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Water adsorption in ideal and defective UiO-66 structures

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Abstract

We combine experiments and simulations to study the adsorption of water in several UiO-66 frameworks (ideal and defect-containing structures). We propose a new set of charges for the frameworks that accurately provides the water-structure interaction at the molecular level. The new set is suitable for predicting water adsorption in the ideal UiO-66 structure, providing for the first time, good agreement between experimental and calculated isotherms. The proposed procedure for tuning the point charges of the framework to achieve agreement with experiments is universal and can easily be extended to other MOFs. We explore the structural characteristics in terms of adsorption of water and the potential application of these materials to water harvesting from air. Our results show that the number of introduced defects significantly affect water sorption properties, which results in shifting steep water uptake and increasing saturation loading. Additional performed experiments, such as Ar sorption and the use of the QE-TPDA method allow for a broad characterization of structure-containing defects and the impact that these defects exert on the properties of the materials.

1. Introduction

The metal-organic framework (MOF) UiO-66 [1], is being one of the most studied materials in recent years. The structure, which contains zirconium-based [Zr6O4(OH)4]12 clusters and derived from benzene-1, 4-dicarboxylic (terephthalic) acid (H2bdc) (Fig. 1) is well known for its hydrothermal stability [1–3] and is being used in a wide range of applications ranging from gas adsorption and storage [4–6] to catalytic reactions [7–10]. Recently, although its stability in air is limited [3], it has also been found to be suitable for use in regions with a moderate humidity of approximately 40% [11–13]. UiO-66 is also an example of a material that, contains structural defects, e.g. lack of organic linkers [14–18]. Although the defective frameworks may reveal more desirable behavior, their thermal stability decreases as the number of defects increases [2]. That is why quantifying and understanding the relation between the number of defects and the stability of the material is a crucial issue. Several works have already focused on the adsorption of water in this zirconium MOFs [19–22], however, those allowing to understand the mechanism of water adsorption and introducing defects at the molecular level, are few and far between. For instance, the work of Ghosh et al. [23] shows the influence of defects in the adsorption of water in UiO-66 and the discordance between experiments and simulations. The authors proved that the ideal UiO-66 exhibits hydrophobic behavior, and the missing organic linkers in UiO-66 make the MOF more hydrophilic. Using the same models, Hosseini et al. [24] explored the influence of water and the effect of the defects type on the CO2 adsorption mechanism. Liang et al. [25] synthesized several defective UiO-66 structures and measured the effect of defects in the adsorption of CO2 and water in UiO-66 structures. This work showed that the defect-free UiO-66 allows the separation of carbon dioxide below 1 bar, and defective UiO-66 is superior for high-pressure storage. Planchais et al. [26] and more recently, Wang et al. [27], studied the dynamic properties of water within the UiO-66 MOF by combining classical and DFT calculations, which allowed to explain the self-diffusion mechanism and interaction between water and UiO-66 framework. They used models, Lennard-Jones (L-J) parameters, and charges from the...
There is no evidence of good performance for water. Molecular simulations of water adsorption are challenging due to the nature of the water molecule itself and the high cost of computing power. The choice of the appropriate model of the water molecule and the development of the specific parameters and charges, i.e., the model of guest-host interactions, is often not trivial. Existing force fields and models in many cases fail to reproduce experimental measurements, and to the best of our knowledge, there is no published work showing good agreement between experimental and simulated adsorption isotherms of water in UiO-66. In fact, Hossain et al. [24] compared simulated adsorption isotherms with experimental isotherms of water, finding an acceptable agreement for structure with defects but not for defect-free UiO-66 framework. Recently, Sladekova et al. [29] carried out a simulation study where they analyzed the effect of the set of charges assigned to the atoms of the structure on the adsorption of water and CO₂ in several MOFs. They used set of charges obtained with four types of methods (DDEC [30], CBAC [31], CHELP [32] and REPEAT [33]) and overall, they found little difference in the water adsorption regarding the charges. However, they could not identify the best set as the isotherms were not compared to experimental results. Besides, there are not previous attempts to modify the parameters of the Lennard-Jones interaction or the framework charges in order to reproduce the experimental isotherm. A large number of structures containing defects were modeled for another zirconium material MOF-801 [34], but experimental results could not be reproduced with molecular simulations, which limits the possibility of interpreting physical properties such as heat of adsorption. Only the quantitative and qualitative reproduction of the experiment with simulations allows for a full picture of the molecular mechanism of adsorption and, therefore, a complete understanding of the process.

The main purpose of this work is to bridge the gap between experiments and simulation on the water adsorption in UiO-66 structures that contain structural defects as well as in the defect-free UiO-66 structure. Furthermore, we investigated the effect exerted by each structures on water adsorption. For this, it was necessary to develop a new set of charges by tuning the set of point charges obtained using the Eqq method [35]. With this approach, it was possible to fit the shape of the calculated isotherm to the experimental data and hence, a thorough investigation of the impact of the introduced defects and analysis of various approaches in the context of the set used. The final set is being used to explore the performance of the UiO-66 structures for heat transformation [36], adsorption chilling and most important: harvesting water vapor from the air, which is regarded as a promising way of addressing the problem of drinking water shortages experienced by people living in dry parts of the world [37–40]. High content of moisture in the atmosphere, reaching 10% of the available freshwater pool [41], makes it a valuable water resource, especially in the landlocked countries that cannot resort to desalination of seawater [42,43]. Among different technologies being developed for water harvesting, those based on water physisorption on judiciously chosen adsorbents seem very interesting. Metal-organic frameworks, comprising metal cations (or their clusters) interlinked by organic ligands, are at present considered the best materials for this application [44–46]. MOFs may exhibit outstanding uptake of water and usually require low energy to release it due to low adsorption enthalpy [11]. This may be very useful in places with large difference between daytime and nighttime temperatures, where water can be captured at night and released during a day. In fact, water-harvesting pilot devices employing MOFs as adsorbents have been already proven effective in the field tests in desert conditions, even at low relative humidity of 20% [11–13]. Materials used for this application must fulfill several criteria, such as e.g., low pressure condensation in pores, high water uptake, hydrothermal stability, and non-toxicity [46].

2. Experimental

All chemicals and solvents were purchased from commercial sources (Merck, Avantor) and were used without further purification. The series of UiO-66 samples with varying content of defects were synthesized based on the published method [2].

ZrCl₄ (621 mg, 2.66 mmol), 35% HCl (0.47 ml, 5.3 mmol) and H₂bdcc (885 mg, 5.32 mmol) were dissolved in 16 ml of N,N'-dimethylformamide (DMF), transferred to 25 ml Teflon liners and heated for 24 h in stainless steel autoclaves at 100, 160 or 220 °C, yielding UiO-66,100, UiO-66,160 and UiO-66,220, respectively. The temperatures of synthesis were chosen according to the data available in the literature [2]. The resulting solids were filtered, washed by adding 30 ml of DMF with stirring at 100 °C for 90 min, and filtered again. Prior to activation at low temperatures, the samples were exchanged with methanol for 24 h at 60 °C. After that, each sample was washed three times with methanol, filtered and dried for 2–3 h at 80 °C. The synthesis yields were as follows: 0.634 g, 65.8% for UiO-66,220, 0.833 g, 81.0% for UiO-66,160 and 0.878 g, 62.7% for UiO-66,100.

FTIR spectra were recorded on a Thermo Scientific Nicolet iS10 FT-IR spectrophotometer equipped with an id7 diamond ATR attachment in a wavenumber range from 4000 to 400 cm⁻¹ with 32 scans. Powder X-ray diffraction (PXRD) patterns were recorded at room temperature (295 K) on a Rigaku Miniflex 600 diffractometer with Cu Kα radiation (λ = 1.5418 Å) in a 2θ range from 3° to 45° with a 0.02° step and 3°/min scan speed. Variable temperature powder X-ray diffraction measurements were performed using Anton Paar BTS500 attachment with a heating range from 40 to 460 °C and 30 °C step. At each temperature the samples were conditioned for 10 min prior to the measurement.

Scanning electron microscopy (SEM) images were recorded on a Tescan Vega3 LMU instrument with a LaB6 emitter (voltage of 4 kV). The samples were coated with gold before imaging to reduce charging of the crystals. Adsorption isotherms were measured using static volumetric Autosorb IQ apparatus (Quantachrome Instruments) at 77 K for nitrogen, 87 K for argon and 293 K for water. Prior to the measurements, all samples were activated under vacuum for 1 h at 60 °C, and 2 h at 150 °C (2 °C/
min). Specific surface areas were determined from N\textsubscript{2} isotherms using the BET method [47]. Pore volumes were obtained using the t-plot method. Pore size distribution was determined based on Ar adsorption measurement at 87 K with the NLDFT method [48,49] (using Ar@87 K, zeolite/silica for cylindrical/spherical pores NLDFT adsorption model provided by ASiQwin/Quantachrome software).

Adsorption of water and stability of the studied materials in subsequent cycles of adsorption and desorption was investigated with the quasi-equilibrated temperature programmed desorption and adsorption (QE-TPDA) technique [50,51]. Prior to the measurement, a sample of 1.2, 1.1 and 1.4 mg of UiO-66_100, UiO-66_160 and UiO-66_220 respectively, was activated by heating in a flow (6.5 cm\textsuperscript{3}/min) of pure helium (purity 5.0, Air Products) at 108 °C

For 30 min (ramp 10 °C/min), and then cooled down. After the activation, the gas flow was switched to helium containing water vapor saturated at room temperature, which results in isothermal adsorption at RT. After stabilization of the thermal conductivity detector (TCD) signal, indicating the end of the adsorption process, the actual QE-TPDA experiment was performed by heating and cooling the sample in the flow of He/H\textsubscript{2}O mixture according to the linear temperature program with different temperature changing rates. Sorption capacities were determined by integrating desorption maxima over the range from 25 °C to 108 °C, and recalculating the obtained areas by adequate calibration constant [52]. Desorption and adsorption integral profiles (that may be regarded as approximate isobars) were calculated from the integrated QE-TPDA desorption and adsorption profiles recorded with 1 °C/min, 1.5 °C/min, and 2 °C/min rate. The inlet pressure was 2.7 kPa for UiO-66_100 and 2.6 kPa for UiO-66_160 and UiO-66_220.

3. Computational details

Regarding computational details, we used the TiP4P-Ew [53] model for the water molecule (we previously tested several water models such as SPC/E [54], PPC [55], TiP4P [56], TiP5 - Ew [57]), which is a rigid planar four-site interaction model. It consists of a single van der Waals interaction center located at the atom of oxygen, while the atoms of hydrogen and the dummy free electron have positive and doubled negative charges, respectively (Fig. S1 in the ESI) [53].

The structures were modeled as rigid crystals, where framework atoms were placed at crystallographic positions. L-J parameters for the framework were taken from the DREIDING [58] force field for all the atoms, except for zirconium, which was taken from the UFF [59]. Point charges for the framework charges were developed by modifying the set of charges obtained using the EQeq method [35]. The exact procedure is described in the Results and discussion section. The atom types of our model are shown in Fig. S2 in the Supporting information, and a full set of charges is available in Table S1 of the ESI. Interactions between guest and host were calculated with the standard Lorentz-Berthelot mixing rules. The Lennard-Jones potential is cut and shifted at a cutoff distance of 12 Å. Therefore, tail corrections are not needed. Coulombic interactions were computed by using the Ewald summation method with a relative precision of 10^-6.

Adsorption isotherms and isobars were calculated using Monte Carlo simulations in the grand-canonical ensemble (GCMC), where the chemical potential, volume and temperature are fixed [60]. In our simulations, the pressure is related to the fugacity using the Peng-Robinson equation of state, and absolute adsorption is directly related to excess adsorption using the equation [60]:

$$\theta_{\text{excess}} = \theta_{\text{absolute}} \frac{PV}{\varepsilonRT}$$

where P, V, and T are the pressure, volume, and temperature of the system, R is the gas constant, and \(\varepsilon\) is the gas compressibility. Simulations were performed applying periodic boundary conditions in a 2 × 2×2 unit cell simulation box. Each simulation was carried out by running 5×10\textsuperscript{4} initialization cycles and 5×10\textsuperscript{5} production cycles of translation, rotation, swap and reinsertion trial moves, where all probabilities were equal.

Heats of adsorption were obtained from MC simulations in the canonical ensemble and carried out at zero coverage using the Widom particle-insertion method [61]. Pore volumes and helium void fractions (HVF) were obtained using helium probes and the aforementioned Widom particle-insertion method. All the simulations were performed using the RASPA code [62].

4. Results and discussion

To propose a set of charges suitable for molecular simulation in the water-UiO-66 system, we needed the experimental isotherms in the ideal structure (defect-free) and in the structures with defects. For this, we created three Uio-66 materials with different defect content, replacing the bdc linker with four hydroxyl groups. The number of defects depends mostly on the temperature during synthesis – the lower temperature, the more defective the structure. This was confirmed by FTIR-ATR spectroscopy (Fig. 2). Higher intensity of the band in the range of 2750–3750 cm\textsuperscript{-1} in defective structures is associated with the larger number of –OH groups. Structures of the studied Uio-66 were also studied by powder X-Ray diffraction (PXRD) patterns. For the most defective Uio-66_100 symmetry forbidden low-angle reflections are observed (indicated by vertical dashed lines in Fig. S3 in the ESI). For Uio-66_220, no evidence of the presence of defects was found thus it is assumed to be an ideal structure.

To characterize the porosity of the Uio-66 materials used, we measured adsorption isotherm of nitrogen (Fig. 3). Based on them, textural properties were determined (Table 1). The values of BET surface areas (calculated from the ranges: Uio-66-220: p/p0 = 1.6×10\textsuperscript{-2} – 3.0×10\textsuperscript{-2}, Uio-66-160: p/p0 = 1.8×10\textsuperscript{-2} – 3.1×10\textsuperscript{-2}, Uio-66-100: p/p0 = 2.6×10\textsuperscript{-2} – 5.0×10\textsuperscript{-2}) and the pore volumes are very similar for Uio-66-220 and Uio-66-160 while, the most defected Uio-66-100 adsorbs significantly more N\textsubscript{2}. The obtained BET surfaces are in line with the literature, where the values were around 1470 m\textsuperscript{2}/g for Uio-66-100, 1240 m\textsuperscript{2}/g for Uio-66-160 and 1110 m\textsuperscript{2}/g for Uio-66-220 [2]. Additionally, for this sample, adsorption on the surface can be observed at p/p0 close to 1. This behavior results from the highly developed external surface of the Uio-66-100 material, and thus – the fine crystallinity of the obtained phase.
Table 1  
Characteristics of ideal and defected UiO-66, where PV is the micropore volume and BET the surface area.

<table>
<thead>
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<th>PV (cm$^3$/g)</th>
<th>BET (m$^2$/g)</th>
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<tbody>
<tr>
<td>UiO-66_220</td>
<td>0.353</td>
<td>1115</td>
</tr>
<tr>
<td>UiO-66_160</td>
<td>0.376</td>
<td>1197</td>
</tr>
<tr>
<td>UiO-66_100</td>
<td>0.460</td>
<td>1646</td>
</tr>
</tbody>
</table>

The conducted SEM imaging (ESI, Fig. S4) shows that UiO-66_100 is characterized by the smallest crystallite size (about 0.1–0.3 μm), compared to the other phases, whose crystallites are in the range 0.5–0.9 μm in size. From these considerations it follows, that the higher the synthesis temperature, the greater the tendency to aggregate, and form larger crystals. Similar results were obtained for adsorption of argon (ESI, Fig. S5). These parameters are the indication of a defects concentration that is in line with PXRD at low angle pattern (ESI, Fig. S3). For all the samples, a multistep adsorption is observed in the microporous pressure range (10$^{-6}$ – 10$^{-2}$) showing that UiO-66 is not a typical microporous material with uniform pores. In Fig. S6 in the ESI, we presented pore size distributions of the studied materials based on Ar adsorption. We found two types of micropores at 7 Å and 9 Å, that may correspond to the two types of cavities present in the UiO-66 structure. However, the pore size distribution of UiO-66 100 differs from the others, showing larger micropores (7.5–11 Å and 17 Å). This is another confirmation of the largest number of defects in the material synthesized at the lowest temperature.

Experimental adsorption isotherms of water in the ideal and defective structures are presented in Fig. 4. In the ideal structure, the steep water uptake occurs at a relative partial pressure p/p$^0$ between 0.25 and 0.4. This step occurs at much lower pressures (0.1 < p/p$^0$ < 0.35) in the most defective structure ( UiO-66_100). As can be observed in Fig. 4, there is a shift to the left on the isotherms of the defective structures. The introduction of defects by removing organic linkers causes the remaining site to be terminated with –OH groups. These additional –OH groups increase the hydrophilicity of the framework and cause changes in the shape of the isotherm. Another effect is that capacity of UiO-66 is much higher for the defected material, most likely due to larger voids available for water molecules. As observed in Table 1, the introduction of defects increases the specific surface area (SSA) of the materials. It is clear that it is impossible to obtain materials with different concentration of defects and similar SSA. However, just for theoretical purposes, it is possible to compare the water adsorption of materials with similar SSA by modifying the water isotherm respect to the SSA of the samples. In that case (Fig. S7 in the ESI), at low pressure, the water adsorption is still higher in the most defective structure (UiO-66_100) than in the others, while at high pressure, the defect-free material would exhibit the maximum water adsorption capacity per a given SSA value. These results are in line with previous works that indicate that both uptake pressure and saturation loading for water can be controlled by changing the numbers of defects..

To gain insight into the characteristics of the material, adsorption isotherms of water were supplemented by the QE-TPDA measurements for water (Fig. 5). The profiles consist of desorption maxima and adsorption minima, which correspond to the momentary amount of water vapor that is desorbed or adsorbed in the studied materials at a given pressure. It is noteworthy that desorption maxima are shifted by 25–35 K to higher temperatures when compared to adsorption minima and this effect is greater for faster heating/cooling. On the one hand, it can be related to the dynamic nature of the QE-TPDA measurements. In line with Le Chatelier’s principle, increase of the adsorptive partial pressure during heating suppresses desorption, shifting its maxima to higher temperatures, while its decrease during cooling results in a reverse shift. On the other hand, a hysteresis between desorption and adsorption may be an intrinsic feature of an adsorbent-adsorbate system, resulting from different mechanisms of adsorption and desorption. Indeed, it is observed in the adsorption isotherms of water obtained for UiO-66 by standard volumetric measurements (ESI, Fig. S8).

The QE-TPDA profiles (Fig. 5) provide insights on the adsorption and desorption mechanisms. Two desorption maxima (at 319 and 323 K for 1/K/min) accompanied by two adsorption minima (at 303 and 310 K), clearly discernible in the profile for UiO-66_220, recorded at 1K/min, indicate the presence of two adsorption states in roughly equal proportions. They are also present in UiO-66_160, but with a proportion of the high temperature state. For UiO-66_100, the low temperature part of the profile forms only a broad shoulder, and the high temperature peak is shifted to 328 K. Additionally, a broad high temperature shoulder, most probably corresponding to the strongest adsorption sites related to the structural defects, appears above 331 K. The integral desorption and adsorption curves (ESI, Fig. S9) calculated form the QE-TPDA profiles reproduce well the results of static isothermal measurements, enhancing the adsorption of water in the defected materials UiO-66_160 and UiO-66_100.

To reproduce experimental data, we first calculated the water isotherms in the defect-free structure with universal force fields commonly used in the literature. The L-J parameters for the framework were taken from the DREIDING [58] force field, except for those for zirconium...
atoms, which were taken from the UFF [59]. Point charges for the framework atoms were taken from Yang et al. [28], where they used electrostatic potential (ESP) charges obtained with ChelpG method [63]. We used the UiO-66 structure without defects (labeled as UiO-66_0). As shown in Fig. S10, we were unable to reproduce the experimental results with these sets of L-J parameters and charges. For accurate predictions, we could modify the parameters of L-J interaction or focus on the coulombic interaction. In this type of systems (water-metal clusters), electrostatic interactions are usually dominant [64]. Based on this knowledge and with the aim of continuing to use universal force fields, we chose to provide a new set of charges that, in combination with the TIP4P-Ew water model and L-J parameters from UFF and DREIDING force fields, allowed the prediction of the experimental data. Firstly, the charges were calculated by using the equilibration method based on Ewald sums (EQeq) [35] but they do not lead to an agreement with experimental data (See Fig. 6a). Then all framework charges were increased by 10, 20, 30, 40, and 50% to achieve a match with experimental results for the low pressure range (See Fig. S11 in ESI). This procedure showed that the charges increased by 40% match the

Fig. 5. QE-TPDA profiles of water vapor measured at a heating/cooling rate of 1, 1.5 and 2 K/min for UiO-66,220 (a), UiO-66,160 (b) and UiO-66,100 (c) samples (UiO-66,220: sample mass 1.4 mg, inlet pressure 2.6 kPa; UiO-66,160: 1.1 mg, 2.6 kPa; UiO-66,100: 1.2 mg, 2.7 kPa).

Fig. 6. Experimental and calculated adsorption isotherms (a) and isobars (b) of water vapor in the defect-free UiO-66 structure, at 293 K and 2.6 kPa respectively. Closed symbols stand for adsorption, open symbols for desorption.
experimental isotherm in the p/p₀ range of 0.0–0.2. However, after calculating the entire isotherm (p/p₀ from 0.0 to 1.0), these point charges appeared to be inadequate. We found that the water molecules accumulate in the proximity of the metal cluster, neutralizing it to extent, so the charges obtained by equilibration method underestimate the charge of zirconium atom and its surroundings. Therefore, we increased the charges within the metal-cluster (in the same range as for the framework, by 10, 20, 30, 40 and 50%), leaving linker charges determined by EQeq method intact. As a result, we obtained a relatively high value of the charge of the oxygen atoms between Zr atoms. However, the charges increased by 40% on the zirconium atom and its surroundings allowed to reproduce the experimental isotherm, but now in the entire pressure range (Fig. S11 in ESI). The EQeq model overestimates  valence character of the bonds, as a result of which the ionic (oxide) MOF nodes interact too weakly with polar adsorbate particles. Following this strategy for determining charges, allowed us to eliminate the EQeq drawback to such an extent, that the isotherms obtained satisfactorily reproduce the experiment. Moreover, it can be easily applied to other MOF materials, after prior optimization. We followed the same procedure and applied it successfully for defect modelling in UiO-66. The final set of point charges for all structures (ideal and defective) is listed in Table S1 in the Supporting Information.

The calculated isotherms (initial and final) are compared with the experimental isotherm obtained for the defect-free material UiO-66_220 in Fig. 6a. We found very good agreement between the desorption branch of the experimental isotherm and the simulation results obtained using the new set of charges. Suitability of the developed set of charges in describing this adsorbate-adsorbent system is further corroborated by high similarity of the QE-TPDA-based integral desorption profile and the simulated adsorption isobar (Fig. 6b).

Fig. 7 shows Average Occupation Profiles for the UiO-66_0 structure determined from calculations at 300, 700 and 1700 Pa, which represent distribution maps of around 100, 800 and 1000 water molecules per unit cell, respectively. Water molecules first accumulate in metal-cluster surroundings, because oxygen atoms in zirconium clusters are hydrophilic adsorption centers. Moreover, metal-cluster has a character of an oxide as indicated by the charges from the force field, so both Zr and O atoms cause accumulation of water molecules in this area. Two different adsorption states can be seen – the first in which the molecules surround the metal-cluster, and the second at high pressures, when they fill the spaces around the linkers. These two different states were also observed on QE-TPDA profiles (Fig. 5).

Apart from the ideal UiO-66 structure, we have also investigated the influence of the introduced structural defects on sorption properties. Five models of a defected structure were proposed. In three models one (UiO-66_1), two (UiO-66_2) and eight (UiO-66_8) linkers randomly distributed in the 2 × 2 × 2 crystal structure supercell were missing, and the positions of the terminal hydrogens were optimized. Additionally, we used the defect distribution data pro-posed by Ghosh et al. [23] with 32 linkers missing in 2 × 2 × 2 supercell, in two variants – adjacent (UiO-66_32a) and not adjacent (UiO-66_32). Each missing bdc linker was compensated by four hydroxyl groups. A graphic representation of the distribution of defects in the structure is shown in Fig. S12 in the ESI. Characteristics of the tested systems are provided in Table 2. The volume of micropores and helium void fraction increases with the number of defects, what nicely match the experimental porosity characterization (Table 1)

After removing the bdc linkers, coordination of [Zr₄O₄(OH)₄]₁²⁻ clusters were complemented by hydroxyl groups. This creates an excess local charge that can be compensated in two ways by distributing it on all atoms of the structure or on the added – OH groups. Analysis of adsorption isotherms for UiO-66_1, UiO-66_2 and UiO-66_8 (ESI, Fig. S13) shows that as the defects are introduced, the range of low pressures where adsorption is low, becomes narrower. In addition, the saturation loading and the heat of adsorption (Table 2) increases. This indicates that the UiO-66 framework becomes more hydrophilic (Fig. 8).

It may be noted that with a small number of defects, the difference in the shape of the isotherm between two different charge arrangements is quite small. It becomes significant only when thirty-two defects are introduced, and there the placement of the charge on the –OH groups can be described as more appropriate, as it more closely reproduces the UiO-66 100 isotherm, which contains the largest number of defects (ESI, Fig. S14). The only deviation from the trend can be noticed for UiO-66_32a, when charge is distributed on every atom in the structure. However, in this case, the interference is very large, because a channel along the b-axis is formed throughout the structure. The available space in the structure is reduced by 25% in each unit cell, because the charge of the –OH groups within the defect is not changed. Thus, water molecules still first tend to be near the Zr atom, and there are less available parts of the structure of UiO-66_32a, so the shape of the isotherm is different (ESI, Fig. S14b). By analyzing Radial Distribution Functions (RDFs) for the two structures with the highest number of defects, it can be observed that despite the larger surface area available within the defect, water molecules accumulate at a distance of ca. 3 Å from the zirconium atoms that are fully coordinated by bdc linkers. Within the defects, the molecules accumulate at a distance of ca. 4.5 Å from the zirconium atom. Diagrams showing the radial distances of the oxygen atom in the water molecule from the zirconium atom with the missing linker and the one fully coordinated are shown in Fig. 9.

Fig. 10 shows Average Occupation Profiles determined from calculations at 5, 100 and 1700 Pa for the UiO-66_32 structure with different charge distributions. The profiles confirm earlier assumptions that in the case of distribution of charges on all atoms in the structure, water molecules first accumulate near the Zr atoms. If excess charge is placed on the –OH groups within the defect, water molecules first fill the void created after removing the linker, and then the spaces near the metal
mechanism differs significantly, which accounts for the differences on -OH groups, at 100 Pa.

Table 2
Characteristics of the structures used in this work, where PV is pore volume and HVF is helium void fraction. All parameters are given for 2 × 2 × 2 supercells.

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<thead>
<tr>
<th></th>
<th>UIO-66_0</th>
<th>UIO-66_1</th>
<th>UIO-66_2</th>
<th>UIO-66_8</th>
<th>UIO-66_32a</th>
<th>UIO-66_32</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of defects</td>
<td>0</td>
<td>1</td>
<td>2</td>
<td>8</td>
<td>32</td>
<td>32*</td>
</tr>
<tr>
<td>Number of OH groups</td>
<td>128</td>
<td>132</td>
<td>136</td>
<td>160</td>
<td>256</td>
<td>256</td>
</tr>
<tr>
<td>HVF</td>
<td>0.5071</td>
<td>0.5084</td>
<td>0.5090</td>
<td>0.5149</td>
<td>0.5372</td>
<td>0.5395</td>
</tr>
<tr>
<td>PV (cm³/g⁻¹)</td>
<td>0.4071</td>
<td>0.4089</td>
<td>0.4101</td>
<td>0.4194</td>
<td>0.4577</td>
<td>0.4597</td>
</tr>
<tr>
<td>Heat of adsorption (kJ·mol⁻¹)</td>
<td>46.51</td>
<td>50.70</td>
<td>51.69</td>
<td>52.91</td>
<td>54.20</td>
<td>57.71</td>
</tr>
<tr>
<td>Cell angles (°) (α – β – γ)</td>
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<td>90</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>Framework density (kg·m⁻³)</td>
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<td>1243</td>
<td>1241</td>
<td>1228</td>
<td>1174</td>
<td>1174</td>
</tr>
</tbody>
</table>

Fig. 8. Calculated adsorption isotherms of water in all of the structures with extra charge distributed on –OH groups, at 293.15 K.

Fig. 9. Radial Distribution Functions showing the distance from defective (top) and non-defective (bottom) zirconium atom to oxygen atom from water, for UIO-66_32 and UIO-66_32a structures with extra charges distributed on –OH groups, at 100 Pa.

linkers. Still, in the case of charges distributed on all atoms in the framework, the molecules also accumulate near the metal-clusters at low pressures. This behavior is similar to that of UIO-66_32, but the difference is not that significant and is partly suppressed by the accumulation of water molecules within the defects.

5. Conclusions

We developed a methodology for tuning the set of charges of the framework to reproduce experimentally measured adsorption isotherms of water. Designing several structures with a growing number of defects in silico allowed for interpretation of various defect-dependent isotherms. We showed here that the applied concept of tuning charges is an effective strategy in defect modelling. What is more, this set of charges combined with the TIP4P-Ew water model might be suitable for modeling water adsorption in other MOFs containing zirconium in the metal-cluster. The approach reproduces not only maximal amounts of adsorbed water but the whole shapes of experimental isotherms, including a shift of steep water uptakes towards lower pressures with increasing number of defects in the UIO-66 samples. Maximizing this effect is desirable when designing water harvesting materials. Since the concentration and distribution of defects can be fully controlled in a model to fit an experimental isotherm, this procedure can be used to estimate the number of defects in a material. Conversely, by applying the presented methodology, it is possible to predict (to some extent) adsorption properties of a material with a given concentration of defects. The additional information about the location of adsorbed water molecules at a certain pressure can be obtained for an assumed distribution of defects in a model. However, controlling the number and distribution of defects in synthesis is still a key challenge. We have shown here that experiment supported by simulations gives a deeper insight into the composition and distribution of defects in the structure, and its properties. Furthermore, our results support the idea that UIO-66 could be a potential candidate for use in water harvesting by introducing defects to control its hydrophobic or hydrophilic character.

CRediT authorship contribution statement

Gabriela Jajko: Data curation, Formal analysis, Methodology, Writing – original draft. Juan José Gutierrez-Sevillano: Conceptualization, Formal analysis, Funding acquisition, Methodology, Project administration, Software, Supervision, Writing – review & editing. Andrzej Slawecki: Data curation, Methodology. Monika Szufia: Data curation, Methodology. Paweł Kozyra: Funding acquisition, Methodology, Resources, Supervision. Dariusz Matoga: Data curation, Methodology. Wacław Makowski: Funding acquisition, Methodology, Resources, Supervision. Sofia Calero: Conceptualization, Funding acquisition, Methodology, Resources, Software, Supervision, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence
the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.micromeso.2021.111555.

References


Fig. 10. Average occupation profiles of water in the UiO-66_32 structure at 293.15 K with extra charge distributed on every atom (top) and on –OH groups (bottom). The arrow indicates the location of the metal cluster. For easier interpretation, the UiO-66 structure model has been superimposed.