

## Electronic Supporting Information to:

### **How ligands improve the hydrothermal stability and affect the adsorption in the IRMOF family**

Luca Bellarosa,<sup>\*a</sup> Juan José Gutiérrez-Sevillano,<sup>b</sup> Sofía Calero,<sup>b</sup> and Núria López<sup>a</sup>

<sup>a</sup> *Institute of Chemical Research of Catalonia, ICIQ, Av. Països Catalans 16, 43007 Tarragona, Spain; email: [lbellarosa@iciq.es](mailto:lbellarosa@iciq.es)*

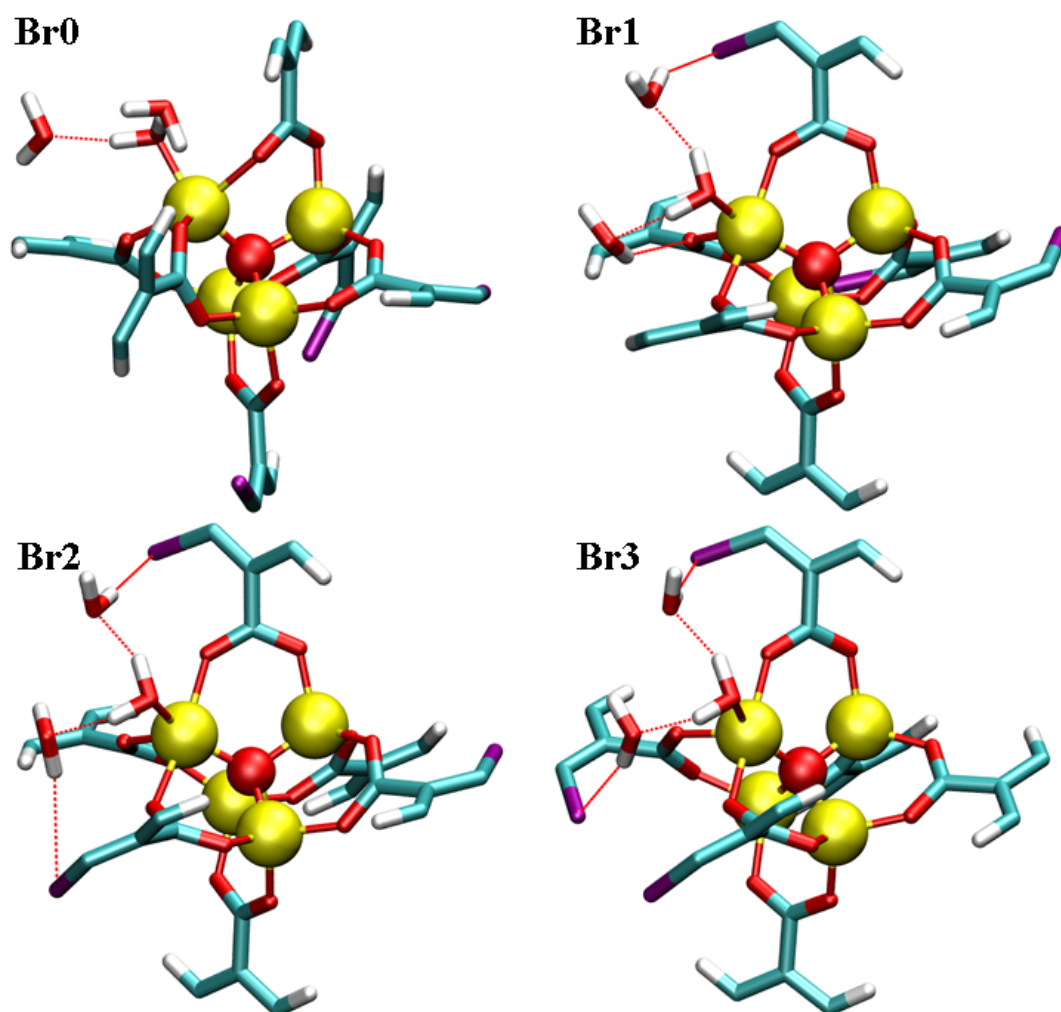
<sup>b</sup> *Department of Physical, Chemical and Natural systems, University Pablo de Olavide, Ctra. de Utrera km. 1, 41013 Seville, Spain.*

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## 1 Initial water configurations

The IRMOF-2 structure consists of a periodic arrangement of  $[\text{Zn}_4(\mu_4\text{-O})(\mu\text{-bdc-Br})_3]_8$  units, see Figure S1 (a). Each unit cell is a cube delimited by eight edges; in each of these edges, the central oxygen  $\text{O}_c$  is surrounded by four Zn atoms and linked by three bdc-Br units. This structure is thus a structural analogue of IRMOF-1 except that one of the H atoms of the terephthalic linker is substituted by Br. The position of Br is scattered, as seen from the X-Ray Diffraction.<sup>1</sup> As shown in the main text of the article, a unit cell of stoichiometry:  $[\text{Zn}_4(\mu_4\text{-O})(\mu\text{-bdc-Br})_3]$  (see Figure 1 (b)) was employed in our initial calculations. The model contains the metal core  $\text{M}_4\text{O}$ , surrounded by six halves of the bromine substituted terephthalic acid, for a total of three bromines per unit cell. This is then repeated in three dimensions to simulate the bulk of an infinite lattice. Due to the disorder generated by the different Br-bdc substituents, four possible conformations were studied accounting for the presence of a variable number of Bromines close to a particular Zn atom (from zero to three, see Figure S2) and labeled **BrN**,  $\text{N}=0\text{-}3$ , being N the number of bromines initially close to the water cluster. Nevertheless, given the low torsional barrier of Br-substituted bdc ( $\sim 0.3$  eV),<sup>2</sup> the configurations can easily transform one to another. The snapshot of all the optimized initial configurations **BrN**,  $\text{N}=0\text{-}3$ , is reported in figure S1.



**Figure S1.** Schematic representation of the IRMOF-2 model lattice with different local configurations at the pocket where the water cluster resides. The number in the label is the number of Br atoms close to the water cluster. Same colour code as Figure S1. H: white sticks; O: red; C: cyan; and Br: purple; Zn: yellow spheres.

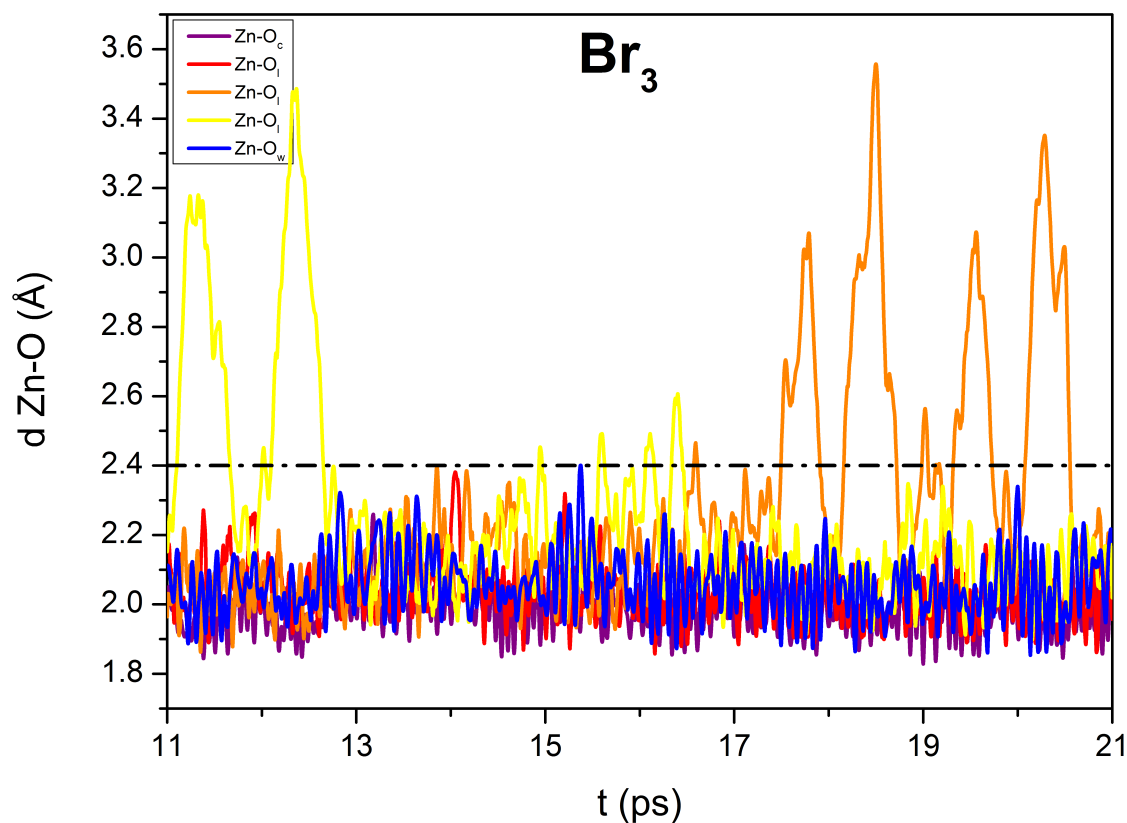
## 2. Details about Born-Oppenheimer Molecular Dynamics

The 11 ps of the four different trajectories have been labeled according to table S1.

**Table S1.** BOMD simulations performed together with the movie file name, split according to its equilibration (*eq*) and the proper run (*md*). **BrN** (N=0-3) refers to the number of bromine atoms close to the water cluster at the beginning of the simulation.

Configuration	Movies
Br0	Br0_eq.mpg / Br0_md.mpg
Br1	Br1_eq.mpg / Br1_md.mpg
Br2	Br2_eq.mpg / Br2_md.mpg
Br3	Br3_eq.mpg / Br3_md.mpg/ Br3_md2.mpg

-) Simulation of the following 10 ps for the Br<sub>3</sub> trajectory



**Figure S2.** Zn-O distances, in Å, during the BOMD simulations, for the next 10 ps of simulation of the conformation **Br<sub>3</sub>**. The dashed black line is the break point of the Zn-O distance. Colour code: Zn-O<sub>c</sub>: magenta; Zn-O<sub>1</sub>: red, orange and yellow; Zn-O<sub>w</sub>: blue line.

From Figure S2 it is possible to see how, even if the bond Zn-O<sub>1</sub> can be broken during the simulation, it is always recovered, leading to an average coordination of 5 for the Zn center.

### 3 Details about Monte Carlo Simulations

Lennard-Jones parameter and point charges used for our models are shown in Tables S2 and S3. The charges were obtained through NBO calculations and adapted to the model used by The heats of the adsorption for several adsorbents on different structures are reported in figure S2.

**Table S2.**  $\epsilon$  and  $\sigma$  Lennard-Jones parameters and charges used for the models of water, methanol, carbon dioxide, and methane.

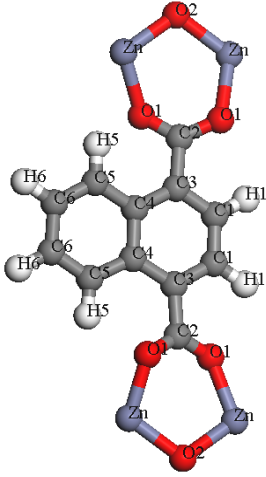
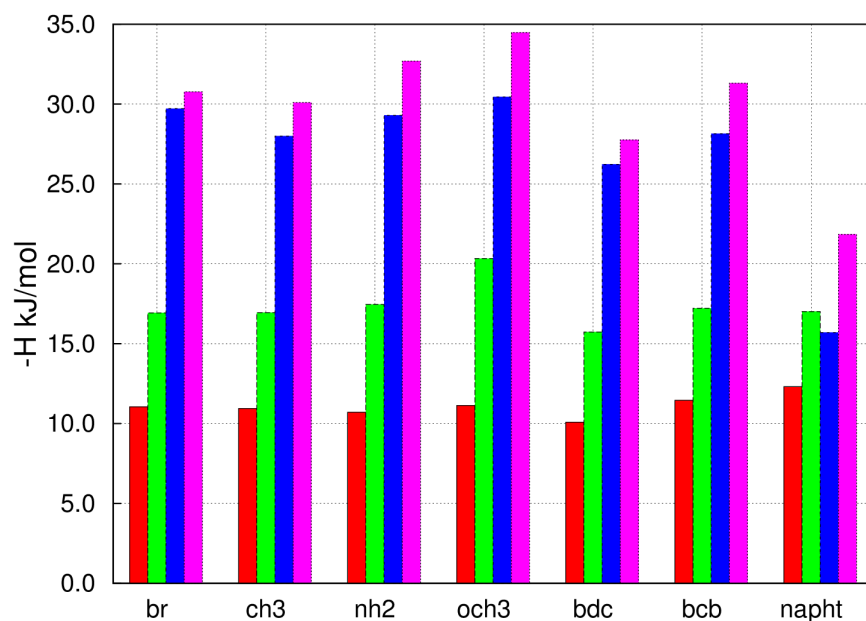
Atom types	$\epsilon/k_B$ (K)	$\sigma$ (Å)	Charge ( e )
C_carbon dioxide	29.933	2.745	0.652
O_carbon dioxide	85.671	3.017	-0.326
CH <sub>4</sub>	158.5	3.72	-
CH <sub>3</sub> _methanol	98.0	3.75	0.265
O_methanol	93.0	3.02	-0.7
H_methanol	-	-	0.435
O_water	89.516	3.097	-
H_water	-	-	0.241
Dummy_water	-	-	-0.241

**Table S3.**  $\epsilon$  and  $\sigma$  Lennard-Jones parameters and charges used for the models of the IRMOF-R substituted structures.

Atom types	$\epsilon/k_B$ (K)	$\sigma$ (Å)	Charge ( e )	
<b>IRMOF-Br</b>				
MOF-Zn	62.4	2.46	1.2	
MOF-O1	48.19	3.03	-0.6	
MOF-O2	48.19	3.03	-1.2	
MOF-C1	47.86	3.47	0.1	
MOF-C2	47.86	3.47	0.6	
MOF-C3	47.86	3.47	0.0	
MOF-C4	47.86	3.47	-0.1	
MOF-Br	186.19	2.99	0.1	
MOF-H1	7.65	2.85	-0.1	
<b>IRMOF-CH<sub>3</sub></b>				
MOF-Zn	62.4	2.46	1.2	
MOF-O1	48.19	3.03	-0.6	
MOF-O2	48.19	3.03	-1.2	
MOF-C1	47.86	3.47	0.1	
MOF-C2	47.86	3.47	0.6	
MOF-C3	47.86	3.47	0.0	
MOF-C4	47.86	3.47	0.0	
MOF-C5	47.86	3.47	-0.03	
MOF-H1	7.65	2.85	-0.1	
MOF-H5	7.65	2.85	0.01	
<b>IRMOF-NH<sub>2</sub></b>				
MOF-Zn	62.4	2.46	1.2	
MOF-O1	48.19	3.03	-0.6	
MOF-O2	48.19	3.03	-1.2	
MOF-C1	47.86	3.47	0.1	
MOF-C2	47.86	3.47	0.6	
MOF-C3	47.86	3.47	0.0	
MOF-C4	47.86	3.47	0.5	
MOF-H1	7.65	2.85	-0.1	
MOF-H2	7.65	2.85	0.125	

<b>IRMOF-OCH<sub>3</sub></b>				
MOF-Zn	62.4	2.46	1.2	
MOF-O1	48.19	3.03	-0.6	
MOF-O2	48.19	3.03	-1.2	
MOF-O3	48.19	3.03	-0.6	
MOF-C1	47.86	3.47	0.1	
MOF-C2	47.86	3.47	0.6	
MOF-C3	47.86	3.47	0.0	
MOF-C4	47.86	3.47	0.15	
MOF-C5	47.86	3.47	0.15	
MOF-H1	7.65	2.85	-0.1	
MOF-H5	7.65	2.85	0.1	
<b>IRMOF-bdc</b>				
MOF-Zn	62.4	2.46	1.2	
MOF-O1	48.19	3.03	-0.6	
MOF-O2	48.19	3.03	-1.2	
MOF-C1	47.86	3.47	0.1	
MOF-C2	47.86	3.47	0.6	
MOF-C3	47.86	3.47	0.0	
MOF-H1	7.65	2.85	-0.1	
<b>IRMOF-bcb</b>				
MOF-Zn	62.4	2.46	1.2	
MOF-O1	48.19	3.03	-0.6	
MOF-O2	48.19	3.03	-1.2	
MOF-C1	47.86	3.47	0.1	
MOF-C2	47.86	3.47	0.6	
MOF-C3	47.86	3.47	0.0	
MOF-C4	47.86	3.47	0.1	
MOF-C5	47.86	3.47	0.0	
MOF-H1	7.65	2.85	-0.1	
MOF-H5	7.65	2.85	-0.05	

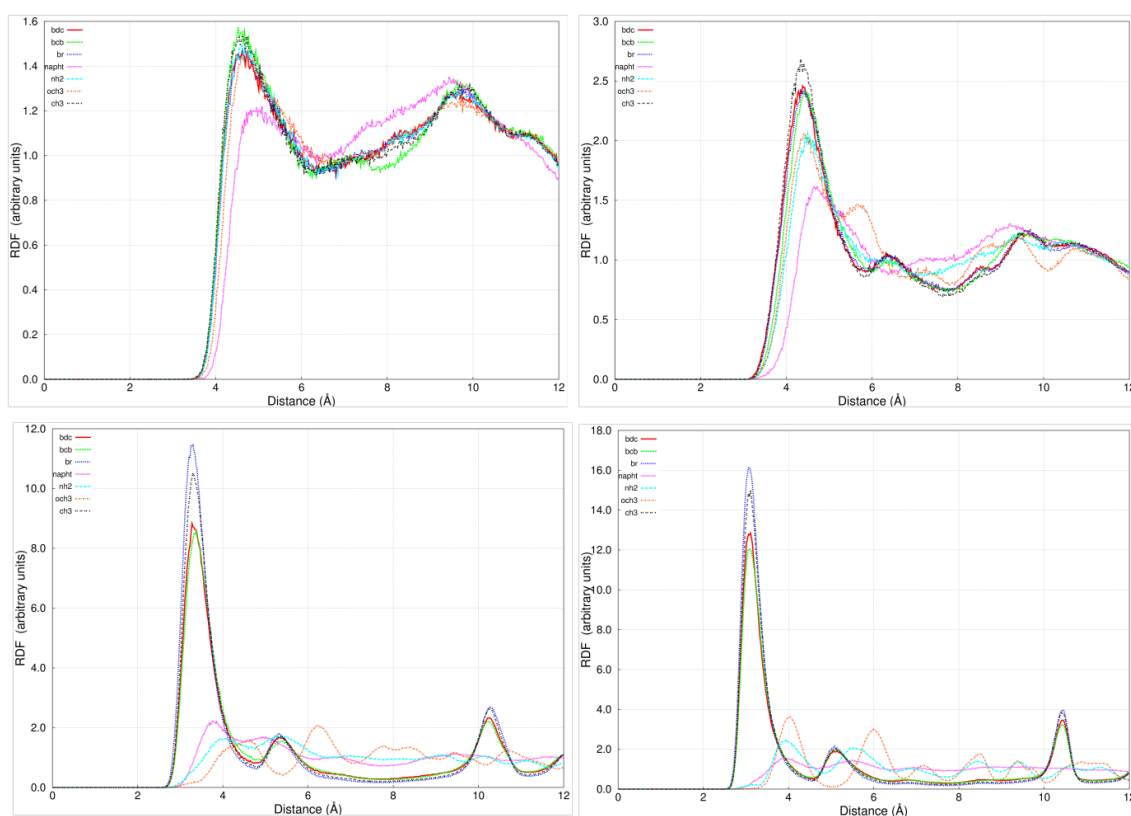
IRMOF-naphthalene			
MOF-Zn	62.4	2.46	1.2
MOF-O1	48.19	3.03	-0.6
MOF-O2	48.19	3.03	-1.2
MOF-C1	47.86	3.47	0.1
MOF-C2	47.86	3.47	0.6
MOF-C3	47.86	3.47	0.0
MOF-C4	47.86	3.47	0.05
MOF-C5	47.86	3.47	0.0
MOF-C6	47.86	3.47	0.0
MOF-H1	7.65	2.85	-0.1
MOF-H5	7.65	2.85	-0.025
MOF-H6	7.65	2.85	-0.025

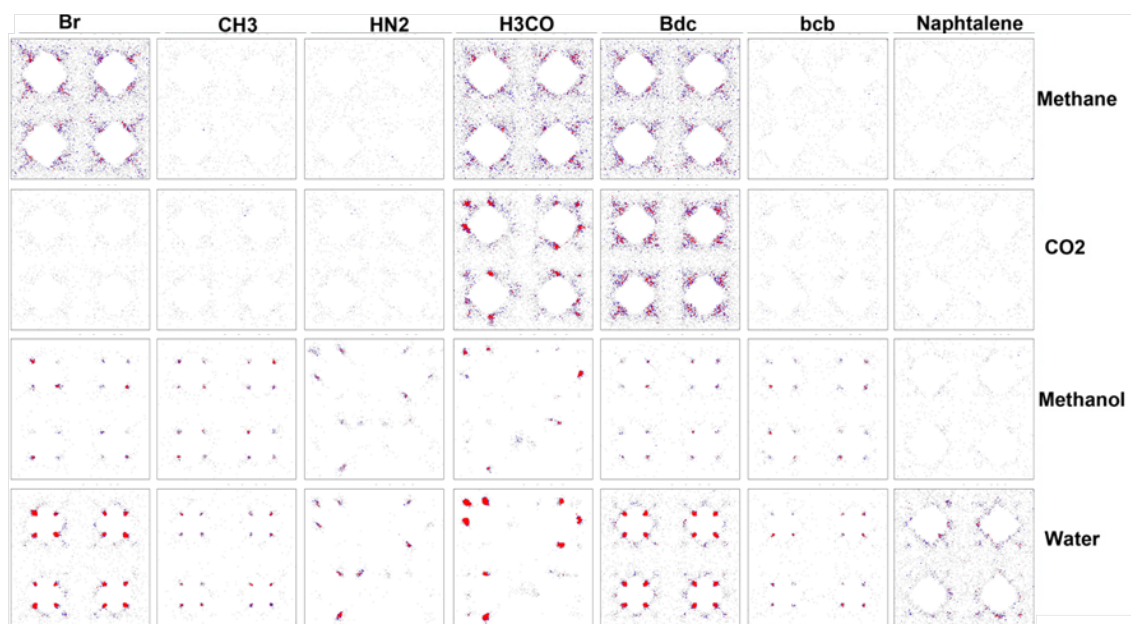
**Figure S3.** Heats of adsorption for methane (red), carbon dioxide (green), water (blue), and methanol (pink) in IRMOF-1 (bdc) and in the IRMOF-R substituted structures.



#### 4 Radial distribution functions (RDF) and adsorption sites



**Figure S4.** C-Zn and O-Zn Radial distribution function at 298 K in functionalized IRMOF-1. a) CH<sub>4</sub>, b) CO<sub>2</sub>, c)CH<sub>3</sub>OH, and d) H<sub>2</sub>O.



**Figure S5.** Average occupation profiles for single molecules at 298 K in functionalized IRMOF-1.

We computed the RDFs of the four molecules to the Zn atoms for a single molecule adsorbed in the structures (Figure S3). We obtained that methane has low interaction

with the metal atoms in all the functionalized structures. Methane molecules are scattered in the whole structure, showing a slight preferential adsorption site around 4.5 Å from the zinc atoms. This spreading can be explained attending to the non-polar nature of the molecule and to the big size of the pore. Similar behavior is observed for carbon dioxide. In this case the interaction with the metal atoms is higher than was methane, but still a wide spread of the molecules is found. The slightly higher interaction can be attributed to the quadrupole moment of the molecule which favours its adsorption closer to the zinc atoms but is not strong enough to avoid the scattering. This behavior is observed for all the functionalized structures as well.

Water and methanol have a different behavior than methane and carbon dioxide. Due to their dipoles both molecules adsorb around 3 Å from the zinc atoms, defining a preferential adsorption site, and showing little scattering inside the structure. This behavior is found in all the structures studied except for functionalized IRMOF-1 with naphthalene, NH<sub>2</sub>, and OCH<sub>3</sub>. With NH<sub>2</sub> and OCH<sub>3</sub>, the preferential adsorption site for water is displaced to a position of 4 Å from the metal centers. In both cases the functional groups modify the previous preferential adsorption site. On the other hand the naphthalene in the functionalized IRMOF-1 deletes the preferential adsorption site and causes that water molecules scatter in the whole structure. Methanol follows a similar behavior than water. This can be observed in Figure S4 where the average occupation profiles for single molecules of water and methanol are shown. Finally we found that the structure with Br is the one which binds stronger water and methanol molecules to the zinc atoms.

### 3. References

1. M. Eddaoudi, J. Kim, N. Rosi, D. Vodak, J. Wachter, M. O'Keeffe and O. M. Yaghi, *Science*, 2002, **295**, 469.
2. E. B. Winston, P. J. Lowell, V. Jaroslav, J. Chocholousová, J. Michl and J. C. Price, *Phys. Chem. Chem. Phys.*, 2008, **10**, 5188.