Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information

The Effects of Framework Dynamics on the Behavior of Water Adsorbed in the [Zn(*l*-L)(Cl)] and Co-MOF-74 Metal-Organic Frameworks

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1 [Zn(*l*-L)(Cl)]

1.1 Water structure

Further insights into the spatial arrangement of the water molecules in [Zn(l-L)(Cl)] can be gained from the analysis of two- and three-dimensional water density distributions in the MOF pores shown in Figures S1-S4. As mentioned in the main text, the water molecules adsorbed in the [Zn(l-L)(Cl)] pores arrange in consecutive layers that are templated by the Zn?Cl groups and propagate along the MOF channels, effectively forming one-dimensional hydrogen-bonded chains that follow the *l*-helicity of the framework. However, although the Zn–Cl groups correspond to the most favorable binding sites in both the flexible and the rigid framework, their interactions with the water molecules are clearly less specific in the latter case, resulting in more diffuse spatial distributions of water inside the pores.

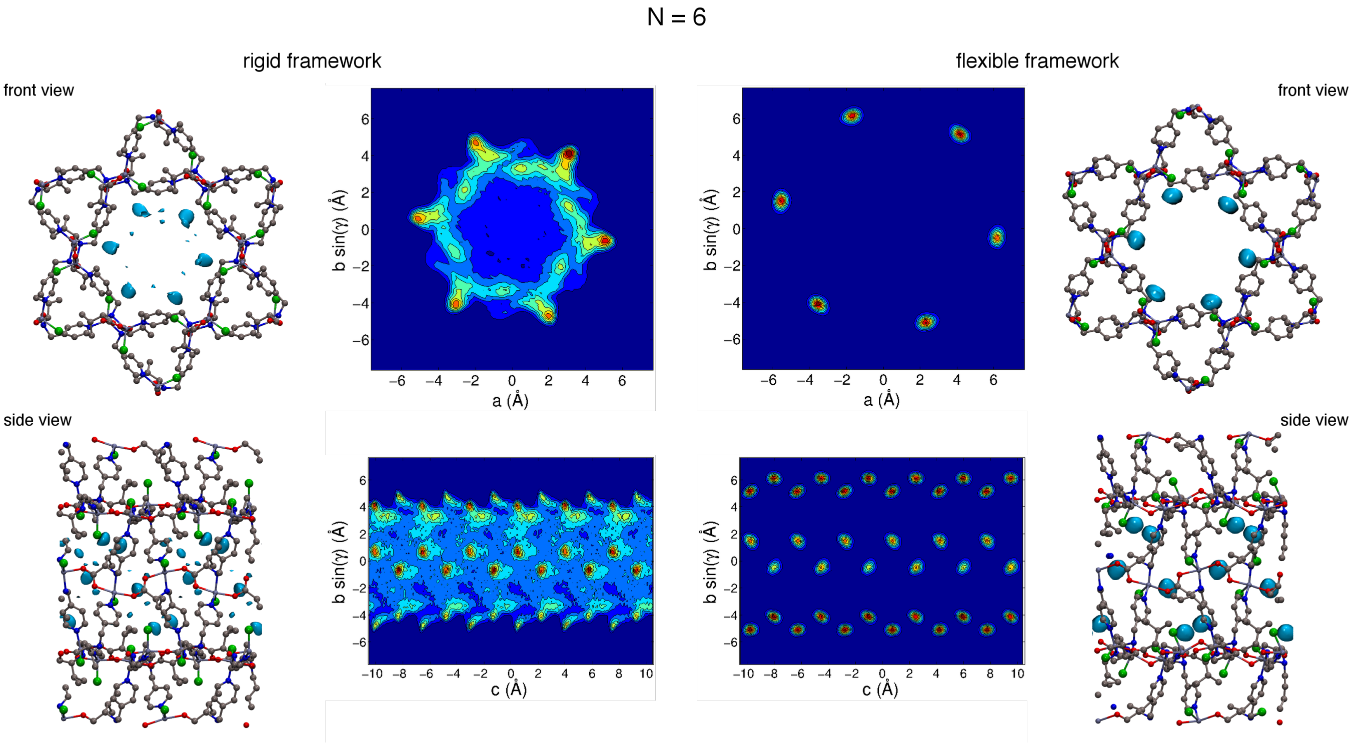

Figure S1 Three- and two-dimensional density distributions of the water oxygen calculated for [Zn(l-L)(Cl)] using both a rigid (first two columns) and a flexible framework (last two columns) for N = 6 water molecules per pore. The top and bottom rows show front and side views of the MOF pores. H atoms are in white, C atoms are in dark gray, N atoms are in blue, O atoms are in red, Cl atoms are in green, and Zn atoms are light violet. The water densities (shown at an isosurface value of 0.16 Å^{-3}) are in light blue.

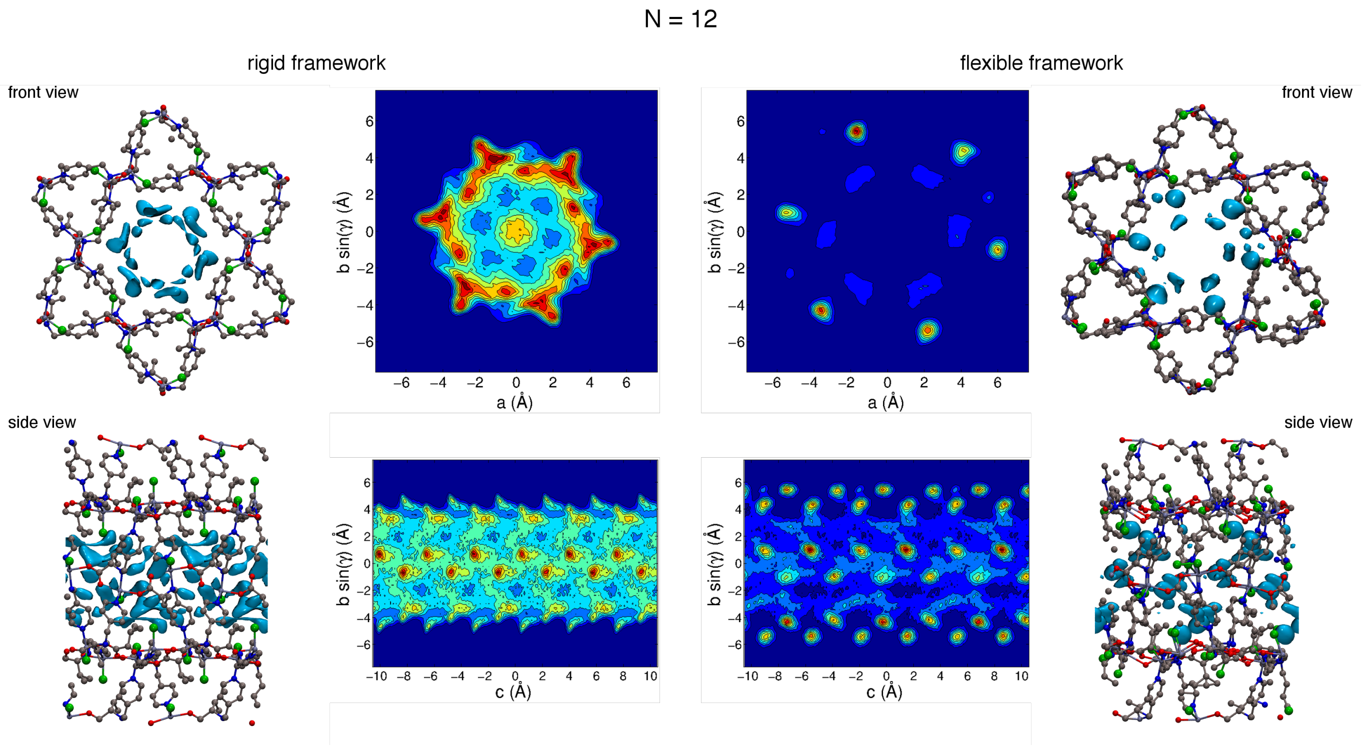

Figure S2 Three- and two-dimensional density distributions of the water oxygen calculated for [Zn(l-L)(Cl)] using both a rigid (first two columns) and a flexible framework (last two columns) for N = 12 water molecules per pore. The top and bottom rows show front and side views of the MOF pores. H atoms are in white, C atoms are in dark gray, N atoms are in blue, O atoms are in red, Cl atoms are in green, and Zn atoms are light violet. The water densities (shown at an isosurface value of 0.16 Å^{-3}) are in light blue.

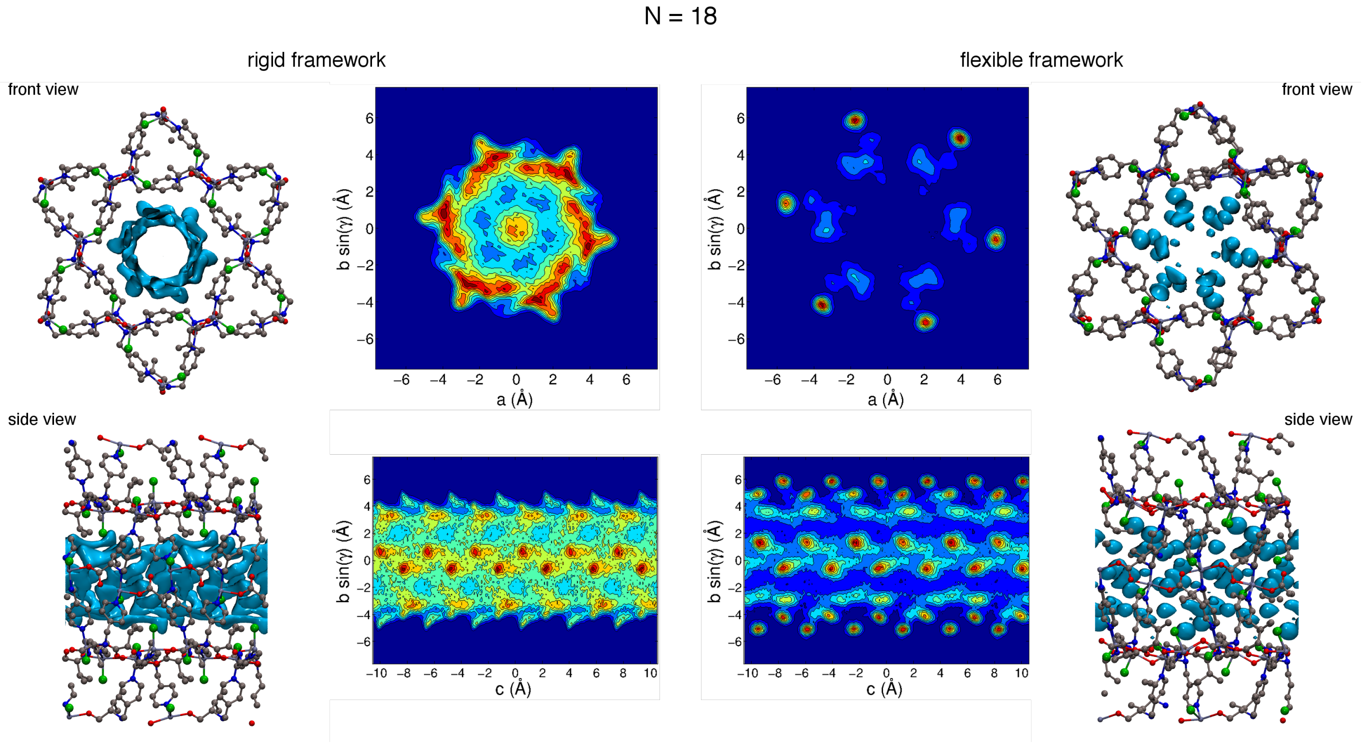

Figure S3 Three- and two-dimensional density distributions of the water oxygen calculated for [Zn(l-L)(Cl)] using both a rigid (first two columns) and a flexible framework (last two columns) for N = 18 water molecules per pore. The top and bottom rows show front and side views of the MOF pores. H atoms are in white, C atoms are in dark gray, N atoms are in blue, O atoms are in red, Cl atoms are in green, and Zn atoms are light violet. The water densities (shown at an isosurface value of 0.16 Å^{-3}) are in light blue.

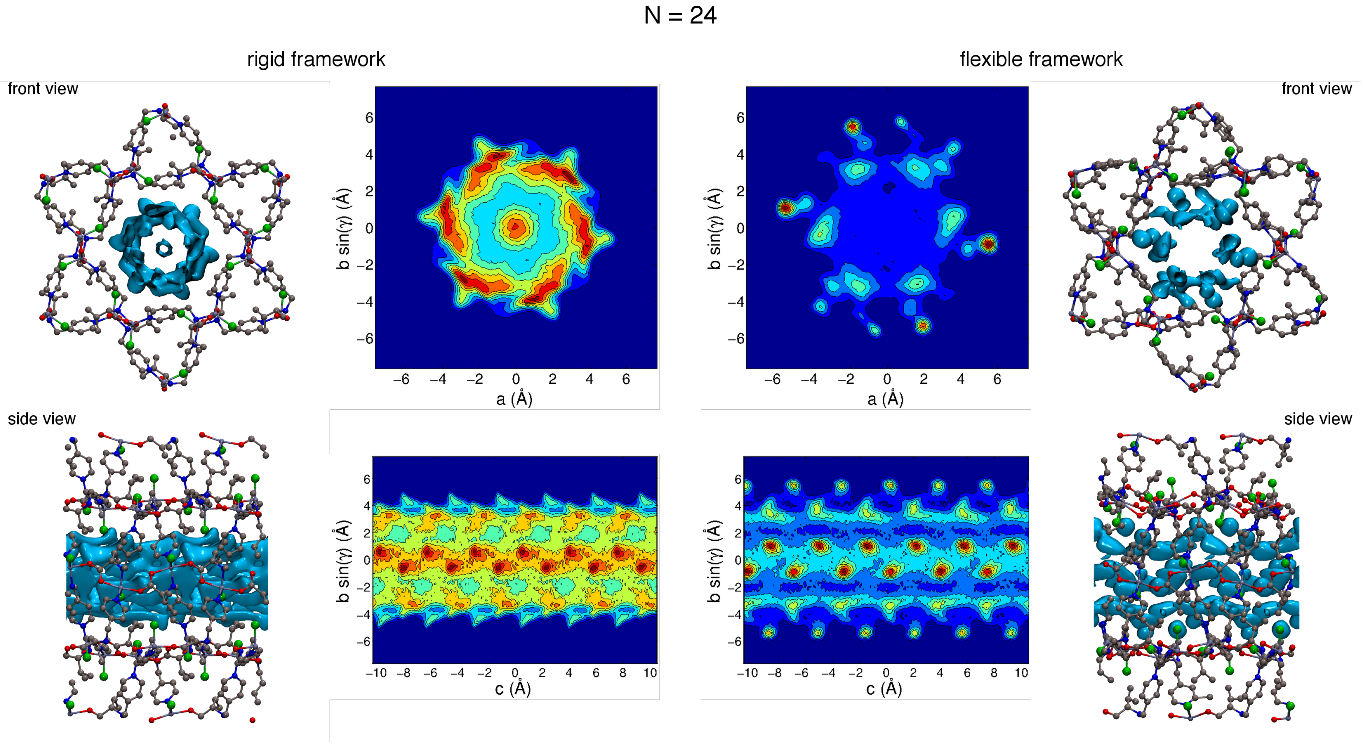

Figure S4 Three- and two-dimensional density distributions of the water oxygen calculated for [Zn(l-L)(Cl)] using both a rigid (first two columns) and a flexible framework (last two columns) for N = 24 water molecules per pore. The top and bottom rows show front and side views of the MOF pores. H atoms are in white, C atoms are in dark gray, N atoms are in blue, O atoms are in red, Cl atoms are in green, and Zn atoms are light violet. The water densities (shown at an isosurface value of 0.16 Å^{-3}) are in light blue.

1.2 Water orientational dynamics

The reorientation decay of $C_2(t)$ was fitted to a tri-exponential function to gain quantitative insights into the hydrogen bonding dynamics of water adsorbed in [Zn(*l*-L)(Cl)]. While only the relevant τ_2 parameters are reported in the main text, all relaxation times are listed in Table S1 and S2.

Table S1 Relaxation time constants, τ_i, obtained from fits to orientational correlation functions $C_2(t)$ calculated for water in flexible [Zn(*l*-L)(Cl)] as a function of number of H_2O molecules per pore.

N	τ_1 (ps)	τ_2 (ps)	τ_3 (ps)
2	0.0569	93.57	>1000
4	0.0544	49.23	300.38
6	0.0497	99.62	750.99
8	0.0013	15.65	179.23
10	0.0021	24.49	216.62
12	0.0011	14.74	179.15
18	0.0026	16.23	210.41
24	0.0107	9.97	89.52

Table S2 Relaxation time constants, τ_i, obtained from fits to orientational correlation functions $C_2(t)$ calculated for water in rigid [Zn(*l*-L)(Cl)] as a function of number of H_2O molecules per pore.

N	τ_1 (ps)	τ_2 (ps)	τ_3 (ps)
2	0.029	8.63	160.72
4	0.138	6.82	88.16
6	0.129	4.70	35.06
8	0.132	3.52	21.19
10	0.156	4.38	22.77
12	0.121	2.84	13.99
18	0.119	3.14	15.52
24	0.167	5.45	22.24

2 Co-MOF-74

2.1 Force field development

For Co-MOF-74, parameterization of all bonds, angles, and dihedrals containing the Co centers were derived from a genetic algorithm fit to *ab initio* calculations carried out for the reduced molecular model shown in Figure S5. A representation of the underlying potential energy surface (PES) was obtained by displacing the central Co atom (colored orange) in three dimensions in increments of 0.05 Å for a total displacement of ± 0.5 Å from the crystal structure reference.[1] The force filed parameters associated with bonds, angles, and dihedrals containing the Co centers were derived form fits to the calculated PES using a genetic algorithm.[2] As described in the main text, the force field parameters describing the intramolecular interactions within the dobdc linkers were taken from the General Amber Force Field (GAFF).[3] All force field parameters are listed in Tables 1-5.

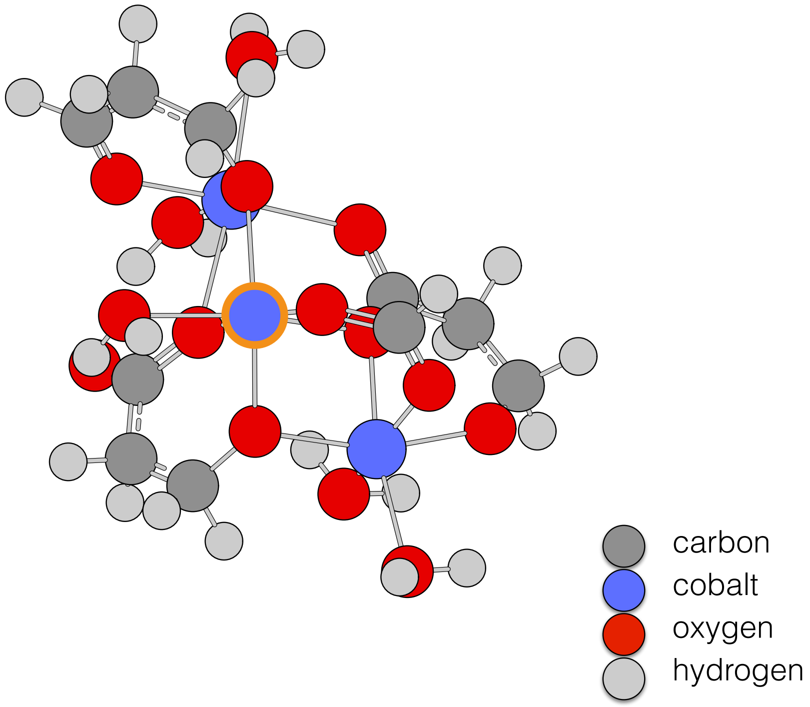

Figure S5 Reduced molecular model for Co-MOF-74 where the carbon (dark grey), cobalt (periwinkle), oxygen (red), and hydrogen (light grey) atoms are shown. The cobalt atom that was displaced in the potential energy scans is highlighted in orange.

The force field parameters describing the interaction of the water molecules with the Co atoms of the framework were obtained from a fit to a 1-dimensional potential energy scan performed using the molecular model of Figure S5 where one water molecule was incrementally moved away from the central Co atom. The calculated potential energy function was then fitted to the following analytical expression

$$U(r_{ij}) = A\exp^{-Br_{ij}} - \frac{C}{(D+r_{ij})^6} \tag{1}$$

where A = 45620.40 kcal mol^{-1}, B = 0.277128 Å^{-1}, C = 137171.00 kcal mol^{-1} Å^6, and D = 1.92618 Å. As described in Figure S6,

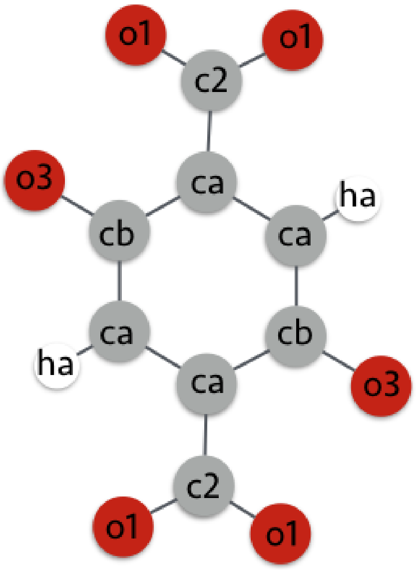

Figure S6 Atom labels used in the definition of the force field parameters for Co-MOF-74 for the organic linker. See text for details.

the atom labels for the force field parameters are shown for 2,5-dioxido-1,4-benzenedicarboxylate. Only one atom type for cobalt was used, Co, and so it is not shown.

Table S3 Electrostatic and Lennard-Jones potentials.

Atom name	Charge	ε (kcal/mol)	$\sigma/2$
Co	1.5780	0.00146124	1.08420
o1	-0.7651	0.08600	1.69983
o3	-0.8822	0.21000	1.47996
c2	0.7173	0.17000	1.50001
ca	-0.2045	0.08600	1.69983
cb	0.3048	0.08600	1.69983
ha	0.2213	0.01570	1.23568

Table S4 Bond potentials: Morse functions. The atom types are defined in Table S3.

Type	D_e	r_0(Å)	α(Å^{-1})
Co-o1	315.932903	1.998278	0.660894
Co-o3	362.942405	2.185981	0.662206

Table S5 Bond potentials: Harmonic functions. The atom types are defined in Table S3.

Type	K_{ij} (kcal/mol Å^2)	r_0(Å)
c2-ca	699.400024	1.487000
c2-o1	1296.000000	1.214000
o3-cb	752.200012	1.370000
ca-cb	823.400024	1.434000
ca-ca	956.799988	1.387000
ca-ha	688.599976	1.087000

Table S6 Angle potentials. The atom types are defined in Table S3.

Type	K_{ijk} (kcal/mol rad^2)	θ(°)
Co-o1-Co	158.969306	90.200136
Co-o1-c2	100.750895	128.137807
Co-o3-cb	91.5568840	126.495318
Co-o3-Co	158.197039	98.327439
o1-Co-o3	60.0203710	93.927311
o1-Co-o1	166.601359	90.952784
o3-Co-o3	90.2478890	164.138608
ca-c2-o1	137.339996	123.400002
o1-c2-o1	156.339996	130.300003
o3-cb-ca	139.639999	115.099998
c2-ca-cb	139.639999	115.099998
c2-ca-ca	129.279999	120.099998
ca-cb-ca	127.879997	117.500000
ca-ca-ha	96.919998	120.000000
ca-ca-cb	131.979996	120.099998
cb-ca-ha	98.139999	120.699997

Table S7 Dihedral potentials. The atom types are defined in Table S3.

Type	K_{ijkl} (kcal/mol)	χ(°)	N
Co-o1-Co-o3	6.944602	180.0000	0
Co-o1-Co-o1	0.338875	180.0000	0
Co-o1-c2-ca	7.815491	180.0000	0
Co-o1-c2-o1	4.222580	180.0000	0
Co-o3-Co-o1	6.028692	180.0000	0
Co-o3-Co-o3	6.068571	180.0000	0
o1-Co-o3-cb	0.068131	180.0000	0
o1-Co-o1-c2	2.995051	180.0000	0
o3-Co-o1-c2	1.377885	180.0000	0
o3-Co-o3-cb	4.022739	180.0000	0
Co-o3-cb-ca	1.050000	180.0000	2
o1-c2-ca-cb	1.000000	180.0000	2
o1-c2-ca-ca	1.000000	180.0000	2
o3-cb-ca-c2	0.700000	180.0000	2
o3-cb-ca-ca	0.700000	180.0000	2
o3-cb-ca-ha	0.700000	180.0000	2
c2-ca-cb-ca	3.625000	180.0000	2
c2-ca-ca-ha	3.625000	180.0000	2
c2-ca-ca-cb	3.625000	180.0000	2
ca-cb-ca-ca	3.625000	180.0000	2
ca-cb-ca-ha	3.625000	180.0000	2
cb-ca-ca-ha	3.625000	180.0000	2
cb-ca-ca-cb	3.625000	180.0000	2
ca-o1-c2-o1	1.100000	180.0000	0
c2-ca-ca-cb	1.100000	180.0000	0
ca-ca-cb-o3	1.100000	180.0000	0
ca-cb-ca-ha	1.100000	180.0000	0

2.2 Water radial distribution functions

As mentioned in the main text, there is little variation in the water structure obtained from simulations with either a flexible or a rigid model of Co-MOF-74. This can be clearly seen in Figure S7 that shows the cobalt-water oxygen (Co-Ow) radial distribution functions calculated at four different loadings, N=18, 36, 54, and 72 using flexible (black) and rigid (red) frameworks.

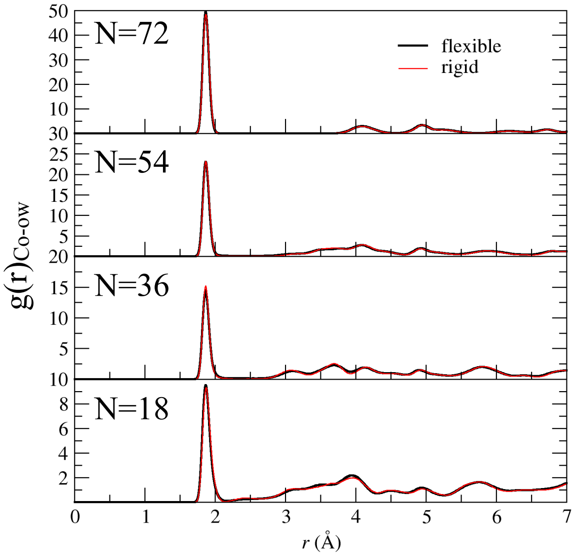

Figure S7 Co-Ow radial distribution functions in the flexible (black) and rigid (red) Co-MOF-74 as a function of water molecules, N, per pore.

2.3 Water orientational dynamics

The reorientation decay of $C_2(t)$ was fitted to a tri-exponential function to gain quantitative insights into the hydrogen bonding dynamics of water adsorbed in Co-MOF-74. While only the relevant τ_2 parameters are reported in the main text, all relaxation times are listed in Table S8 and S9.

Table S8 Relaxation time constants, τ_i, obtained from fits to orientational correlation functions $C_2(t)$ calculated for water in flexible and rigid Co-MOF-74 as a function of number of H_2O molecules per pore.

N	τ_1^{flex} (ps)	τ_2^{flex} (ps)	τ_3^{flex} (ps)	τ_1^{rig} (ps)	τ_2^{rig} (ps)	τ_3^{rig} (ps)
18	<0.01	0.08	985	<0.01	2.35	617
36	<0.01	10.42	246	<0.01	11.97	318
54	<0.01	7.80	1128	<0.01	12.22	3633
72	<0.01	7.30	412	<0.01	7.96	737

Table S9 Relaxation time constants, τ_i, obtained from fits to orientational correlation functions $C_2(t)$ calculated for water in rigid Co-MOF-74 as a function of number of H_2O molecules per pore.

N	τ_1^{flex} (ps)	τ_2^{flex} (ps)	τ_3^{flex} (ps)	τ_1^{rig} (ps)	τ_2^{rig} (ps)	τ_3^{rig} (ps)
36	<0.01	13.43	283	<0.01	10.13	687
54	<0.01	10.41	273	<0.01	29.45	928
72	<0.01	7.49	145	<0.01	10.79	425

References

[1] P. D. C. Dietzel, Y. Morita, R. Blom and H. Fjellvåg, *Angew. Chem. Int. Ed.*, 2005, **44**, 6354–6358.

[2] D. E. Goldberg, *Genetic Algorithms in Search, Optimization and Machine Learning*, Addison-Wesley Longman Publishing Co.,Inc.: Boston, MA, U.S.A., 1st edn., 1989.

[3] J. M. Wang, R. Wolf, J. Caldwell, P. Kollman and D. Case, *J. Comput. Chem.*, 2005, **25**, 1157–1174.