

## Supporting Information for:

# Monte Carlo Simulations of Water Adsorption in Aluminum Oxide Rod-based Metal–Organic Frameworks

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## Supplementary Tables and Figures

**Table S1:** Tabulated crystallographic unit cell parameters and unit cell volume for the *trans* forms (unless otherwise noted) of MOF-303 structures considered in this work. The letter and number in the column headers denote the source of the unit cell parameters: E0, E4, E8, and E40 stand for the unit cells of pristine MOF-303 without any adsorbed water molecules, with 4, 8, and 40 water molecules per unit cell, respectively, extracted from single-crystal X-ray diffraction experiments;<sup>1</sup> while D0 and D4 denote lattice parameters obtained from a full DFT optimization for MOF-303 without any adsorbed water molecules and with 4 water molecules per unit cell, respectively.

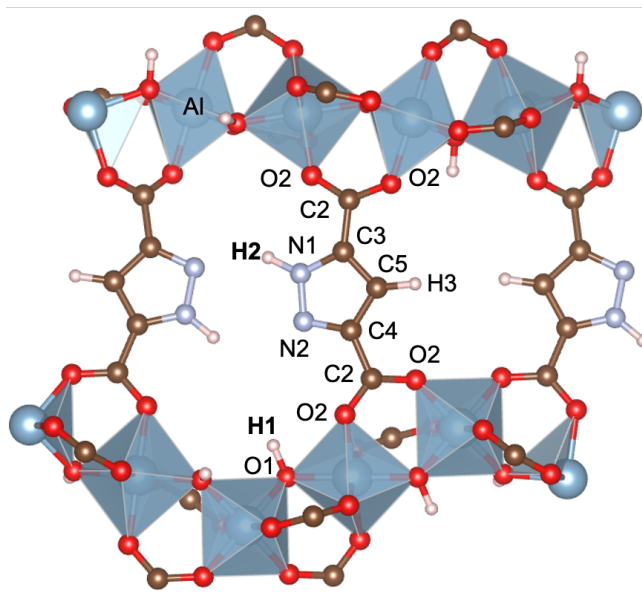
MOF Structure	E0	E4	E8	E40	D0D0	D0D0- <i>cis</i>	D4D4
$a$ (Å)	12.0438 <sub>5</sub>	12.2727 <sub>10</sub>	12.2819 <sub>14</sub>	12.316 <sub>7</sub>	11.897	12.220	12.253
$b$ (Å)	14.9649 <sub>7</sub>	15.4996 <sub>10</sub>	15.5976 <sub>15</sub>	14.893 <sub>8</sub>	15.009	14.621	15.893
$c$ (Å)	14.0794 <sub>7</sub>	13.4203 <sub>12</sub>	13.1958 <sub>16</sub>	13.937 <sub>8</sub>	14.025	13.983	12.820
$\alpha$ (°)	90	90	90	90	90	90	90
$\beta$ (°)	101.929 <sub>2</sub>	103.262 <sub>2</sub>	103.582 <sub>4</sub>	102.278 <sub>8</sub>	101.583	100.573	102.962
$\gamma$ (°)	90	90	90	90	90	90	90
$V$ (Å <sup>3</sup> )	2482.8	2484.8	2457.2	2498.0	2453.4	2455.9	2433.0

**Table S2:** Tabulated energies per unit cell computed from periodic DFT calculations for the pristine (no water) MOF-303 structures in the *trans* and *cis* forms (E0D0, D0D0, and D0D0-*cis*, respectively) and for MOF-303 structures with various water loadings. For the latter, the energy of the “empty” framework after removal of the water molecules without relaxation of the framework atoms is also provided. Furthermore, the probe-occupiable volume (POAV, computed using a spherical probe of 3.154 Å diameter in Zeo++<sup>2</sup>) is reported for the different structural variants. In the structure name, the first letter and number denote the source of the unit cell parameters: E0, E4, E8, and E40 stand for the unit cells of pristine MOF-303 without any adsorbed water molecules, and those with 4, 8, and 40 water molecules per unit cell, respectively, extracted from single-crystal X-ray diffraction experiments;<sup>1</sup> D0, and D4 denote corresponding lattice parameters obtained from a full DFT optimization. The second letter denotes the source for the location of the framework atoms: D for positions resulting from DFT optimization and E for the experimental coordinates of the MOF with no optimization. The second number gives the number of water molecules per unit cell during optimization.

MOF structure	Water loading per unit cell	$E_{\text{lattice}}$ (eV)	$E_{\text{empty}}$ (eV)	$POAV$ (cm <sup>3</sup> /g <sub>MOF</sub> )
E0D0	0	−937.499277	—	0.460
E0D4	4	−997.578020	−936.598125	0.450
E0D8	8	−1055.960772	−935.694280	0.454
E4D4	4	−997.669866	−936.448396	0.438
E4D8	8	−1057.796936	−935.871939	0.429
E8D4	4	−997.619326	−936.370124	0.426
E8D8	8	−1057.796435	−935.773177	0.417
E40D40	40	−1525.78902	−926.765657	0.447
E0E0	4	−985.123773	−925.342094	0.464
E0E0	8	−1043.950222	−925.342094	0.464
E4E4	4	−985.232402	−924.804174	0.450
E4E4	8	−1044.534377	−924.804174	0.450
E8E8	4	−985.299751	−924.819423	0.438
E8E8	8	−1044.671753	−924.819423	0.438
D0D0	0	−937.488916	—	0.452
D0D0- <i>cis</i>	0	−936.555053	—	0.415
D4D4	4	−998.066205	−936.617267	0.416

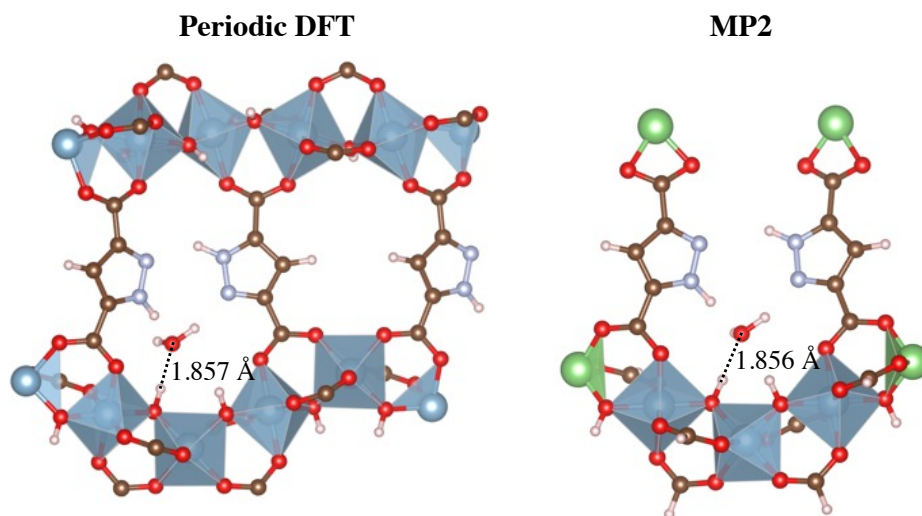
**Table S3:** Lennard-Jones parameters and partial charges used to describe the adsorbate interaction with MOF-303. The DDEC6 charges for the D0D0, E0D0, and E4D4 MOF-303 structures, and the TraPPE–EH charges for pyrazole molecule are also listed with the entries in bold being selected.

Atom type	$\varepsilon / k_B (K)$	$\sigma (\text{\AA})$	$q ( e )$	$q^{\text{DDEC6}} ( e )$			$q^{\text{TraPPE}} ( e )$
				D0D0	E0D0	E4D4	
Al	254.00	4.000	1.64	<b>1.64</b>	<b>1.64</b>	1.65	-
O1	30.19	3.118	-0.98	<b>-0.98</b>	-0.99	-1.01	-
H1 (FF1)	22.14	2.571	0.43	<b>0.43</b>	<b>0.43</b>	<b>0.43</b>	-
H1 (FF2-np)	7.65	2.846					-
H1 (FF2)	0.05	2.846					-
H1 (FF3)	0.00	0.000					-
O2	79.00	3.050	-0.57	-0.59	-0.59	-0.58	-
C2	41.00	3.900	0.704	0.63	0.63	0.63	-
C3	30.70	3.600	0.081	0.03	0.03	0.03	<b>0.081</b>
N1	141.00	3.400	-0.302	-0.07	-0.07	-0.08	<b>-0.302</b>
N2	57.00	3.200	-0.324	-0.19	-0.19	-0.20	<b>-0.324</b>
C4	30.70	3.600	0.06	0.03	0.03	0.02	<b>0.060</b>
C5	30.70	3.600	-0.17	-0.21	-0.21	-0.21	<b>-0.170</b>
H2	12.00	0.500	0.32	0.26	0.27	0.26	<b>0.320</b>
H3	25.45	2.360	0.117	0.16	0.16	0.16	<b>0.117</b>



**Table S4:** Comparison of the  $H_{\text{rod}}\text{--}O_{\text{wat}}$  Lennard-Jones (LJ) interaction energies (in  $\text{kJ mol}^{-1}$ ) between  $\text{Al}(\mu_2\text{-O}[\text{H}])_{\text{rod}}$  and  $O_{\text{water}}$  for water adsorbed at the primary site for the structures optimized using periodic DFT and cluster MP2 methods. The LJ parameters for  $H_{\text{rod}}$  in  $\text{Al}(\mu_2\text{-O}[\text{H}])_{\text{rod}}$  are taken from FF1 (UFF), FF2 (DREIDING-polar), FF2-np (DREIDING-nonpolar), and FF3 (no LJ site) descriptions, while the LJ parameters for  $O_{\text{water}}$  are taken from the TIP4P water model. The LJ parameters for the  $H_{\text{rod}}\text{--}O_{\text{wat}}$  interaction are calculated using the Lorentz-Berthelot mixing rules. Color code: Al (blue octahedra), O (red), N (light blue), C (brown), Li (green), and H (light pink)

FF	LJ parameters for $\text{Al}(\mu_2\text{-O}[\text{H}])_{\text{rod}}$		LJ parameters for $H_{\text{rod}}\text{--}O_{\text{wat}}$ interaction		$H_{\text{rod}}\text{--}O_{\text{wat}}$ LJ interaction energy ( $\text{kJ mol}^{-1}$ )	
	$\epsilon_{\text{H}}/k_{\text{B}}$ (K)	$\sigma_{\text{H}}$ (Å)	$\epsilon_{\text{LB}}/k_{\text{B}}$ (K)	$\sigma_{\text{LB}}$ (Å)	$d_{\text{H-O}} = 1.857 \text{ Å}$	$d_{\text{H-O}} = 1.856 \text{ Å}$
FF1	22.14	2.571	41.556	2.8625	230.2	231.7
FF2-np	7.65	2.846	24.426	3.000	242.3	243.9
FF2	0.05	2.846	1.975	3.000	19.6	19.7
FF3	0.0	0.0	0.0	1.577	0.0	0.0



**Table S5:** Comparison of binding energies (in  $\text{kJ mol}^{-1}$ ) using fixed or (fully or partially) relaxed geometries for a water molecule adsorbed at the primary adsorption site of MOF-303 computed using the three MOF parameter sets (FF1, FF2, and FF3) and the TIP4P water model for the structures E4D4 and D4D4 with the binding energies computed from periodic DFT calculations at the PBE-D3 level and for a cluster model comprising this water adsorption site using second order Møller-Plesset (MP2) theory. For the DFT and MP2 calculations of the X4D4 (X = E or D) MOF structures, the energy is calculated as  $U_{\text{bind}} = [U(\text{X4D4}) - U(\text{E0D0}) - 4 U(\text{isolated water})] / 4$ . For the force field calculations in the  $3 \times 2 \times 3$  MOF supercell, the energy is calculated as  $U_{\text{bind}} = [U(\text{X4D4}) \text{ with water} - U(\text{X4D4 without water})] / 72$ , since the force field does not account for the energy change between  $U(\text{X4D4 without water})$  and  $U(\text{E0D0})$  and  $U(\text{isolated water}) = 0$  for the rigid water models. The single-point energies correspond to the DFT-optimized structure and binding energies are obtained from constrained geometry optimization with the force field allowing only for translation and rotation of rigid water molecules. The internal geometry of the TIP4P water model is used for the force-field-based single-point energies and binding energies.

Method	Energy contribution	E4D4 $U_{\text{bind}} (\text{kJ mol}^{-1})$			D4D4 $U_{\text{bind}} (\text{kJ mol}^{-1})$		
		FF1	FF2	FF3	FF1	FF2	FF3
Force-field-based binding energies from constrained geometry optimization	Inter LJ	-3.6	-1.4	-3.2	-10.2	43.8	11.0
	Coulombic	-55.3	-70.6	-83.6	-31.9	-88.5	-91.5
	Total	-58.9	-72.0	-86.8	-42.1	-44.7	-80.5
Force-field-based single-point energies	Inter LJ	231.7	21.5	1.8	418.7	50.4	16.2
	Coulombic	-82.9	-82.9	-82.9	-88.6	-88.6	-88.6
	Total	148.8	-61.4	-81.1	330.0	-38.3	-72.4
DFT (PBE-D3/850 eV)	-	-72.5			-82.1		
MP2/cc-pVDZ	-	-83.3			-108.8		

**Table S6:** Numerical data for water adsorption/desorption isotherms in structural variants of MOF-333 obtained from  $NpT$ -GEMC simulations for the TIP4P and TIP4P/2005 water models at  $T = 298$  K. The pressure is reported as  $RH$ , where the saturated vapor pressures are  $4.54 \pm 0.12$  and  $0.739 \pm 0.017$  kPa for the TIP4P and TIP4P/2005<sup>3</sup> water models, respectively. The water loading is reported as molecules per unit cell, where the subscripts denote the uncertainty in the last digits.

Structure	E0D0	E0D0	E0D0	E0D0	E0D4
FF-water model	FF1-TIP4P	FF2-TIP4P	FF3-TIP4P	FF3-TIP4P	FF3-TIP4P
	ads	ads	ads	des	ads
$p/p_{\text{sat}}$	$N$	$N$	$N$	$N$	$N$
0.010	0.121 <sub>3</sub>	0.0128 <sub>1</sub>	0.0229 <sub>1</sub>	0.24 <sub>17</sub>	4.189 <sub>1</sub>
0.025	0.360 <sub>3</sub>	0.0329 <sub>2</sub>	0.0590 <sub>4</sub>	0.128 <sub>1</sub>	4.569 <sub>3</sub>
0.051	1.03 <sub>1</sub>	0.0710 <sub>4</sub>	0.130 <sub>1</sub>	-	5.37 <sub>2</sub>
0.077	3.09 <sub>18</sub>	0.114 <sub>1</sub>	0.207 <sub>1</sub>	0.204 <sub>3</sub>	20.16 <sub>53</sub>
0.103	26.84 <sub>18</sub>	0.169 <sub>3</sub>	0.320 <sub>8</sub>	2.46 <sub>1.36</sub>	32.90 <sub>7</sub>
0.128	29.85 <sub>7</sub>	0.236 <sub>8</sub>	0.49 <sub>2</sub>	16.2 <sub>2.7</sub>	34.12 <sub>7</sub>
0.154	30.72 <sub>4</sub>	0.59 <sub>8</sub>	23.7 <sub>2.6</sub>	33.11 <sub>5</sub>	34.85 <sub>5</sub>
0.180	31.40 <sub>4</sub>	23.67 <sub>1.5</sub>	34.11 <sub>4</sub>	34.08 <sub>6</sub>	35.08 <sub>9</sub>
0.205	31.89 <sub>7</sub>	31.18 <sub>33</sub>	34.81 <sub>5</sub>	34.93 <sub>5</sub>	35.75 <sub>5</sub>
0.231	32.15 <sub>6</sub>	32.28 <sub>4</sub>	35.50 <sub>5</sub>	35.34 <sub>9</sub>	36.12 <sub>3</sub>
0.257	32.51 <sub>4</sub>	32.97 <sub>5</sub>	35.80 <sub>6</sub>	35.83 <sub>4</sub>	36.34 <sub>3</sub>
0.282	32.76 <sub>4</sub>	33.48 <sub>5</sub>	36.24 <sub>5</sub>	36.28 <sub>5</sub>	36.72 <sub>5</sub>
0.308	33.17 <sub>4</sub>	33.86 <sub>5</sub>	36.67 <sub>6</sub>	-	36.90 <sub>7</sub>
0.349	33.41 <sub>5</sub>	34.49 <sub>6</sub>	37.12 <sub>5</sub>	-	37.25 <sub>9</sub>
0.380	33.67 <sub>6</sub>	34.72 <sub>6</sub>	37.30 <sub>3</sub>	-	37.41 <sub>6</sub>
0.411	33.71 <sub>5</sub>	35.08 <sub>4</sub>	37.65 <sub>4</sub>	-	37.66 <sub>5</sub>
0.452	33.99 <sub>5</sub>	35.58 <sub>4</sub>	37.84 <sub>2</sub>	-	37.85 <sub>6</sub>
0.482	34.14 <sub>3</sub>	35.65 <sub>5</sub>	38.08 <sub>5</sub>	-	38.05 <sub>5</sub>
0.513	34.31 <sub>2</sub>	35.82 <sub>4</sub>	38.27 <sub>5</sub>	-	38.26 <sub>12</sub>
0.616	34.50 <sub>3</sub>	36.39 <sub>5</sub>	38.74 <sub>3</sub>	-	38.55 <sub>7</sub>
0.770	35.08 <sub>4</sub>	37.08 <sub>3</sub>	39.37 <sub>2</sub>	-	39.07 <sub>6</sub>
0.924	35.42 <sub>3</sub>	37.54 <sub>2</sub>	39.83 <sub>3</sub>	-	39.50 <sub>5</sub>

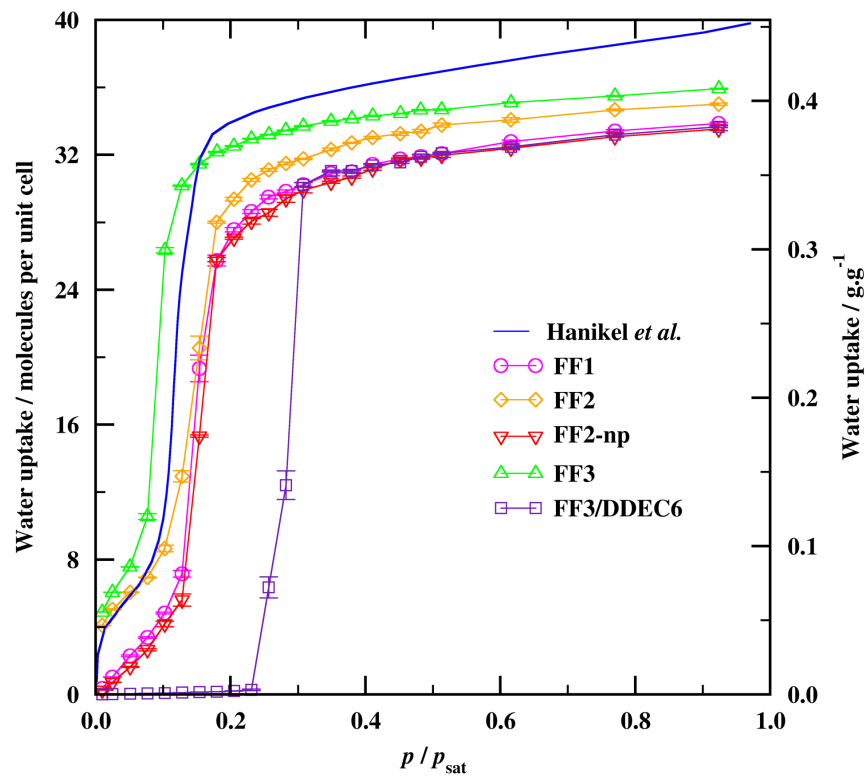
**Table S6:** Continued.

Structure	E4E4	D4D4	E4D4	E4D4	E4D4
FF-water model	FF3-TIP4P	FF3-TIP4P	FF3-TIP4P	FF3-TIP4P	FF3-TIP4P/2005
	ads	ads	ads	des	ads
$p/p_{\text{sat}}$	$N$	$N$	$N$	$N$	$N$
0.010	4.242 <sub>6</sub>	3.96 <sub>1</sub>	4.884 <sub>6</sub>	4.96 <sub>6</sub>	4.80 <sub>1</sub>
0.025	5.19 <sub>1</sub>	4.060 <sub>5</sub>	6.055 <sub>7</sub>	6.20 <sub>15</sub>	-
0.051	7.20 <sub>2</sub>	4.26 <sub>2</sub>	7.56 <sub>1</sub>	7.88 <sub>29</sub>	7.32 <sub>6</sub>
0.077	16.18 <sub>27</sub>	4.95 <sub>9</sub>	10.55 <sub>17</sub>	11.03 <sub>44</sub>	23.75 <sub>58</sub>
0.103	30.27 <sub>10</sub>	22.63 <sub>26</sub>	26.34 <sub>16</sub>	26.44 <sub>27</sub>	32.03 <sub>7</sub>
0.128	32.17 <sub>6</sub>	28.53 <sub>10</sub>	30.17 <sub>3</sub>	30.22 <sub>7</sub>	32.60 <sub>6</sub>
0.154	32.97 <sub>5</sub>	29.65 <sub>10</sub>	31.45 <sub>4</sub>	31.45 <sub>4</sub>	33.08 <sub>6</sub>
0.180	33.70 <sub>2</sub>	30.75 <sub>17</sub>	32.17 <sub>3</sub>	32.06 <sub>6</sub>	33.21 <sub>9</sub>
0.205	34.05 <sub>4</sub>	31.42 <sub>7</sub>	32.52 <sub>3</sub>	32.54 <sub>3</sub>	33.61 <sub>5</sub>
0.231	34.43 <sub>4</sub>	31.98 <sub>11</sub>	32.95 <sub>3</sub>	32.98 <sub>3</sub>	33.72 <sub>5</sub>
0.257	34.79 <sub>4</sub>	32.10 <sub>11</sub>	33.20 <sub>2</sub>	33.18 <sub>6</sub>	33.88 <sub>3</sub>
0.282	34.97 <sub>4</sub>	32.55 <sub>11</sub>	33.45 <sub>2</sub>	33.52 <sub>4</sub>	33.99 <sub>6</sub>
0.308	35.27 <sub>3</sub>	32.76 <sub>13</sub>	33.70 <sub>3</sub>	-	34.17 <sub>7</sub>
0.349	35.56 <sub>3</sub>	33.19 <sub>6</sub>	33.99 <sub>4</sub>	-	34.42 <sub>5</sub>
0.380	35.78 <sub>5</sub>	33.7 <sub>1</sub>	34.14 <sub>2</sub>	-	34.52 <sub>3</sub>
0.411	35.89 <sub>3</sub>	33.82 <sub>4</sub>	34.31 <sub>3</sub>	-	34.66 <sub>5</sub>
0.452	36.16 <sub>4</sub>	33.87 <sub>8</sub>	34.45 <sub>2</sub>	-	34.74 <sub>8</sub>
0.482	36.32 <sub>2</sub>	34.12 <sub>7</sub>	34.66 <sub>3</sub>	-	34.87 <sub>6</sub>
0.513	36.37 <sub>4</sub>	34.57 <sub>12</sub>	34.68 <sub>3</sub>	-	34.97 <sub>3</sub>
0.616	36.87 <sub>5</sub>	34.78 <sub>5</sub>	35.10 <sub>3</sub>	-	35.26 <sub>2</sub>
0.770	37.34 <sub>3</sub>	35.23 <sub>5</sub>	35.49 <sub>2</sub>	-	35.68 <sub>5</sub>
0.924	37.72 <sub>4</sub>	35.91 <sub>6</sub>	35.92 <sub>3</sub>	-	36.02 <sub>5</sub>

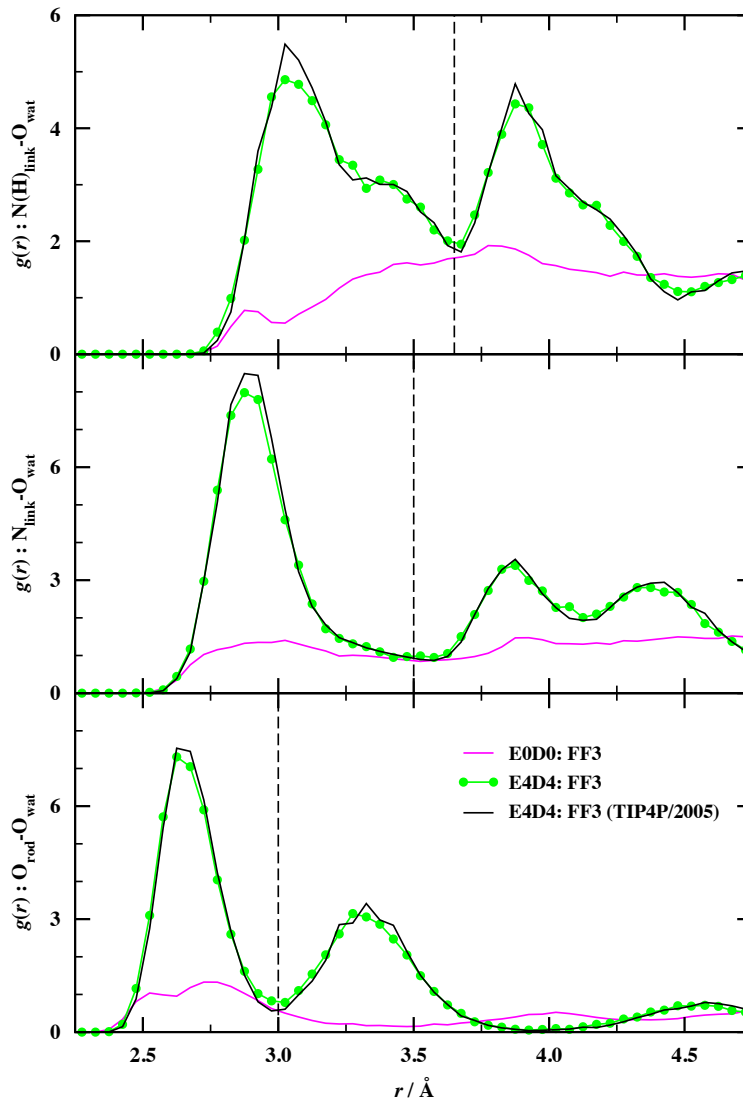


**Table S6:** Continued.

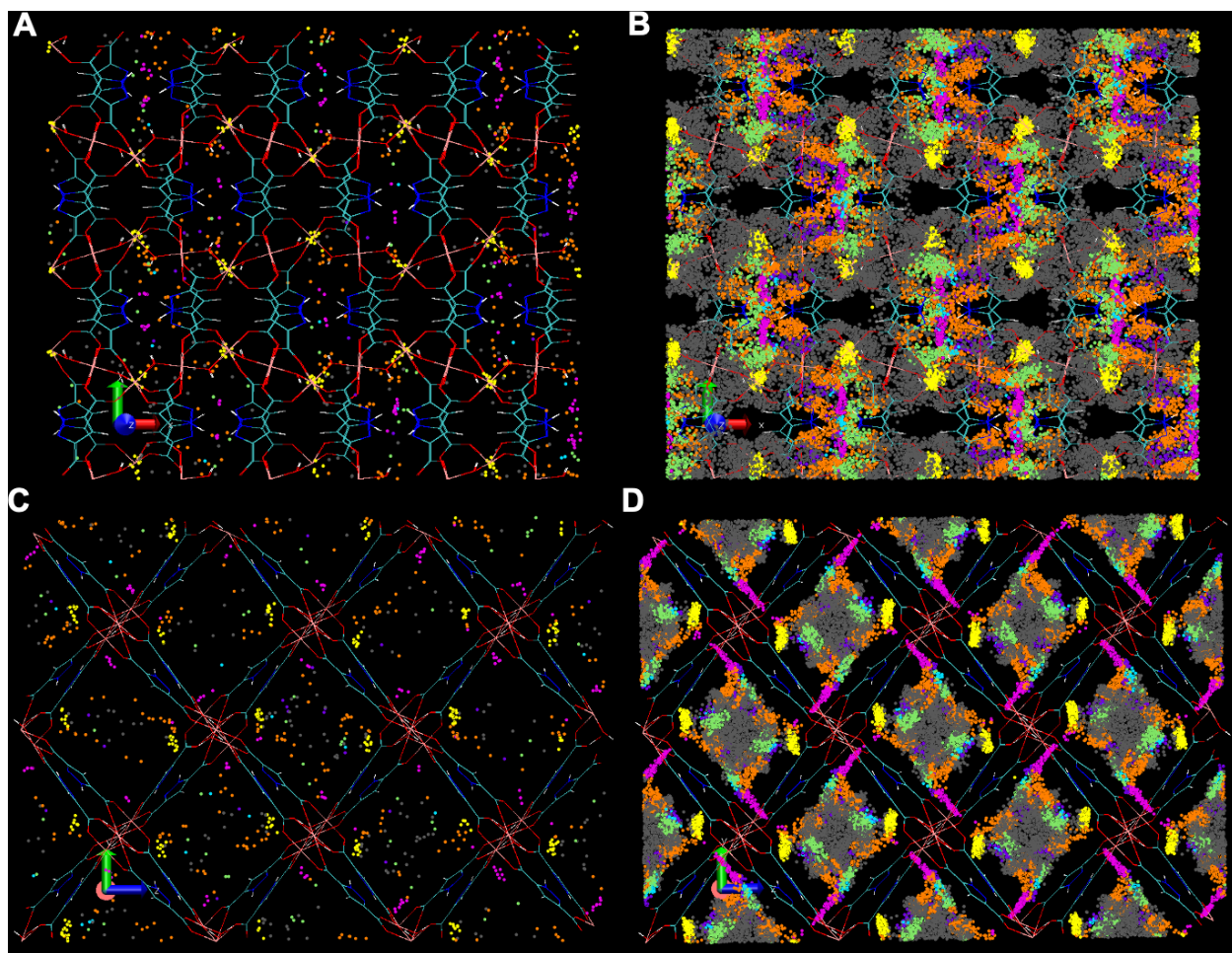
Structure	E4D4	E4D4	E4D4	E4D4
FF-water model	FF1-TIP4P	FF2-TIP4P	FF2-np-TIP4P	FF3/DDEC6-TIP4P
	ads	ads	ads	ads
$p/p_{\text{sat}}$	$N$	$N$	$N$	$N$
0.010	0.35 <sub>1</sub>	4.10 <sub>1</sub>	0.250 <sub>3</sub>	0.0071 <sub>1</sub>
0.025	1.03 <sub>1</sub>	5.04 <sub>4</sub>	0.71 <sub>1</sub>	0.0180 <sub>2</sub>
0.051	2.29 <sub>6</sub>	6.06 <sub>1</sub>	1.63 <sub>3</sub>	0.0382 <sub>2</sub>
0.077	3.37 <sub>4</sub>	6.93 <sub>2</sub>	2.65 <sub>6</sub>	0.0595 <sub>1</sub>
0.103	4.82 <sub>5</sub>	8.65 <sub>19</sub>	4.18 <sub>17</sub>	0.080 <sub>1</sub>
0.128	7.16 <sub>20</sub>	12.93 <sub>33</sub>	5.60 <sub>36</sub>	0.110 <sub>2</sub>
0.154	19.33 <sub>79</sub>	20.54 <sub>70</sub>	15.32 <sub>6</sub>	0.138 <sub>2</sub>
0.180	25.73 <sub>33</sub>	28.01 <sub>6</sub>	25.79 <sub>13</sub>	0.160 <sub>4</sub>
0.205	27.55 <sub>12</sub>	29.37 <sub>11</sub>	27.06 <sub>6</sub>	0.20 <sub>1</sub>
0.231	28.63 <sub>11</sub>	30.52 <sub>8</sub>	28.06 <sub>16</sub>	0.27 <sub>4</sub>
0.257	29.50 <sub>11</sub>	31.10 <sub>9</sub>	28.55 <sub>21</sub>	6.35 <sub>63</sub>
0.282	29.83 <sub>9</sub>	31.48 <sub>8</sub>	29.39 <sub>21</sub>	12.41 <sub>85</sub>
0.308	30.22 <sub>14</sub>	31.76 <sub>4</sub>	29.91 <sub>16</sub>	30.22 <sub>12</sub>
0.349	30.89 <sub>14</sub>	32.32 <sub>8</sub>	30.37 <sub>6</sub>	31.038 <sub>63</sub>
0.380	30.99 <sub>8</sub>	32.71 <sub>3</sub>	30.68 <sub>7</sub>	31.042 <sub>92</sub>
0.411	31.42 <sub>2</sub>	33.03 <sub>7</sub>	31.15 <sub>7</sub>	31.38 <sub>10</sub>
0.452	31.76 <sub>5</sub>	33.25 <sub>11</sub>	31.71 <sub>9</sub>	31.55 <sub>6</sub>
0.482	31.89 <sub>5</sub>	33.40 <sub>10</sub>	31.80 <sub>3</sub>	31.88 <sub>14</sub>
0.513	32.07 <sub>8</sub>	33.77 <sub>12</sub>	31.96 <sub>12</sub>	32.09 <sub>6</sub>
0.616	32.78 <sub>9</sub>	34.07 <sub>13</sub>	32.39 <sub>9</sub>	32.47 <sub>11</sub>
0.770	33.41 <sub>8</sub>	34.67 <sub>5</sub>	33.07 <sub>2</sub>	33.19 <sub>7</sub>
0.924	33.86 <sub>7</sub>	35.00 <sub>7</sub>	33.53 <sub>8</sub>	33.66 <sub>5</sub>



**Figure S1:** Water adsorption isotherms computed at  $T = 298$  K in the E4D4 structure of MOF-303 using the FF1, FF2, FF2-np (using the DREIDING LJ parameters for non-polar hydrogen atoms for  $H_{rod}$ ), FF3, and FF3/DDEC6 (using DDEC6 partial charges for all framework atoms) models. The TIP4P water model was used to describe the interactions of water. Numerical data are reported in **Table S6**.



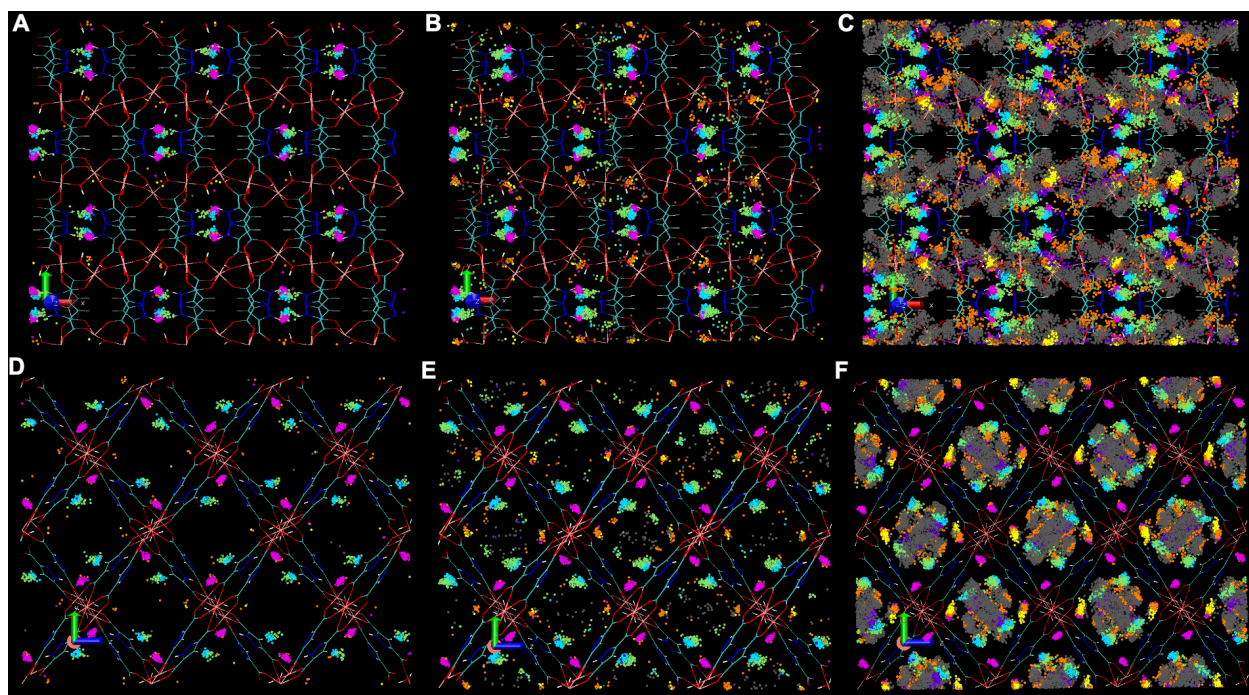
**Figure S2:** Radial distribution function ( $g(r)$ ) plots computed to describe the interactions between the oxygen atom of the adsorbed water molecules ( $O_{\text{wat}}$ ) and the donor/acceptor functionalities of MOF-303 [ $N(\text{H})_{\text{linker}}$  (top),  $N_{\text{linker}}$  (middle), and  $O_{\text{rod}}$  (bottom)] obtained for the E4D4 structure with the FF3-TIP4P model at a loading of 7.56 water molecules per unit cell, for the E4D4 structure with the FF3-TIP4P/2005 model at a loading of 7.32 water molecules per unit cell, and for the E0D0 structure with the FF3-TIP4P model at a loading of 34.8 water molecules per unit cell (note that the steep adsorption step for the E0D0 structure leads to a jump from 2 to 34 water molecules per unit cell). The vertical dashed line indicates the cutoff distance used to determine the presence of a hydrogen bond.



**Figure S3.** Spatial distribution of water molecules in the E0D0 MOF-303 structure at loadings of 0.49 (A,C) and 34.8 (B,D) molecules per unit cell obtained from GEMC simulations using the FF3-TIP4P force field. Inclined views along the  $c$ -direction (top) and corresponding projections on the  $b$ - $c$  plane (bottom) are shown. The MOF backbone is represented as lines, and the O-atom positions of the adsorbed water molecules (taken from 100 GEMC configurations) are shown as point clouds. Coloring of the water points according to the types of adsorbing sites and hydrogen bonds: primary and secondary adsorption sites in magenta and cyan, respectively, other color codes are reported in **Table S7**.

**Table S7.** Label, color code, presence of hydrogen bonds with different framework functionalities, and occupancy per unit cell at representative *RH* values for different water adsorption sites in the E0D0 structure of MOF-303. N(H)<sub>linker</sub> and N<sub>linker</sub> donors and acceptors are distinguished based on belonging to the primary or secondary patch ( $d_{\text{N(H)}-\text{N}} = 3.4$  and  $3.1 \text{ \AA}$ , respectively). The first minima of the corresponding X–O<sub>wat</sub> radial distribution functions (where X = N(H)<sub>linker</sub>, N<sub>linker</sub>, O<sub>rod</sub>, or O<sub>wat</sub>) are used as maximum distance to determine the presence of a hydrogen bond (Figure S2).

Color	N(H) <sub>linker</sub>	N <sub>linker</sub>	O <sub>rod</sub>	<i>RH</i> = 12.8%	<i>RH</i> = 20.5%
<i>Primary patch</i>					
magenta	yes	yes	yes	0.07	2.13
orange	yes	yes	no	0.02	0.45
orange	yes	no	yes	0.00	0.03
orange	yes	no	no	0.01	1.58
orange	no	yes	yes	0.03	0.24
orange	no	yes	no	0.08	3.99
<i>Secondary patch</i>					
violet	yes	yes	yes	0.00	0.04
cyan	yes	yes	no	0.01	0.50
violet	yes	no	yes	0.00	0.00
violet	yes	no	no	0.01	0.92
violet	no	yes	yes	0.00	0.12
lime	no	yes	no	0.03	4.13
<i>Other</i>					
yellow	no	no	yes	0.14	3.21
gray	no	no	no	0.10	17.51



**Figure S4.** Spatial distribution of water molecules in the E4D4 MOF-303 structure at loadings of 4.80 (A,D), 7.32 (B,E), and 33.6 (C,F) molecules per unit cell obtained from GEMC simulations using the FF3-TIP4P/2005 force field. Inclined views along the *c*-direction (top) and corresponding projections on the *b-c* plane (bottom) are shown. The MOF backbone is represented as lines, and the O-atom positions of the adsorbed water molecules (taken from 100 GEMC configurations) are shown as point clouds. Coloring of the water points according to the types of adsorption sites and hydrogen bonds: primary and secondary adsorption sites in magenta and cyan, respectively, other color codes are reported in **Table S8**.

**Table S8.** Color code, presence of hydrogen bonds with different framework functionalities, and occupational factors per unit cell at representative  $RH$  values for different water adsorption sites in the E4D4 structure of MOF-303 obtained for the TIP4P/2005 water model.  $N(H)_{\text{linker}}$  and  $N_{\text{linker}}$  donors and acceptors are distinguished based on belonging to the primary or secondary patch ( $d_{N(H)-N} = 3.9$  and  $3.5$  Å, respectively). The first minima of the corresponding X–O<sub>wat</sub> radial distribution functions (where X =  $N(H)_{\text{linker}}$ ,  $N_{\text{linker}}$ , O<sub>rod</sub>, or O<sub>wat</sub>) are used as maximum distance to determine the presence of a hydrogen bond (**Figure S2**).

Color	$N(H)_{\text{linker}}$	$N_{\text{linker}}$	O <sub>rod</sub>	$RH = 1.0\%$	$RH = 5.1\%$	$RH = 20.5\%$
<i>Primary patch</i>						
magenta	yes	yes	yes	3.95	3.97	4.15
orange	yes	yes	no	0.04	0.04	0.07
orange	yes	no	yes	0.03	0.22	1.66
orange	yes	no	no	0.00	0.03	0.70
orange	no	yes	yes	0.01	0.00	0.01
orange	no	yes	no	0.01	0.06	1.32
<i>Secondary patch</i>						
violet	yes	yes	yes	0.00	0.00	0.00
cyan	yes	yes	no	0.41	1.44	2.06
violet	yes	no	yes	0.00	0.00	0.00
violet	yes	no	no	0.02	0.05	0.85
violet	no	yes	yes	0.00	0.00	0.00
lime	no	yes	no	0.32	1.27	4.03
<i>Other</i>						
yellow	no	no	yes	0.01	0.08	1.74
gray	no	no	no	0.02	0.21	17.02

**Table S9:** Tabulated crystallographic unit cell parameters, unit cell volume, and lattice energy computed from periodic DFT calculations for the pristine (no water) MOF-333 structure (E5D0) and in the presence of 4 water molecules per unit cell (E5D4) in *cis* and *trans* arrangements of the FDC linkers. The unit cell parameters are taken from single-crystal X-ray diffraction experiments with 5 water molecules per unit cell (E5).<sup>1</sup> The energy of the “empty” framework after removal of the water molecules without relaxation of the framework atoms is also provided. Furthermore, the probe-occupiable volume (POAV), computed using a spherical probe of 3.154 Å diameter in Zeo++,<sup>2</sup> is reported for the different structural variants.

MOF Structure	<i>cis</i> -MOF-333		<i>trans</i> -MOF-333	
	E5D0	E5D4	E5D0	E5D4
$a$ (Å)	12.239 <sub>2</sub>	12.239 <sub>2</sub>	12.239 <sub>2</sub>	12.239 <sub>2</sub>
$b$ (Å)	15.074 <sub>3</sub>	15.074 <sub>3</sub>	15.074 <sub>3</sub>	15.074 <sub>3</sub>
$c$ (Å)	13.651 <sub>3</sub>	13.651 <sub>3</sub>	13.651 <sub>3</sub>	13.651 <sub>3</sub>
$\alpha$ (°)	90	90	90	90
$\beta$ (°)	101.878 <sub>8</sub>	101.878 <sub>8</sub>	101.878 <sub>8</sub>	101.878 <sub>8</sub>
$\gamma$ (°)	90	90	90	90
$V$ (Å <sup>3</sup> )	2464.6	2464.6	2464.6	2464.6
$E_{\text{lattice}}$ (eV)	−928.707234	−988.335862	−928.815677	−988.151588
$E_{\text{empty}}$ (eV)	−928.707234	−928.393910	−928.815677	−928.558653
$POAV$ (cm <sup>3</sup> /g <sub>MOF</sub> )	0.407	0.406	0.419	0.412



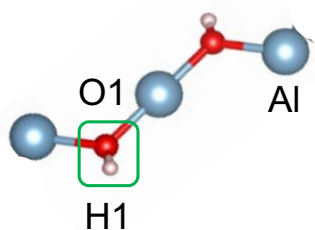
**Table S10:** Comparison of binding energies (in kJ mol<sup>-1</sup>) using fixed or (fully or partially) relaxed geometries for a water molecule adsorbed at the primary adsorption site of MOF-333 computed using the three MOF parameter sets (FF1, FF2, and FF3) and the TIP4P water model for structures E5D4 with binding energies computed from periodic DFT calculations at the PBE-D3 level and for a cluster model comprising this water adsorption site using second order Møller-Plesset (MP2) theory. For the DFT and MP2 calculations of the E5D4 MOF structures, the energy is calculated as  $U_{\text{bind}} = [U(\text{E5D4}) - U(\text{E5D0}) - 4 U(\text{isolated water})] / 4$ . For the force field calculations in the  $3 \times 2 \times 3$  MOF supercell, the energy is calculated as  $U_{\text{bind}} = [U(\text{E5D4}) \text{ with water} - U(\text{E5D4} \text{ without water})] / 72$ , since  $U(\text{isolated water}) = 0$  for the rigid water models. The single-point energies correspond to the DFT-optimized structure and binding energies are obtained from constrained geometry optimization with the force field allowing only for translation and rotation of rigid water molecules. The internal geometry of the TIP4P water model is used for the force-field-based single-point energies and binding energies.

Method	Energy contribution	E5D4 ( <i>cis</i> ) $U_{\text{bind}}$ (kJ mol <sup>-1</sup> )			E5D4 ( <i>trans</i> ) $U_{\text{bind}}$ (kJ mol <sup>-1</sup> )		
		FF1	FF2	FF3	FF1	FF2	FF3
Force-field-based binding energies from constrained geometry optimization	Inter LJ	-5.1	-4.4	-6.3	-8.6	-8.0	-7.2
	Coulombic	-37.3	-48.1	-58.3	-29.0	-39.2	-51.4
	Total	-42.4	-52.5	-64.7	-37.6	-47.2	-58.6
Force-field-based single-point energies	Inter LJ	429.3	55.1	20.2	437.9	52.1	16.1
	Coulombic	-49.5	-49.5	-49.5	-43.9	-43.9	-43.9
	Total	379.8	5.6	-29.3	394.0	8.2	-27.8
DFT (PBE-D3/850 eV)	-	-59.4			-55.0		
MP2/ccPVDZ	-	-67.7			-65.5		

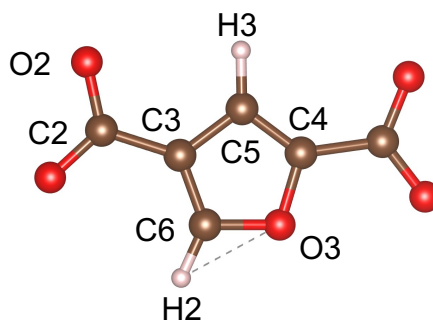
**Table S11:** Lennard-Jones parameters and partial charges used to describe the adsorbate interaction with MOF-333.

Atom type	$\varepsilon / k_{\text{B}}(\text{K})$	$\sigma(\text{\AA})$	$q( e )$
Al	254.00	4.000	1.64
O1	30.19	3.118	-0.98
H1 (FF1)	22.14	2.571	0.43
H1 (FF2)	0.05	2.846	0.43
H1 (FF3)	0.00	0.000	0.43
O2	79.00	3.050	-0.57
C2	41.00	3.900	0.703
C3	30.70	3.600	-0.135
C6	30.70	3.600	0.016
O3	70.00	2.600	-0.193
C4	30.70	3.600	0.016
C5	30.70	3.600	-0.135
H2	25.45	2.360	0.101
H3	25.45	2.360	0.114

**Infinite Al(OH) rods**

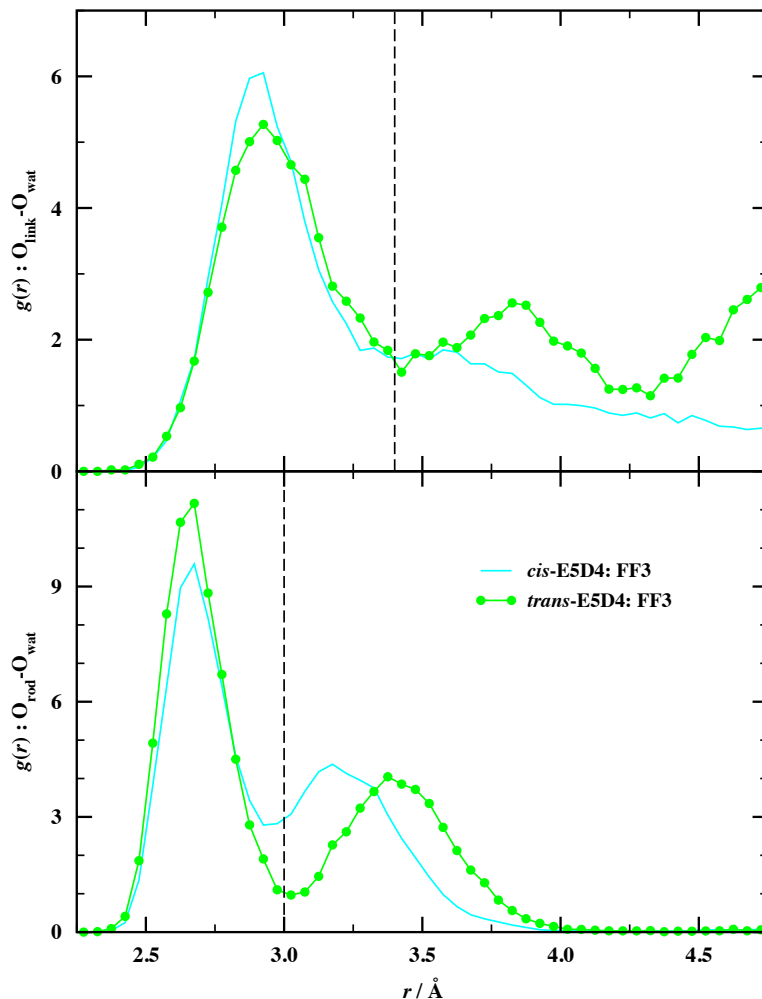


**FDC linkers**



**Table S12:** Numerical data for water adsorption/desorption isotherms in structural variants of MOF-333 obtained from  $NpT$ -GEMC simulations for the TIP4P water model at  $T = 298$  K. The pressure is reported as  $RH$ , where the saturated vapor pressure is  $4.54 \pm 0.12$  kPa for the TIP4P water model. The water loading is reported as molecules per unit cell, where the subscripts denote the uncertainty in the last digits.

Structure	E5D0 ( <i>cis</i> )	E5D0 ( <i>cis</i> )	E5D4 ( <i>cis</i> )	E5D0 ( <i>trans</i> )	E5D4 ( <i>trans</i> )
FF-water model	FF2-TIP4P	FF3-TIP4P	FF3-TIP4P	FF3-TIP4P	FF3-TIP4P
	ads	ads	ads	des	ads
$p/p_{\text{sat}}$	$N$	$N$	$N$	$N$	$N$
0.051	0.0623 <sub>2</sub>	2.490 <sub>5</sub>	5.483 <sub>6</sub>	0.176 <sub>1</sub>	3.632 <sub>3</sub>
0.077	0.0940 <sub>3</sub>	3.120 <sub>8</sub>	5.966 <sub>4</sub>	0.267 <sub>1</sub>	3.799 <sub>2</sub>
0.103	0.126 <sub>1</sub>	3.576 <sub>9</sub>	6.345 <sub>7</sub>	0.347 <sub>4</sub>	3.904 <sub>2</sub>
0.128	0.159 <sub>1</sub>	3.931 <sub>7</sub>	6.70 <sub>1</sub>	0.442 <sub>3</sub>	3.992 <sub>3</sub>
0.154	0.1920 <sub>4</sub>	4.278 <sub>12</sub>	7.12 <sub>4</sub>	0.522 <sub>6</sub>	4.08 <sub>1</sub>
0.180	0.228 <sub>1</sub>	4.64 <sub>2</sub>	7.94 <sub>11</sub>	0.604 <sub>4</sub>	4.22 <sub>2</sub>
0.205	0.269 <sub>3</sub>	5.36 <sub>19</sub>	23.60 <sub>27</sub>	0.693 <sub>5</sub>	4.30 <sub>2</sub>
0.231	0.302 <sub>1</sub>	28.35 <sub>87</sub>	28.25 <sub>15</sub>	0.787 <sub>6</sub>	4.91 <sub>25</sub>
0.257	0.345 <sub>3</sub>	30.50 <sub>5</sub>	29.42 <sub>7</sub>	0.885 <sub>9</sub>	24.2 <sub>1,9</sub>
0.282	0.41 <sub>1</sub>	31.04 <sub>4</sub>	30.05 <sub>4</sub>	1.002 <sub>19</sub>	29.84 <sub>14</sub>
0.308	0.44 <sub>1</sub>	31.38 <sub>4</sub>	30.52 <sub>6</sub>	1.04 <sub>1</sub>	30.72 <sub>9</sub>
0.349	0.66 <sub>8</sub>	31.98 <sub>4</sub>	31.06 <sub>3</sub>	1.49 <sub>12</sub>	31.07 <sub>6</sub>
0.380	8.1 <sub>2,9</sub>	32.21 <sub>3</sub>	31.31 <sub>3</sub>	29.63 <sub>8</sub>	31.49 <sub>8</sub>
0.411	28.0 <sub>1,3</sub>	32.42 <sub>3</sub>	31.65 <sub>3</sub>	29.96 <sub>10</sub>	31.59 <sub>6</sub>
0.452	30.28 <sub>3</sub>	32.72 <sub>5</sub>	31.86 <sub>3</sub>	30.25 <sub>4</sub>	32.02 <sub>6</sub>
0.482	30.62 <sub>3</sub>	32.94 <sub>6</sub>	32.11 <sub>3</sub>	30.46 <sub>7</sub>	32.19 <sub>6</sub>
0.513	30.86 <sub>3</sub>	33.07 <sub>5</sub>	32.36 <sub>4</sub>	30.57 <sub>7</sub>	32.40 <sub>9</sub>
0.616	31.35 <sub>4</sub>	33.51 <sub>3</sub>	32.75 <sub>5</sub>	31.18 <sub>5</sub>	32.88 <sub>5</sub>
0.770	31.99 <sub>3</sub>	34.09 <sub>3</sub>	33.32 <sub>3</sub>	31.77 <sub>3</sub>	33.19 <sub>3</sub>
0.924	32.49 <sub>4</sub>	34.48 <sub>4</sub>	33.81 <sub>5</sub>	32.26 <sub>11</sub>	33.74 <sub>4</sub>



**Figure S5:** Radial distribution function ( $g(r)$ ) plots computed to describe the interactions between the oxygen atom of the adsorbed water molecules ( $O_{\text{wat}}$ ) and the donor/acceptor functionalities of MOF-333 [ $O_{\text{linker}}$  (top), and  $O_{\text{rod}}$  (bottom)] obtained for the E5D4 structures of MOF-333 with the FF3-TIP4P model at a loading of 7.56 water molecules per unit cell in the *cis* arrangement of the FDC linkers, and at a loading of 4.22 water molecules per unit cell in the *trans* arrangement of the FDC linkers. The vertical dashed line indicates the cutoff distance used to determine the presence of a hydrogen bond.

## References:

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- (3) Chen, J. L.; Xue, B.; Mahesh, K.; Siepmann, J. I. Molecular Simulations Probing the Thermophysical Properties of Homogeneously Stretched and Bubbly Water Systems. *J. Chem. Eng. Data* **2019**, *64*, 3755–3771. DOI: 10.1021/acs.jced.9b00284.