interest for characterization of the mechanical behaviours of this class of materials under different conditions which have been discussed in theory by Cheetham *et al.*<sup>1</sup>. In recent years, more results are reported especially the research of our team and co-

workers in the flexible MOFs as MIL-53 (MIL stands for Materials of the Institute Lavoisier) serious and the MIL-47, which we pull it from the rigid to flexible field<sup>2</sup>. Indeed, the mechanical constraint can load on the MOFs in terms of tension, compression, shear, bending, torsion, impact or any combinations of the above, depending on the explored applications and the nature/magnitude of the loads. The properties of the MOFs were intensively explored under low mechanical loads within the elastic limit where the deformation is usually relatively small and reversible. In this content, a series of experimental techniques including, the high-pressure x-ray diffraction, and the neutron diffraction were employed sometimes in tandem with quantum as well as force field based molecular simulations to determine the corresponding elastic properties of MOFs. In this review we mainly discussed about the bulk modulus (K), the inverse of compressibility, corresponding to a measure of the mechanical resilience of the MOF framework against volumetric changes under uniform hydrostatic pressure.

**Quan Xu**

*Quan Xu received his Ph.D. degree from the Department of Materials Science and Engineering, University of North Texas in 2013. He is an Associate Professor in Institute of New Energy, China University of Petroleum (Beijing). His research interest focuses on the development of membrane catalysis technology, bioinspired materials, nanomaterials for environmental applications and bio-devices.*

In the typical industrial processing and applications explored so far by the collaborators of the group (gas/vapour adsorption-separation), the MOFs undergo many cycles of pressurization/compression in hydrostatic conditions and indeed the K elastic property is the most relevant mechanical properties of the host framework to be characterized. In this review, we have a global overview of the literature dealing with this elastic property. Other mechanical properties such as the hardness, a measure of the framework resilience towards permanent plastic deformation, the yield

strength and the fracture toughness are much more scarcely explored so far in the fields of MOFs<sup>1</sup> and thus they are not further detailed here.

Above the estimation of these elastic properties, the structural behaviour for a series of both rigid and flexible MOFs was intensively characterized by mercury porosimetry, x-ray and neutron diffraction experiments under moderate and high applied pressures. These different characterization focus on the loss of crystallinity, the framework collapse and even the amorphization of a series of MOFs under hydrostatic compression using specific cells including the Diamond Anvil cells (DAC). Finally, the promising future of some MOFs for mechanical energy absorption related applications are discussed and proposed.

## Structural behavior of MOFs under applied pressures

### 1. Rigid MOFs

Cu-BTC (BTC for benzene-1,3,5-tricarboxylate) is the one of the first investigated rigid MOFs by high pressure x-ray diffraction experiments. Chapman *et al.*<sup>3, 4</sup> first revealed that Cu-BTC showed a linear framework compression up to ~2 GPa in the absence or in the presence of Fluorinert as pressure-transmitting media which is assumed to not enter the pore. A relative small unit cell variation of ~6% was evidenced and this phenomenon was fully reversible although some changes in sample morphology were observed depending on the rate of pressure release. This experimental observation was further confirmed by molecular dynamics simulations based on a flexible force field to represent the MOF framework<sup>3, 4</sup> emanating from two different groups.

Moggach *et al.*<sup>5</sup> further conducted high pressure single crystal measurements on MOF-5 in the presence of diethylformamide (DEF) which is supposed to enter the pores. They reported Density Functional Theory (DFT) calculations for the empty solid as it was the only way to probe the mechanical properties of this solid in the absence of guest molecules, the size of its pore being too large to avoid the inclusion of the pressure-

transmitting media they currently used. They predicted a gradual decrease of the unit cell volume up to 14% at 3.2 GPa, this compressibility being mediated through the Zn-O bonds. Above this critical pressure, this solid was shown to be amorphous.

High-pressure x-ray powder diffraction measurements were also performed by Chapman *et al*<sup>6</sup> on the ZIF-8 (ZIF for Zeolitic Imidazolate Framework) solid under an applied pressure up to 1 GPa without fluid (non-hydrostatic) or with the non-penetrating inert fluid, the Fluorinert in order to focus only on the intrinsic high-pressure behavior of this MOF. As illustrated in Figure 1, they reported that the framework compresses rapidly with a unit cell variation of 5% over 0.3 GPa while for a pressure above 0.34 GPa an irreversible structural transition occurs corresponding to an amorphization of the structure which however retains some structural order.

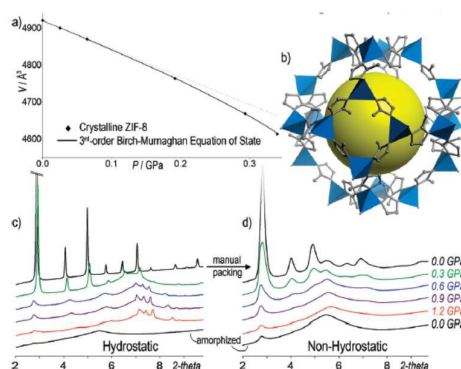


Figure 1: Relative change in lattice parameters for ZIF-8 up to 0.34 GPa before the amorphization occurs as evidenced by the high pressure diffraction data recorded under hydrostatic and non-hydrostatic compression ( $\lambda=0.60511\text{\AA}$ ) (adapted from Ref.<sup>6</sup>).

The  $\text{Zn}(\text{Im})_2$  phase and its  $\text{LiB}(\text{Im})_4$  boron imidazolate frameworks analogues with alternate Zn cations being replaced by Li and B, respectively, were also explored by high pressure single crystal diffraction<sup>7</sup>. It was the first article reported that the Zn-phase undergoes a phase transition in the range of 0.54-0.84 GPa corresponding to a relative volume change of 9% while the tetragonal symmetry is maintained<sup>7</sup>. The  $\text{LiB}(\text{Im})_4$  was established to be more mechanical resilient with a similar phase transition occurring at higher pressure (1.69 GPa) with a smaller unit cell volume change

(~6%). These data were further discussed in light of complementary results issued from nano-indentation measurements and DFT calculations.

High-pressure single crystal experiments reported recently by Moggach *et al*<sup>8</sup> also evidenced an amorphization of the scandium terephthalate  $\text{Sc}_2\text{BDC}_3$  (BDC for 1,4-benzene dicarboxylate) in the presence of the non-penetrating Fluorinert at the same range of applied pressure (0.4 GPa) which was this time fully reversible once the applied pressure was released.

Another MOF labeled as ZAG-4 (ZAG stands for Zinc alkyl gate) which is comprised of Zn-O-P-O 8-membered rings fused through zinc into a 1-D chain was also recently investigated as single crystal using a 4:1 methanol/ethanol mixture as transmitting medium<sup>9</sup>. This material showed a gradual decrease of its unit cell volume up to 10 GPa corresponding to a relative change of 27% without any loss of crystallinity. This transformation was shown to be fully reversible, the quality of the single crystal being intact after a release of the pressure.

## 2. Flexible MOFs

The first work on the very well-known breathing MIL-53(Cr) was reported in 2010 by the Madirel group in Marseille. Beurroies *et al*<sup>10</sup> evidenced by mercury porosimetry experiments an apparent volume of intruded Hg at about 55 MPa that does not correspond to any porosity of this solid (Figure 2). Such a signature was assigned to a structural transition involving a unit cell volume change of ~38% which was not confirmed by further analysis.

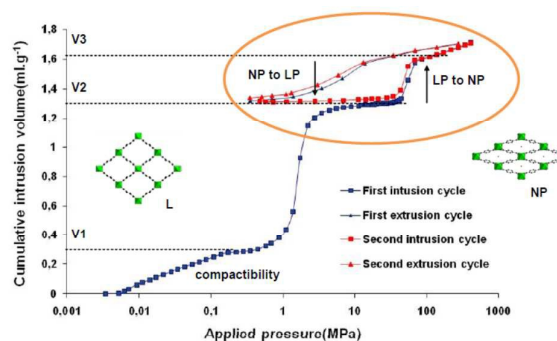




Figure 2: Cumulative volume of intruded mercury in a two cycles Intrusion–extrusion as a function of the applied pressure obtained for the MIL-53(Cr) sample (adapted from Ref.<sup>10</sup>).

A computational approach based on Molecular Dynamics simulations using a flexible force field for the framework was further performed by the group and provided the first theoretical confirmation that this experimental findings can be assigned to a sudden contraction of the structure under an applied external pressure about 50 MPa (Figure 3) corresponding to a structural transition between a large pore and a closed pore forms which involves a unit cell volume change (32%) of similar magnitude than the one obtained by porosimetry measurements<sup>10, 11</sup>. This structural switching was predicted to be fully reversible consistent again with the experimental results. Additionally, the incorporation of CO<sub>2</sub> within the pores was shown to induce an additional internal stress on the framework that leads to (i) a significant decrease of the external pressure required to induce the structural switching of the MIL-53(Cr) and (ii) an irreversible structural transformation as depicted in Figure 3<sup>11</sup>.

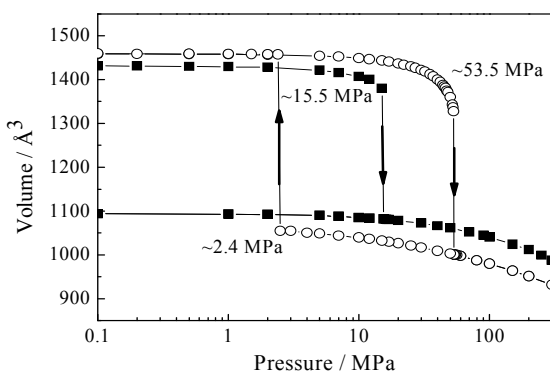


Figure 3: Evolution of the simulated unit cell volume for MIL-53(Cr) as a function of the external applied pressure at 300 K (bare form: empty circle symbols; loaded with 1 CO<sub>2</sub>/u.c. : solid square symbols) (Reproduced from Ref. 11 with permission from The Royal Society of Chemistry)

In complement to this, the MIL-47(V) solid which has been shown to behave as rigid in the presence of guest molecules<sup>12-15</sup>, was later explored under applied pressure using a combination of mercury porosimetry, Raman spectroscopy, high pressure x-ray diffraction

and molecular dynamics simulations. Here one should notice that silicone oil was used as a pressure-transmitting medium as its kinetic diameter largely exceeds the window size of MIL-47(V) which ensures that it does not penetrate the pores. This joint experimental/ computational effort was able for the first time in this class of solids to unambiguously assign the apparent volume of intruded Hg occurring at ~125 MPa to a reversible structural transition between a large pore and a closed pore versions (Figure 4)<sup>2</sup>.

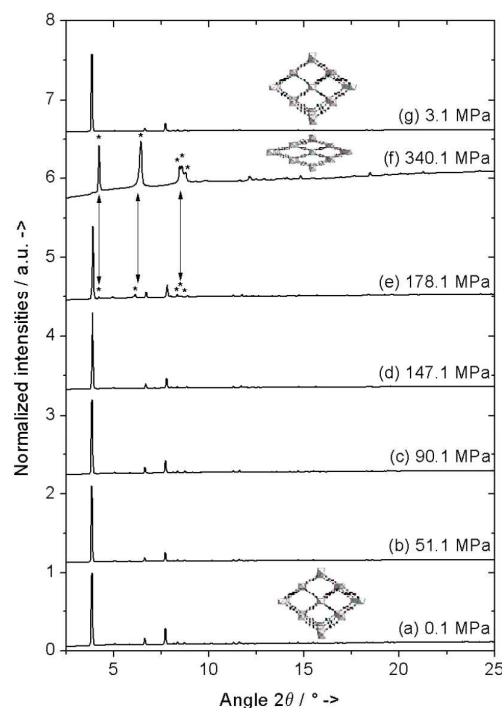


Figure 4: X-ray diffraction patterns of the MIL-47(V) as a function of the applied pressure. Compression (a) 0.1 MPa, (b) 51.1 MPa, (c) 90.1 MPa, (d) 147.1 MPa, (e) 178.1 MPa, (f) 340.1 MPa and decompression (g) 3.1 MPa. The asterisks correspond to the Bragg peaks characteristic of the close pore form of the solid ( $\lambda=0.709622 \text{ \AA}$ ). (Reproduced from Ref. 2 with permission from The Royal Society of Chemistry.)

A very recent high-pressure x-ray powder diffraction reported on the aluminium version of MIL-53<sup>16</sup> in the presence of mineral oil as non-penetrating media confirms the presence of a structural transition from a large pore to a closed pore form but unexpectedly as shown in Figure 5. (i) This phase transition occurs with a gradual decrease of the unit cell volume which

drastically deviates with the sudden transition evidenced for MIL-53(Cr)/MIL-47(V) and (ii) the volume of the closed pore form is only attained at about 6 GPa vs 0.3 GPa for MIL-53(Cr)/MIL-47(V). The amino-functionalized MIL-53(Al) also showed a similar profile of the pressure dependence of the unit cell volume. Such a behavior can be only possible if we assume that mineral oil enters the pore of the MIL-53(Al)-NH<sub>2</sub> structure as this solid is known to exist only in a closed pore form when its pores are empty. The authors further demonstrated that both materials maintain their crystallinity up to high applied pressure (6 and 11 GPa for the pristine and the functionalized solids respectively).

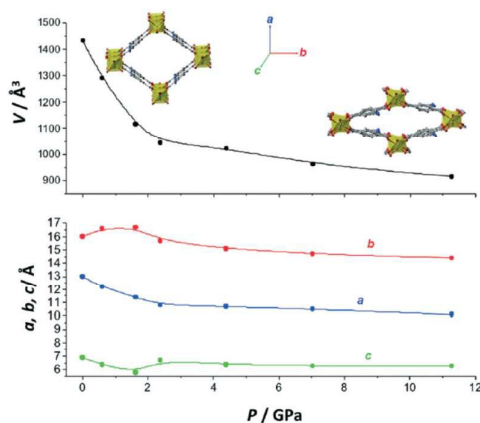


Figure 5: Evolution of the unit cell volume and cell parameters for MIL-53(Al) as a function of the external applied pressure at ambient temperature (Reproduced from Ref. 16 with permission from The Royal Society of Chemistry.).

Another contribution on this family of MIL-53 solids comes from Gascon *et al*<sup>17</sup>, who reported a high pressure x-ray powder diffraction on the very closed pore of MIL-53(In) functionalized with amino function (similar structure than the non-modified MIL-53(Fe)) with the use of mineral oil as non-penetrating media. Figure 6 clearly shows that the crystallinity of this solid is only slightly affected at high pressure ~23 GPa and that the compression of the framework is fully reversible up to pressures of 15 GPa.

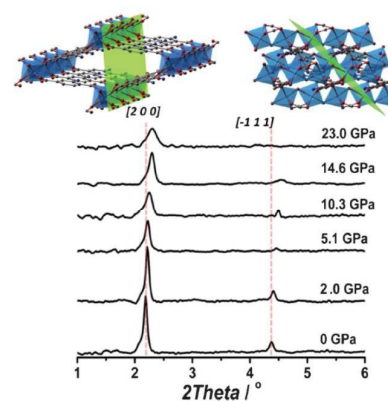


Figure 6: X-ray diffraction patterns of the MIL-53(In)-NH<sub>2</sub> as a function of the applied pressure. The planes correspond to the main reflections as depicted in green ( $\lambda=0.709622 \text{ \AA}$ ) (Reproduced from Ref. 17 with permission from The Royal Society of Chemistry).

### 3. Impact of the presence of guest molecules

The studies related to the guest dependent pressure behaviour of these solids are still rather scarce. They mainly focused on (i) rigid or semi-flexible MOF frameworks (MOF-5, Cu-BTC, ZIF-8), and (ii) a limited set of guest molecules (alcohol/water, diethylformamide, I<sub>2</sub>) used experimentally as pressure transmitting fluids which penetrate the pores. Further, the mechanical properties of these guest loaded MOFs were primarily characterized in the high pressure domain (>1 GPa).

Chapman *et al*<sup>1, 18</sup> revealed for instance by high pressure x-ray diffraction measurements that the incorporation of a mixture of methanol-ethanol-water (MEW) and isopropyl alcohol (IPA) into the pores of Cu-BTC induces a unit cell variation profile which differs with the one obtained with the non-penetrating Fluorinert liquid. The existence of a transition between two distinct regions of near linear compressibility was then observed (see Figure 7) and it could be ascribed to a structural change from a pore filling to a pore emptying states, the value of the transition pressure being higher when the larger isopropyl alcohol molecule is considered. A detailed structural analysis was latter provided by Graham *et al*<sup>19</sup> using high pressure x-ray diffraction experiments performed on single crystals.

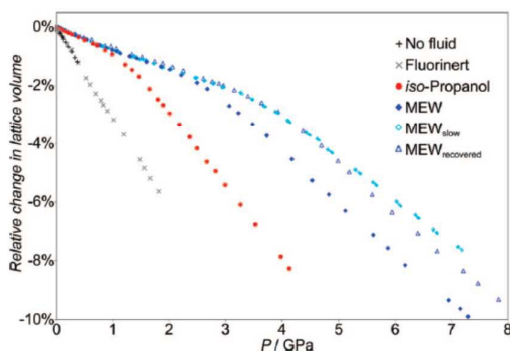


Figure 7: Relative change in lattice parameters for Cu-BTC compressed in the presence of MEW and isopropyl alcohol (IPA) as a function of the pressure, showing two linear regions of compression (adapted from Ref.<sup>18</sup>).

Moggach *et al*<sup>5</sup> further evidenced by means of high pressure single crystal measurements that diethylformamide adsorbed in MOF-5 tends to stabilize the framework by significantly decreasing the magnitude of the unit cell volume change when the pressure increases and also shifting the onset of the amorphization at higher pressure (see Figure 8).<sup>5</sup>

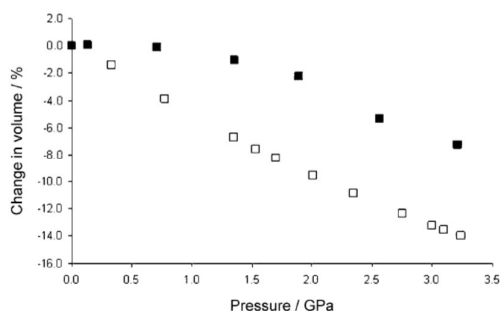


Figure 8: Relative change in lattice parameters for MOF-5 compressed in the absence (empty squares: DFT calculations) and in the presence of DEF (filled squares: experiments) as a function of the pressure (adapted from Ref.<sup>5</sup>).

High-pressure x-ray diffraction experiments using single crystals were performed by Moggach *et al*<sup>20</sup> on ZIF-8 using methanol and ethanol as hydrostatic medium which penetrate into the pores under applied pressure. They found a structural transition in the range 0.90 - 1.47 GPa between two phases (I and II) characterized by the same cubic symmetry (space group  $I43m$ ) but with different twist of the imidazolate ligands in order

to slightly increase the accessible pore volume as illustrated in Figure 9. This transition involves a local rearrangement of the structure which involves only a tiny change of the unit cell volume ( $\sim 1.5\%$ ). This guest assisted structural transition also called “gate closing/opening” thus increases the size and the shape of the narrow channels that connect the pores leading to an overall increase of the pore volume. This structural transformation was shown to be fully reversible once the applied pressure is released. It was also reported that the incorporation of pentane/isopentane instead of methanol/ethanol within the pore of ZIF-8 does not lead to any phase transition under applied pressure which emphasizes that this structural modification is really driven by the nature of the penetrating media. Compared to the empty case which shows an amorphization at low pressure (0.34 GPa), here one observes that the inclusion of guest molecules allow ZIF-8 to be much more mechanical stable up to high pressure.

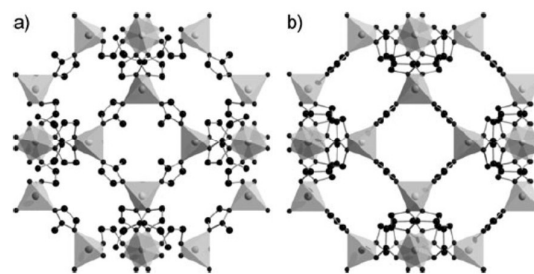


Figure 9: Comparison between the structures of ZIF-8 at ambient pressure (phase I) and at 1.47 GPa (phase II) showing the change in orientation of the imidazolate linkers (adapted from Ref.<sup>20</sup>).

In complement to this contribution, Cheetham *et al*<sup>21</sup> explored by high-pressure single crystal and powder diffraction the mechanical behaviour of ZIF-4. They reported a reversible amorphization of this structure which occurs at different applied pressure depending on the nature and size of the pressure transmitting fluid. In some cases the solid undergoes a structural transition from its initial form (orthorhombic symmetry) to the ZIF-4(I) phase (monoclinic symmetry) corresponding to a unit cell volume change of  $\sim 15\%$ .

Moggach et al<sup>8</sup> further showed that while the empty scandium terephthalate  $\text{Sc}_2\text{BDC}_3$  structure shows a reversible amorphization at 0.4 GPa, the crystallinity of the same solid containing methanol in its pore is retained up to 3 GPa (Figure 10). This increase of mechanical stability was explained by the well-ordered arrangement of methanol within the pores predicted by Monte Carlo simulations which tend to reinforce the resilience of the pore wall.

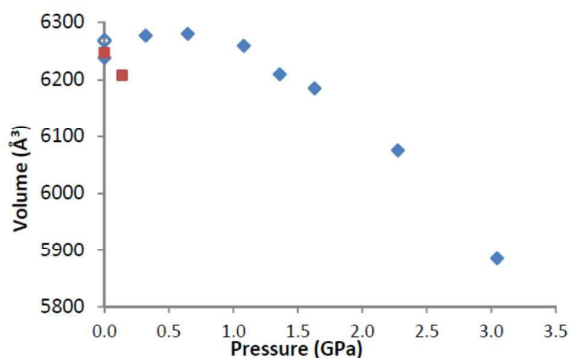


Figure 10: Change in unit cell volume for  $\text{Sc}_2\text{BDC}_3$  compressed in the absence (red squares) and in the presence of methanol (blue lozenges) as a function of the pressure (adapted from Ref.<sup>8</sup>).

Finally, in the case of the highly flexible solid MIL-53(Al)- $\text{NH}_2$ , Gascon et al<sup>16</sup> reported that the use of ethanol instead of mineral oil as pressure-transmitting media drastically changes the pressure dependence profile for the unit cell volume as illustrated in Figure 11. In the case of ethanol, the structural transition between the large pore and the close pore form is not anymore observed (rather a continuous decrease). This was assigned to the formation of densely packed ethanol in the pores which would prevent the structural transition<sup>16</sup>.

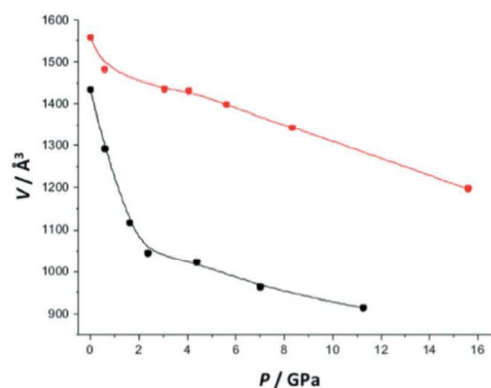


Figure 11: Change in unit cell volume for MIL-53(Al)- $\text{NH}_2$  compressed in the presence of mineral oil (black circles) and of ethanol (red circles) as a function of the pressure (Reproduced from Ref. 16 with permission from The Royal Society of Chemistry )

### Elastic properties of MOFs in hydrostatic conditions

As mentioned in the introduction, one of the most convenient parameters to characterize the mechanical properties of MOFs under uniform hydrostatic pressure is the bulk modulus,  $K$ . The values reported so far in the literature for the different MOFs introduced above were obtained by (i) using a 2nd/3rd order Birch-Murnaghan equation of states<sup>22, 23</sup> to fit the pressure dependence of the unit cell volume or (ii) calculating the product of the initial volume of the MOF structure by the derivative of pressure over the volume. These two approaches were also applied when force-field based molecular dynamics simulations were undertaken. In complement to this, Density Functional Theory calculations were intensively employed to predict the bulk modulus of additional MOFs including the series of IRMOFs, DUTs and UiO-66(Zr)s. These calculations also employ Birch-Murnaghan equation of states to fit the total energy of the structure vs the strain corresponding to the application of a uniform hydrostatic pressure. Table 1 summarizes the experimental and theoretical values obtained for the MOFs in the absence of guest molecules within their pores. It can be observed that only a few results were collected experimentally. The  $K$  values are widely distributed depending on the topology, the density, the



connectivity and the rigid/flexible nature of the MOF frameworks. It can also be observed that the rigid frameworks are obviously more resilient to the deformation and indeed a higher value of  $K$  (lower compressibility) is obtained which make these materials more attractive for further industrial applications. Apart from the direct correlation between a high value of bulk modulus and a low density of the material, the resulting  $K$  values for MOFs are more generally lower than the ones reported for the other well-known family of porous solids, the zeolites (30-70  $\text{GPa}^{-1}$ ) which are usually characterized by a higher framework densities.

In order to clarify the analysis of the data, we also report in Table 2, the  $K$  values for some MOFs which contain guest molecules or solvent used as pressure-transmitting fluid inside their pores. As already emphasized above, the usual trend is an improvement of the mechanical resilience of the MOF framework in the presence of guest which leads to higher values of  $K$ . Interestingly one can observe that some values of  $K$  become even higher than those reported for the denser zeolites which make these considered solids with optimal features for further industrial applications.

We could note that for the same MOFs the  $K$  values get from the experimental and theoretical calculation method could be different, especially for the UIO-66, we trust our experimental data is more acceptable. So if without regarding for the effect of the guest molecules within their pores, the HKUST-1(Cu-BTC) has the biggest bulk modulus among all the results we reported in this article. And with the values in the Table 1 and Table 2, we could clearly conclude that the introduction of the guest molecules within their pores could increase the bulk modulus, the guest molecules share some pressure make the materials more elastic. The differences of bulk modulus between different MOFs should be related to the topology structure, the metal centre, the organic linker, the functionalization group, the chemical environment, but how they affect and which is the main effect still need more targeted and strict experiment to investigate. In our following

report we will discuss deeply how the different metal centres and functionalization affect the mechanical behaviour of MOFs.

Table 1: List of the bulk moduli determined for a series of MOFs without any guest molecules within their pores. (All the experimental values are reported at ambient temperature, Density Functional Theory (DFT) calculations correspond to data at 0 K while forcefield based Molecular Dynamics (MD) are reported also at ambient temperature.

Materials	Framework dynamics	Bulk modulus (GPa)	Method	Reference
MOF-5	Rigid	~17.0	DFT	<sup>24</sup>
	Rigid	~18.2	DFT	<sup>25</sup>
	Rigid	~18.5	DFT	<sup>26</sup>
	Rigid	~17.0	DFT	<sup>27</sup>
	Rigid	~20.0	Forcefield Energy Minimization	<sup>4</sup>
	Rigid	~4.0	MD	<sup>4</sup>
	Rigid	~14.4	Forcefield Energy Minimization	<sup>28</sup>
	Rigid	~15.34	DFT	<sup>29</sup>
	Rigid	~16.66	MD	<sup>30</sup>
IRMOF-8	Rigid	~11.28	MD	<sup>30</sup>
IRMOF-14	Rigid	~10.05	MD	<sup>30</sup>
MOF-C22	Rigid	~6.88	MD	<sup>30</sup>
MOF-C30	Rigid	~4.11	MD	<sup>30</sup>
MOF-177	Rigid	~10.10	DFT	<sup>29</sup>
DUT-6	Rigid	~10.73	DFT	<sup>29</sup>
MOF-14 (interpenetrated)	Rigid	~14.8	DFT	<sup>31</sup>
MOF-14 (single net)	Rigid	~5.5	DFT	<sup>31</sup>
DUT-34	Rigid	~9.1	DFT	<sup>31</sup>
DUT-23	Rigid	~13.2	DFT	<sup>31</sup>

ARTICLE

Journal Name

HKUST-1(Cu-BTC)	Rigid	~30.7	Experiment (No fluid)	<sup>18</sup>
	Rigid	~29.5	Experiment (Fluorinert)	<sup>18</sup>
	Rigid	~25	DFT	<sup>32</sup>
	Rigid	~35.2	MD	<sup>3</sup>
	Rigid	~24.53	DFT	<sup>33</sup>
UiO-66	Rigid	~41.01	DFT	<sup>33</sup>
		~15	Experiment (silicon oil AP100)	Our work
Hf- UiO-66	Rigid	~39.49	DFT	<sup>33</sup>
Ti- UiO-66	Rigid	~42.07	DFT	<sup>33</sup>
UiO-67	Rigid	~17.15	DFT	<sup>33</sup>
UiO-68	Rigid	~14.40	DFT	<sup>33</sup>
ZIF-4-1	Rigid	~15.2	Experiment (Daphne Oil 7474)	<sup>21</sup>
ZIF-4	Rigid	~7.78	Experiment (Daphne Oil 7474)	<sup>21</sup>
Zn(Im) <sub>2</sub>	Rigid	~14	Experiment (Anhydrous 2-propanol)	<sup>34</sup>
LiB(Im) <sub>4</sub>	Rigid	~16.6	Experiment (Anhydrous 2-propanol)	<sup>35</sup>
ZIF-8	Rigid	~6.5	Experiment (Fluorinert)	<sup>6</sup>
	Rigid	~9.23	DFT	<sup>36</sup>
	Flexible	~7.75	Experiment (No fluid)	<sup>36</sup>
NH <sub>2</sub> -MIL-53(In)	Flexible	~10.09	Experiment (Mineral oil)	<sup>17</sup>
MIL-53(Cr)(Large-pore form)	Flexible	~1.8	MD	<sup>11</sup>

Table 2: List of the bulk moduli (K) determined for a series of MOFs with the presence of guest molecules within their pores. (The experiments and the molecular dynamics were done at ambient temperature).

Material	Guest molecules	Bulk modulus (GPa)	Method	Reference
NH2-MIL-53(Al)( Large-pore form, 0 to 2 GPa)	mineral oil	~7.4	Experiment	<sup>16</sup>
NH2-MIL-53(Al)( Large-pore form, 2 to 11 GPa)	mineral oil	~71	Experiment	<sup>16</sup>
NH2-MIL-53(Al)( Large-pore form, 2 to 11 GPa)	Ethanol	~85	Experiment	<sup>16</sup>
MIL-53(Cr)(Large-pore form)	CO2	~0.75(300K)	MD	<sup>11</sup>
HKUST-1(Cu-BTC)	isopropyl alcohol	~117.6	Experiment	<sup>18</sup>
		~25.9		
	methanol-ethanol-water	~116.0	Experiment	<sup>18</sup>
		~33.6		
methanol-ethanol-water (slow)	~114.5	Experiment	<sup>18</sup>	
	~41.9			
methanol-ethanol-water (recovered)	~134.4	Experiment	<sup>18</sup>	
	~32.5			
ZAG-4	Methanol, ethanol	~11.7	Experiment	<sup>9</sup>
ZIF-4-I	methanol : ethanol	~16.45	Experiment	<sup>21</sup>
MOF-5	diethyl formamide (DEF)	22.3-242.5	Experiment	<sup>5</sup>



### Outlook of application: Promising MOFs for mechanical energy absorption/storage

The highly flexible structural behavior of MIL-53(Cr) under mechanical stimuli led the group in Madirel (Université Aix-Marseille) to propose the use of such materials to store the energy in play during the transition between the large pore and the closed pore forms discussed above<sup>10</sup>. This mechanical way to store the energy is complementary to the strategy previously envisaged with the intrusion-extrusion of water at high pressure in hydrophobic solids including mesoporous silica<sup>37</sup> and zeosil<sup>38</sup> (hydrophobic zeolites) and even more recently MOFs with ZIF-8 which showed a shock-absorber behavior at about 27 MPa with a stored energy of 13 J·g<sup>-1</sup><sup>39</sup>. Very recently Patarin *et al* reported that ZIF-8 upon high pressure intrusion–extrusion of aqueous KCl, LiCl, and NaCl solutions of variable concentration can even show higher stored energy sometimes slightly exceeding 20 J·g<sup>-1</sup><sup>40</sup>.

The energy storage capacity of MIL-53(Cr) was thus estimated by the following relationship which corresponds to a work:  $W = P \times \Delta V$  where  $P$  corresponds to the transition pressure and  $\Delta V$  the unit cell volume between the large pore and the closed pore forms. The resulting value of 12 J·g<sup>-1</sup> was revealed to be similar to the best performances reported so far for some of the hydrophobic materials including silica, silicalite and zeosil (~4-12 J·g<sup>-1</sup>)<sup>38, 39, 41, 42</sup> and also for ZIF-8 (13 J·g<sup>-1</sup>)<sup>39, 43</sup>.

Indeed MOFs were already in the good range of performance and because of their extraordinary number of possible structures and chemical compositions, there was at that time a serious hope of obtaining even better performance. This was later confirmed by the exploration of MIL-47(V)<sup>2</sup> in the group which showed an almost similar volume change between the large pore and the closed pore forms while the transition pressure was much higher (125 MPa vs 55 MPa) leading to an even higher absorbed mechanical energy (33 J·g<sup>-1</sup>). In both MIL-53(Cr) and MIL-47(V) cases, the structural transformation was

shown to be reversible and associated with a relatively large hysteresis which makes these materials potentially attractive for energy absorption applications in the form of nano-dampers.

With our research results it could be indeed pointed out that MOF structures do not collapse even under very high pressures up to 5 GPa, which emphasizes the stability of this material upon mechanical pressure, an indispensable prerequisite for further applications. The observation highlights the interest of selecting this family of MOFs compared to other relatively flexible MOFs such as some ZIFs that show an irreversible amorphization even at moderate pressure as discussed above<sup>20</sup>. Moreover, the long term stability of silicalite and hydrophobic samples in water is limited<sup>44, 45</sup>, whereas the applications we mention here for MOFs are expected to be realized in inert fluids.

The general reports are mainly purely force on the physical characteristics such as the unit cell dimensions etc. Still few work was involved to discuss the effect of chemical composition or chemical environment on the elasticity of the MOFs materials. In fact, in our study we have investigated the impact of different metal centres and functionalization on the mechanical behaviour of MOFs, the results show the modifications of the chemical composition could obviously change the pressure domain of stability and compressibility, these will be reported minutely in my next paper soon. The researches of the effect of chemical composition or chemical environment on the elasticity will complete our knowledge on the physic properties of the MOFs materials, and this information also needs to be considered in the design of MOFs for further applications.

These preliminary results pave the way towards either the tuning of existing MOFs or the design of novel ones able to maximize the energy storage capacity which can be achieved by combining large unit cell variations and high transition pressures. Besides the interest of MOFs in terms of nano-springs/dampers, the challenge is to also imagine a way to get a system with an irreversible structural transition in order to absorb the mechanical

energy during the compression without any further release.

### Acknowledgment

We thank the National Nature Science Foundation of China (No. 51505501) for the support.

### Notes and references

- J. C. Tan and A. K. Cheetham, *Chem. Soc. Rev.*, 2011, **40**, 1059-1080.
- P. G. Yot, Q. Ma, J. Haines, Q. Yang, A. Ghoufi, T. Devic, C. Serre, V. Dmitriev, G. Férey, C. Zhong and G. Maurin, *Chemical Science*, 2012, **3**, 1100-1104.
- L. Zhao, Q. Yang, Q. Ma, C. Zhong, J. Mi and D. Liu, *J Mol Model*, 2011, **17**, 227-234.
- J. A. Greathouse and M. D. Allendorf, *The Journal of Physical Chemistry C*, 2008, **112**, 5795-5802.
- A. J. Graham, D. R. Allan, A. Muszkiewicz, C. A. Morrison and S. A. Moggach, *Angew. Chem.-Int. Edit.*, 2011, **50**, 11138-11141.
- K. W. Chapman, G. J. Halder and P. J. Chupas, *Journal of the American Chemical Society*, 2009, **131**, 17546-17547.
- T. D. Bennett, J.-C. Tan, S. A. Moggach, R. Galvelis, C. Mellot-Draznieks, B. A. Reisner, A. Thirumurugan, D. R. Allan and A. K. Cheetham, *Chemistry-a European Journal*, 2010, **16**, 10684-10690.
- A. J. Graham, A.-M. Banu, T. Düren, A. Greenaway, S. C. McKellar, J. P. S. Mowat, K. Ward, P. A. Wright and S. A. Moggach, *Journal of the American Chemical Society*, 2014, DOI: 10.1021/ja411934f.
- K. J. Gagnon, C. M. Beavers and A. Clearfield, *Journal of the American Chemical Society*, 2013, **135**, 1252-1255.
- I. Beurroies, M. Boulhout, P. L. Llewellyn, B. Kuchta, G. Férey, C. Serre and R. Denoyel, *Angew. Chem.-Int. Edit.*, 2010, **49**, 7526-7529.
- Q. Ma, Q. Yang, A. Ghoufi, G. Férey, C. Zhong and G. Maurin, *Dalton Transactions*, 2012, **41**, 3915-3919.
- I. Deroche, S. Rives, T. Trung, Q. Yang, A. Ghoufi, N. A. Ramsahye, P. Trens, F. Fajula, T. Devic, C. Serre, G. Férey, H. Jobic and G. Maurin, *Journal of Physical Chemistry C*, 2011, **115**, 13868-13876.
- S. Rives, H. Jobic, F. Ragon, T. Devic, C. Serre, G. Férey, J. Ollivier and G. Maurin, *Microporous Mesoporous Mat.*, 2012, **164**, 259-265.
- S. Rives, H. Jobic, D. I. Kolokolov, A. A. Gabrienko, A. G. Stepanov, Y. Ke, B. Frick, T. Devic, G. Férey and G. Maurin, *Journal of Physical Chemistry C*, 2013, **117**, 6293-6302.
- F. Salles, H. Jobic, T. Devic, P. L. Llewellyn, C. Serre, G. Férey and G. Maurin, *ACS Nano*, 2009, **4**, 143-152.
- P. Serra-Crespo, A. Dikhtiarenko, E. Stavitski, J. Juan-Alcaniz, F. Kapteijn, F.-X. Coudert and J. Gascon, *CrystEngComm*, 2014, DOI: 10.1039/C4CE00436A.
- P. Serra-Crespo, E. Stavitski, F. Kapteijn and J. Gascon, *Rsc Advances*, 2012, **2**, 5051-5053.
- K. W. Chapman, G. J. Halder and P. J. Chupas, *Journal of the American Chemical Society*, 2008, **130**, 10524-10526.
- A. J. Graham, J. C. Tan, D. R. Allan and S. A. Moggach, *Chem Commun (Camb)*, 2012, **48**, 1535-1537.
- S. A. Moggach, T. D. Bennett and A. K. Cheetham, *Angew. Chem.-Int. Edit.*, 2009, **48**, 7087-7089.
- T. D. Bennett, P. Simoncic, S. A. Moggach, F. Gozzo, P. Macchi, D. A. Keen, J. C. Tan and A. K. Cheetham, *Chemical Communications*, 2011, **47**, 7983-7985.
- F. D. Murnaghan, *Proceedings of the National Academy of Sciences of the United States of America*, 1944, **30**, 244-247.
- F. Birch, *Physical Review*, 1947, **71**, 809-824.
- M. Mattesini, J. M. Soler and F. Ynduráin, *Phys. Rev. B*, 2006, **73**, 094111.
- W. Zhou and T. Yildirim, *Physical Review B*, 2006, **74**.
- A. Samanta, T. Furuta and J. Li, *The Journal of Chemical Physics*, 2006, **125**, -.
- D. Bahr, J. Reid, W. Mook, C. Bauer, R. Stumpf, A. Skulan, N. Moody, B. Simmons, M. Shindel and M. Allendorf, *Physical Review B*, 2007, **76**.
- M. Tafipolsky and R. Schmid, *The Journal of Physical Chemistry B*, 2009, **113**, 1341-1352.
- B. Lukose, B. Supronowicz, P. St. Petkov, J. Frenzel, A. B. Kuc, G. Seifert, G. N. Vayssilov and T. Heine, *physica status solidi (b)*, 2012, **249**, 335-342.
- S. S. Han and W. A. Goddard, *The Journal of Physical Chemistry C*, 2007, **111**, 15185-15191.
- N. Klein, I. Senkovska, I. A. Baburin, R. Gruenker, U. Stoeck, M. Schlichtenmayer, B. Streppel, U. Mueller, S. Leoni, M. Hirscher and S. Kaskel, *Chemistry-a European Journal*, 2011, **17**, 13007-13016.
- M. Tafipolsky, S. Amirjalayer and R. Schmid, *The Journal of Physical Chemistry C*, 2010, **114**, 14402-14409.
- H. Wu, T. Yildirim and W. Zhou, *The Journal of Physical Chemistry Letters*, 2013, **4**, 925-930.
- E. C. Spencer, R. J. Angel, N. L. Ross, B. E. Hanson and J. A. K. Howard, *Journal of the American Chemical Society*, 2009, **131**, 4022-4026.
- T. D. Bennett, J. C. Tan, S. A. Moggach, R. Galvelis, C. Mellot-Draznieks, B. A. Reisner, A. Thirumurugan, D. R. Allan and A. K. Cheetham, *Chemistry*, 2010, **16**, 10684-10690.
- J.-C. Tan, B. Civalieri, C.-C. Lin, L. Valenzano, R. Galvelis, P.-

## ARTICLE

Journal Name

- F. Chen, T. D. Bennett, C. Mellot-Draznieks, C. M. Zicovich-Wilson and A. K. Cheetham, *Physical Review Letters*, 2012, **108**, 095502.
37. B. Lefevre, A. Saugey, J. L. Barrat, L. Bocquet, E. Charlaix, P. F. Gobin and G. Vigier, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 2004, **241**, 265-272.
38. V. Eroshenko, R.-C. Regis, M. Soulard and J. Patarin, *Journal of the American Chemical Society*, 2001, **123**, 8129-8130.
39. L. Tzani, M. Trzpit, M. Soulard and J. Patarin, *The Journal of Physical Chemistry C*, 2012, **116**, 20389-20395.
40. G. Ortiz, H. Nouali, C. Marichal, G. Chaplais and J. Patarin, *The Journal of Physical Chemistry C*, 2014, **118**, 7321-7328.
41. B. Lefevre, A. Saugey, J. L. Barrat, L. Bocquet, E. Charlaix, P. F. Gobin and G. Vigier, *The Journal of Chemical Physics*, 2004, **120**, 4927-4938.
42. N. Gokulakrishnan, J. Parmentier, M. Trzpit, L. Vonna, J. L. Paillaud and M. Soulard, *Journal of Nanoscience and Nanotechnology*, 2013, **13**, 2847-2852.
43. G. Ortiz, H. Nouali, C. Marichal, G. Chaplais and J. Patarin, *Physical Chemistry Chemical Physics*, 2013, **15**, 4888-4891.
44. R. Denoyel, P. Llewellyn, I. Beurroies, J. Rouquerol, F. Rouquerol and L. Luciani, *Particle & Particle Systems Characterization*, 2004, **21**, 128-137.
45. T. Karbowiak, C. Paulin, A. Ballandras, G. Weber and J.-P. Bellat, *Journal of the American Chemical Society*, 2009, **131**, 9898-9899.