Supporting Information:

Simulation studies of water adsorption on MIL-101(Cr) revealing the role of inhomoeneous potential field composed of open metal sites and organic linkers

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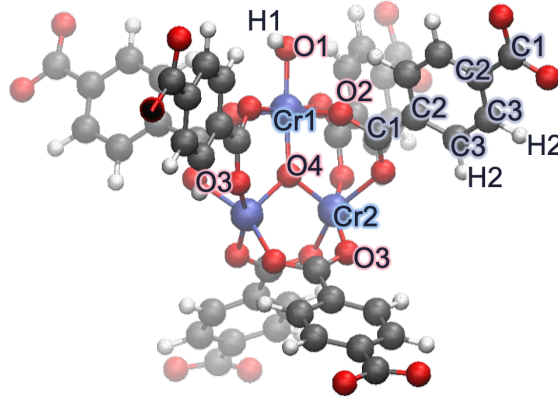E-mail: hiraide@cheme.kyoto-u.ac.jp; nabe@cheme.kyoto-u.ac.jp

Figure S1: Atom types in the MIL-101(Cr) framework.

Table S1: Potential parameters of MIL-101(Cr) without OMS interaction, which was originally reported by De Lange et al.[S1] Atom types of MIL-101(Cr) are shown in Fig. S1.

symbol	$\varepsilon_{\mathrm{ss}}/k_{\mathrm{B}}$ [K]	σ_{ss} [Å]	q [e]
Cr1	7.54829	2.69319	1.28
Cr2	7.54829	2.69319	1.44
O1	48.1581*	3.03315	-0.76
O2	48.1581	3.03315	-0.58
O3	48.1581	3.03315	-0.65
O4	48.1581	3.03315	-0.67
C1	47.8562	3.47299	0.74
C2	47.8562	3.47299	-0.12
C3	47.8562	3.47299	-0.1
H1	–	–	0.35
H2	7.64893	2.84642	0.16

* The value was originally set to zero in their previous work. In this study, to prevent the overlap of O1 and water molecules, the same values as those of the other oxygen atoms were assigned.

Table S2: Potential parameters of MIL-101(Cr) with OMS interaction. Atom types of MIL-101(Cr) are shown in Fig. S1.

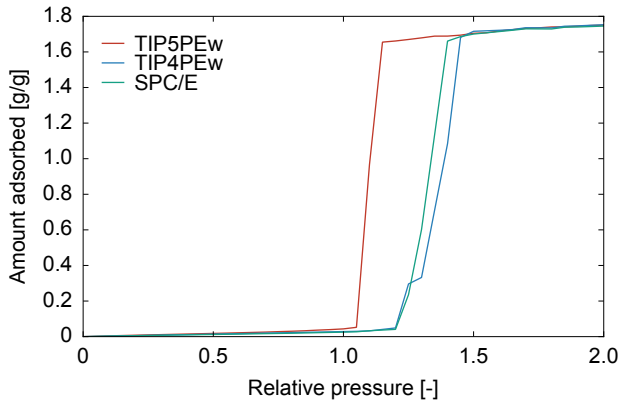| symbol	ε_{ss}/k_B [K]	σ_{ss} [Å]	q [e]
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Cr2	206123.7974	0.64401	1.44
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Figure S2: Calculated adsorption isotherms of TIP5PEw, TIP4PEw, and SPC/E water models on MIL-101(Cr) at 353 K using the atomistic structures after the geometical optimization, where the potential parameters without the OMS interaction (Table S1) were used. The saturated pressures of TIP4PEw and SPC/E were taken from the reports by Vega et al.[S2] and NIST database (https://www.nist.gov/mml/csd/informatics/sat-tmmc-liquid-vapor-coexistence-properties-spce-water-lrc), respectively.
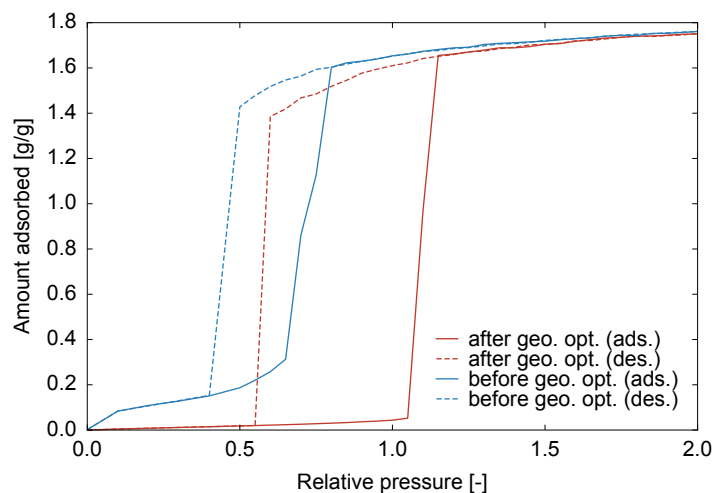
Figure S3: Calculated adsorption/desorption isotherms of water on MIL-101(Cr) at 353 K using the atomistic structures before (blue) and after (red) the geometical optimization, where the potential parameters without the OMS interaction (Table S1) were used.
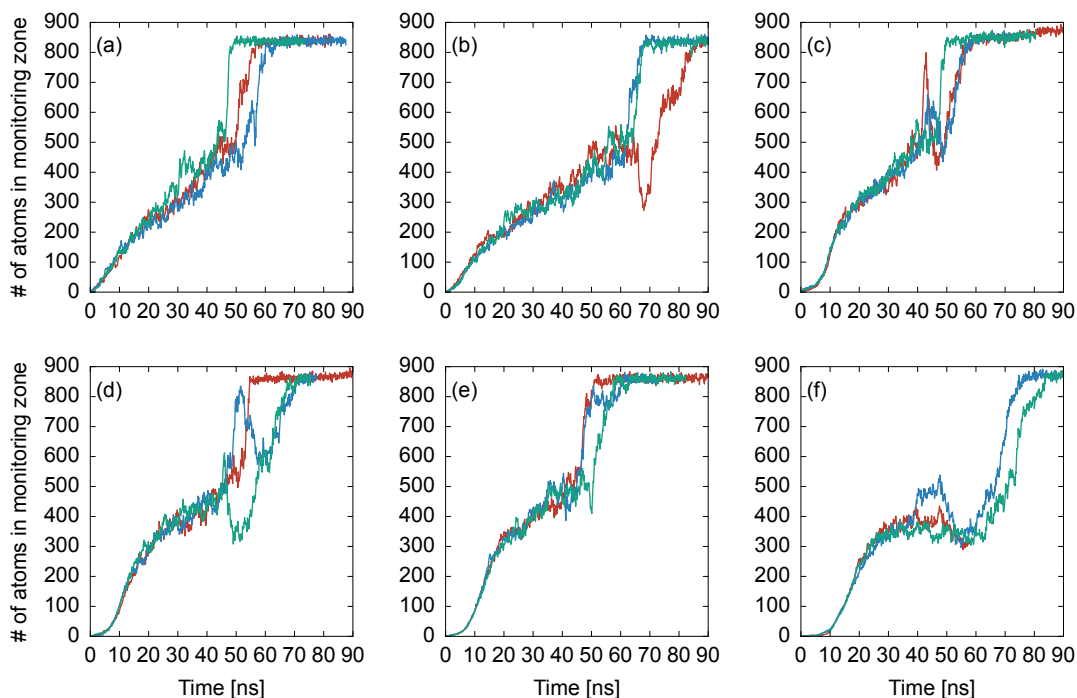

Figure S4: Time evolution of the number of atoms in the monitoring zone for (a) uniform pore model, (b) OMS-2, (c) OMS-3, (d) OMS-4, (e) OMS-5, and (f) OMS-6. The red, blue, and green lines represent the results obtained under the same condition but with different seeds for the random number sequence.
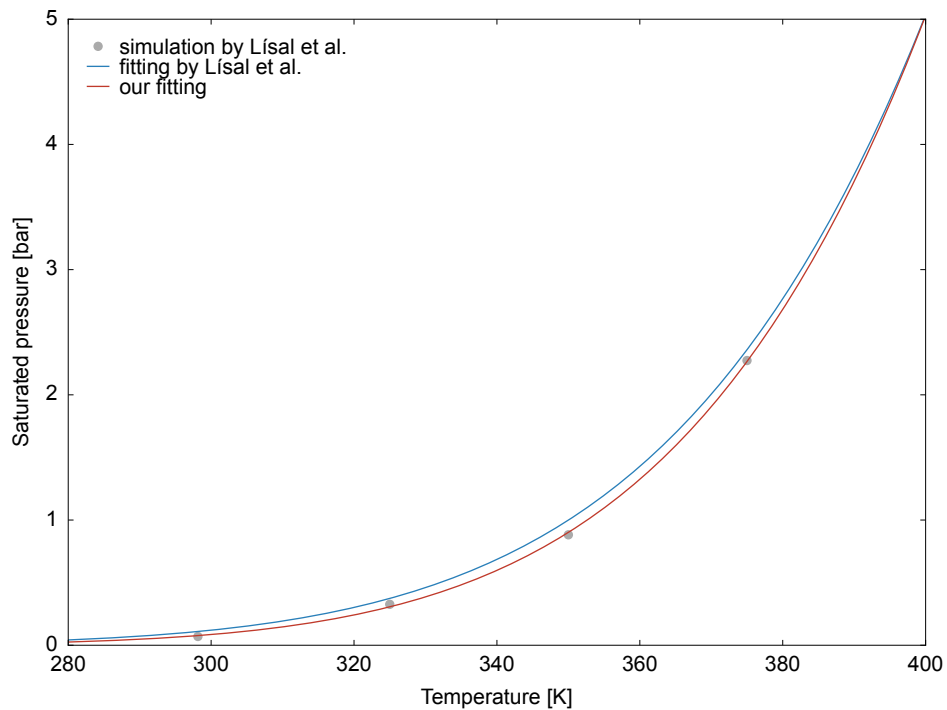
Figure S5: Saturated pressure of TIP5PEw. The gray circles represent simulated values, while the blue line represents the fitted line using the Antoine equation ($\ln P_{\text{sat}}[\text{bar}] = A + B/(T[\text{K}] + C)$), as reported by Lísal et al.[S3] As their fitting was not so accurate around 353 K due to the wide temperature range of data used (298–500 K), we refitted the data within the narrower range of 298–400 K (red line). The original parameters provided by Lísal et al. were $A = 13.642988$, $B = -5073.9387$, and $C = 21.888973$, and our refitted parameters were $A = 12.6097578$, $B = -4065.1598$, and $C = -30.254271$.

S1 Material characterization

A powder X-ray diffraction (PXRD) pattern was recorded on a MiniFlex600 (Rigaku Corp.) operating at $40\,\mathrm{kV}/15\,\mathrm{mA}$ producing Cu Kα radiation ($\lambda = 0.15406\,\mathrm{nm}$) at room temperature ranging from 3° to 55° with the scan rate of 5°/min.

Thermogravimetric analysis (TGA) was performed using a TP-EVO2 SL DyTG/DTA TypeJ (Rigaku Corp.) under nitrogen flow scanning from 25 to 500 °C with a temperature ramp of 1 °C/min.

N_2 adsorption on MIL-101(Cr) was measured at 77 K using a BELSORP-max instrument (MicrotracBEL Corp.). Before the adsorption measurements, MIL-101(Cr) was heated to 373 K for 12 h under a vacuum.

Scanning electron microscopy (SEM) images were obtained using an SU8600 field emission SEM (Hitachi High-Tech Corp.).

These results are shown in Figs. S6 to S9, proving that our synthesized particles are indeed MIL-101(Cr).
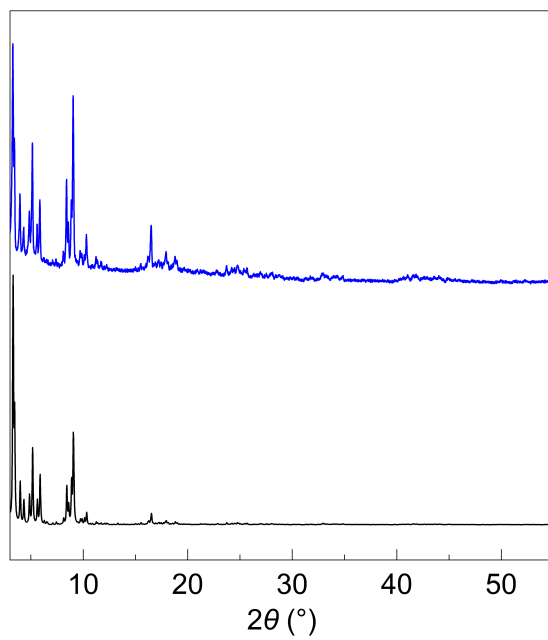
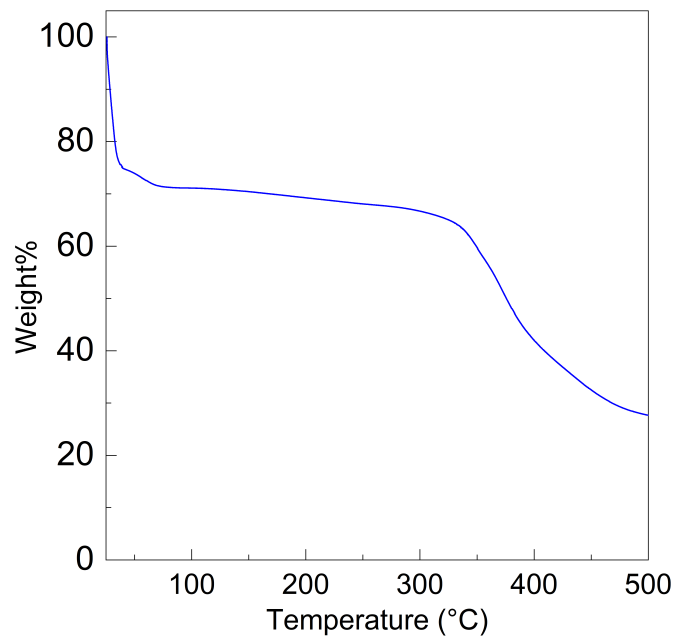Figure S6: PXRD pattern of MIL-101(Cr): top, experimental data; bottom, simulated data.[S4]
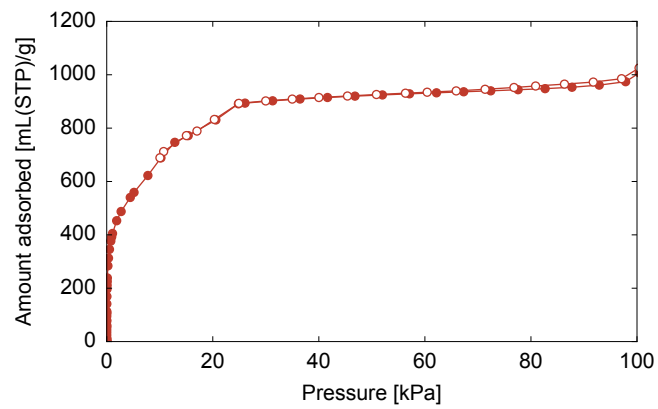

Figure S7: TGA curve of MIL-101(Cr).

Figure S8: N_2 adsorption isotherm on MIL-101(Cr) at 77 K.
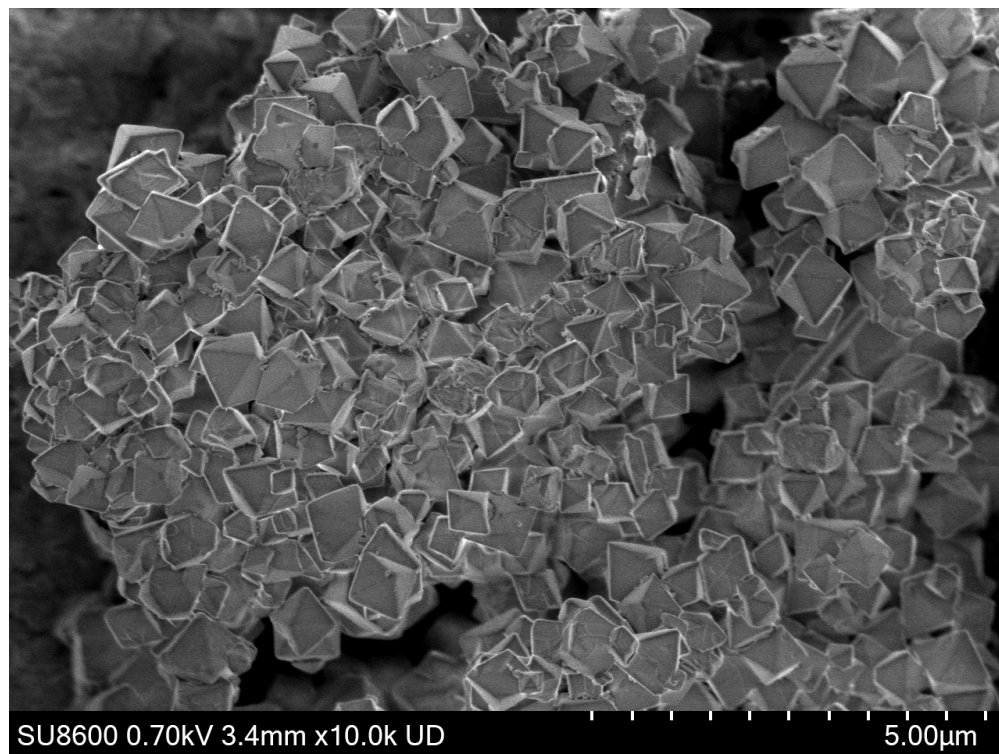

Figure S9: SEM image of MIL-101(Cr).

S2 Validation of the OMS–water interaction potential

Due to the significant computational cost associated with the MP2 calculation, the potential interaction between OMS and water was modeled based on a water molecule with a single orientation, as depicted in Fig. S10a. In order to validate the derived potential model, 10 various cluster models were established by randomly rotating the water molecule, maintaining D_O at 0.22 nm (Fig. S10b–k). The interaction energy between the metal cluster and water molecule, as determined by the MP2 calculation, was then compared to that from the refined force field shown in Table S2.

The results are presented in Table S3, in which coordinates b to k coorespond to Fig. S10b–k. When the interaction energy is relatively low (b–d), both values coincide by approximately 10 kJ/mol. When the interaction energy is large (h–k), although there are large deviations in the values, both the MP2 calculation and the refined force field indicate that the interaction energy is positive, suggesting that the system is unstable. Therefore, the refined force field is qualitatively accurate in expressing the order of the stability of the system and is quantitatively accurate in the neighborhood of the most stable orientation. In light of these results, the refined force field is considered to have reasonable accuracy for use in GCMC simulations to calculate adsorption isotherms.

Table S3: The interaction energy between the metal cluster and water molecule.

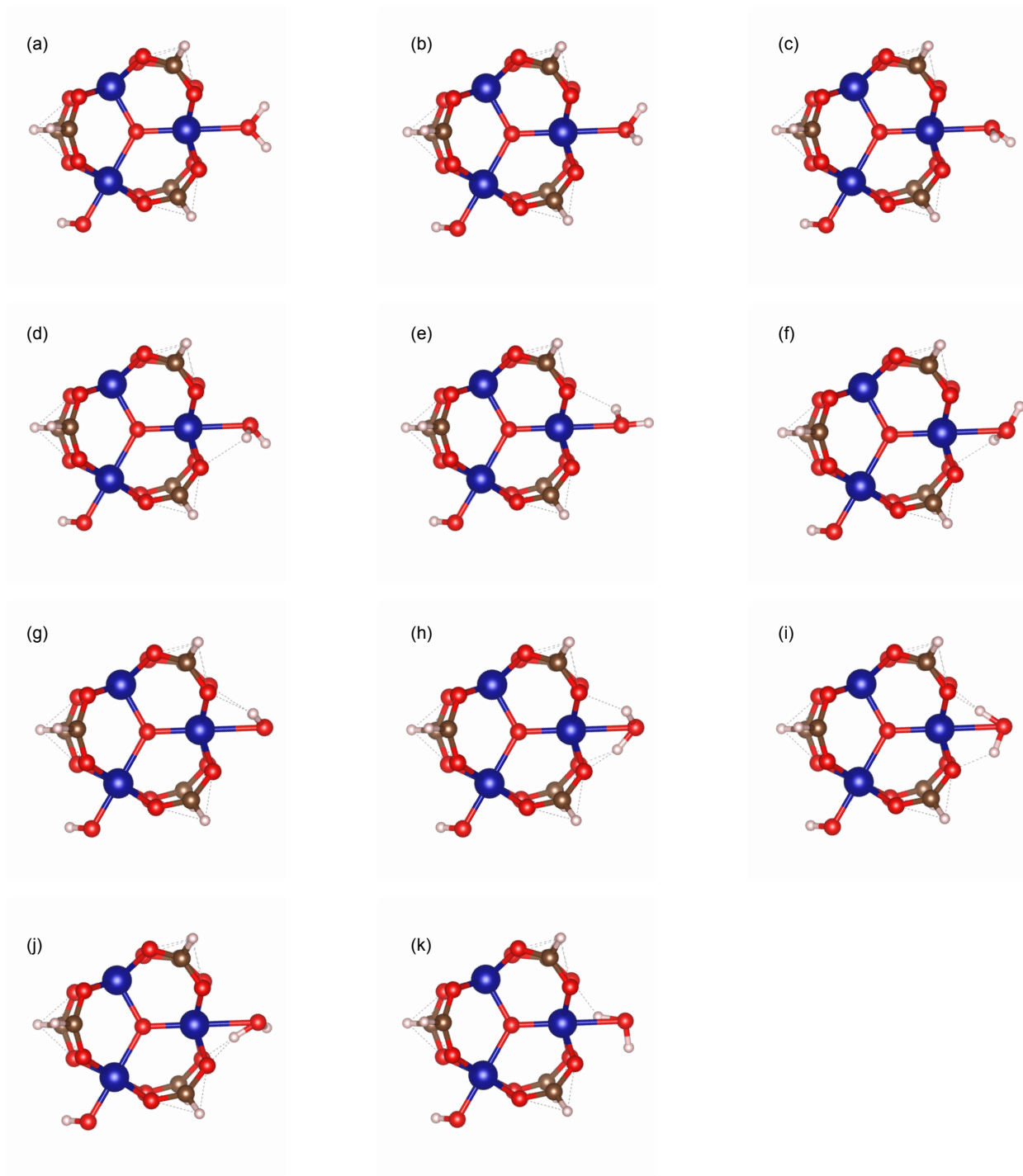| coordinate	MP2 [kJ/mol]	Refined force field [kJ/mol]
a (ref.)	−61.2	−65.4
b	−68.5	−81.6
c	−61.8	−75.3
d	−51.3	−60.7
e	−19.5	−46.6
f	−5.4	−33.1
g	31.2	−5.6
h	89.7	21.4
i	192.5	51.1
j	201.3	43.7
k	339.9	81.1

Figure S10: (a) The cluster model used for constructing the force field with the OMS–water interaction potential. (b–k) The 10 models with different orientations of the water molecule to validate the derived potential model.

References

(S1) De Lange, M. F.; Gutierrez-Sevillano, J.-J.; Hamad, S.; Vlugt, T. J. H.; Calero, S.; Gascon, J.; Kapteijn, F. Understanding Adsorption of Highly Polar Vapors on Mesoporous MIL-100(Cr) and MIL-101(Cr): Experiments and Molecular Simulations. *J. Phys. Chem. C* **2013**, *117*, 7613–7622.

(S2) Vega, C.; Abascal, J. L. F.; Nezbeda, I. Vapor-liquid equilibria from the triple point up to the critical point for the new generation of TIP4P-like models: TIP4P/Ew, TIP4P/2005, and TIP4P/ice. *The Journal of Chemical Physics* **2006**, *125*, 034503.

(S3) Lísal, M.; Nezbeda, I.; Smith, W. R. Vapor-Liquid Equilibria in Five-Site (TIP5P) Models of Water. *J. Phys. Chem. B* **2004**, *108*, 7412–7414.

(S4) Lebedev, O. I.; Millange, F.; Serre, C.; Van Tendeloo, G.; Férey, G. First Direct Imaging of Giant Pores of the Metal-Organic Framework MIL-101. *Chem. Mater.* **2005**, *17*, 6525–6527.