ELECTRONIC SUPPLEMENTARY INFORMATION

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Combined Quantum Mechanical and Molecular Mechanical Method for Metal-Organic Frameworks: Proton Topologies of NU-1000

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Force Field Parameterization

Recently, Bristow et al. developed a transferable force field called BTW-FF[1] for six MOFs including MOF-5, IRMOF-10, IRMOF-14, UiO-66, UiO-67, and HKUST-1. We chose this force field as a starting point for making a force field for NU-1000 because (i) UiO-66 and UiO-67 have the same node structure, $[Zr_6(\mu_3\text{-}O)_8H_4]^{12+}$, as NU-1000, and (ii) BTW-FF uses the functional form of MM3,[2-4] which is available in many programs. For example, *TINKER*[5] contains the full set parameters of the MM3 force field. Therefore, only a small number of parameters, namely those associated with the -OH and $-OH_2$ chemical groups (see Fig. S1) needed to be added.

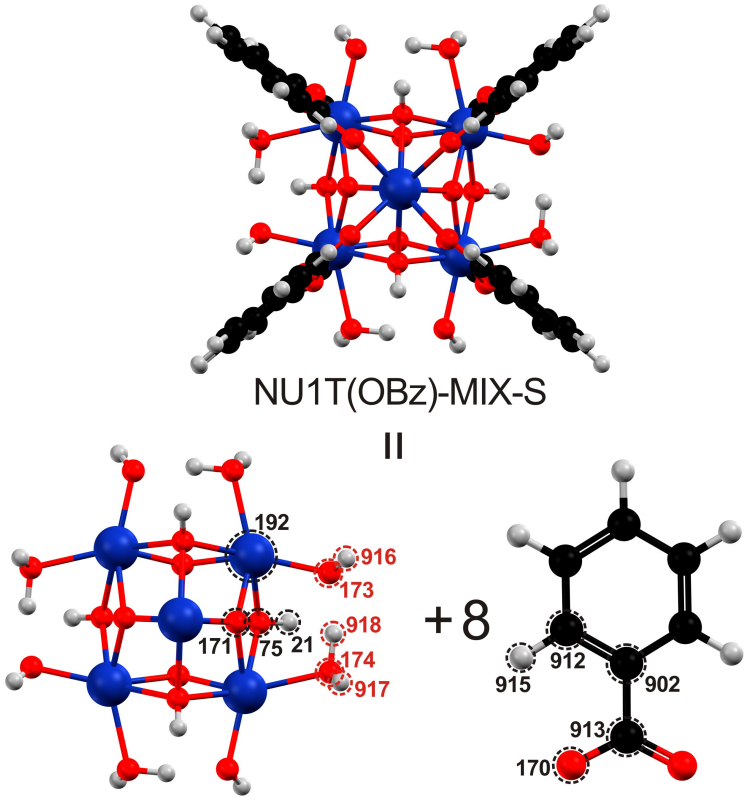

Fig. S1 Atom type definitions for the NU1T(OBz)-MIX-S cluster. The newly added atom types are in red dashed circles, while atom types already included in BTW-FF are in black dashed circles.

In addition to adding the missing parameters, we changed the charge parameters. In particular, considering that CM5[6] charges can predict more accurate dipole moments than other charge models and that accurate bond dipoles are important for describing electrostatic interactions in MOFs with polar bonds, we used averaged CM5 charges for each atom type (see Table S1) to replace the original atomic partial charge parameters in the BTW-FF. We first optimized the NU1T(OBz) structure with the most stable MIX-S topology,[7] using the M06-L functional[8] with the 6-31G(d,p)[9] basis set for H, C, and O and the Stuttgart [8s7p6d1f | 6s5p3d1f] ECP10MDF contracted effective core potential (SDD)[10] basis set for Zr in *Gaussian 09*[11]. Then we obtained the CM5 charges through a single-point calculation on the optimized structure using the M06-L functional with the 6-311+G(df,p)[9] basis set for H, C, and O and the SDD basis set for Zr.

Table S1. CM5 charges for each atom type.

Atom Type	902	912	913	75	170	171	173
Element	C	C	C	O	O	O	O
Charge	-0.014	-0.082	0.270	-0.665	-0.362	-0.777	-0.676
Atom Type	174	21	915	916	917	918	192
Element	O	H	H	H	H	H	Zr
Charge	-0.604	0.343	0.095	0.302	0.337	0.306	1.493

Van der Waals parameters for new atom types of oxygen and hydrogen were taken to be identical to those of other oxygen and hydrogen types in the BTW-FF force field. Equilibrium bond lengths and bond angles were derived from the DFT optimized structure. Then force constants were derived by fitting the classically optimized structure of NU1T(OBz)-MIX-S to its DFT optimized counterpart. The classical calculations were performed in *TINKER 6.3*. The MINIMIZE program of *TINKER* was utilized to perform geometry optimization. All eight phenyl groups of the cluster were fixed during optimization. The derived parameters are summarized in Tables S2 through S7. Combining those parameters, the CM5 charges, and the original parameters in BTW-FF generates a modified version of the BTW-FF force field, which is called the NU1T force field, and which allows calculations on NU-1000. From Fig. S2 and Table S8, we can see that classical optimization on the NU1T(OBz)-MIX-S cluster using the NU1T force field well reproduces the DFT optimized structure with an MUE of 0.011 Å and 1.23 deg for bond lengths and bond angles, respectively. Therefore, it can be concluded that the NU1T force field accurately predicts the NU1T(OBz)-MIX-S structure.

Although parameterization of the NU1T force field is solely based on the NU1T(OBz)-MIX-S structure, the NU1T force field can still be used for QM/MM calculations on the other NU1T(OBz) clusters with different proton topologies because their MM subsystems are almost identical. The NU1T force field is also validated by the encouraging QM/MM results given in the article properly.

Table S2. vdW radii and ε parameters.

Atom Type	Element	vdW radii (Å)	ε (kcal mol^{-1})
173	O	1.820	0.059
174	O	1.820	0.059
916	H	1.620	0.020
917	H	1.620	0.020
918	H	1.620	0.020

Table S3. Hydrogen bonding force constant (*k*) and equilibrium bond length (*r*).

Bond	*k* (kcal mol^{-1}/ Å^2)	*r* (Å)
173 - 918	23.080	1.624

Table S4. Bond stretching force constants (*k*) and equilibrium bond lengths (*r*).

Bond	*k* (kcal mol^{-1}/ Å^2)	r (Å)
916 - 173	3.630	0.963
917 - 174	6.500	0.966
918 - 174	32.800	1.015
173 - 192	10.500	2.108
174 - 192	10.500	2.322

Table S5. Angle bending force constants (*k*) and equilibrium bond angles (θ).

Angle	*k* (kcal mol^{-1}/radian^2)	θ (deg)
916 - 173 - 192	5.099	111.274
917 - 174 - 192	4.500	104.371
918 - 174 - 192	5.000	107.997
170 - 192 - 173	1.000	77.805
170 - 192 - 174	1.000	73.874
171 - 192 - 173	0.000	91.328
171 - 192 - 174	0.000	84.026
173 - 192 - 174	4.630	114.934
917 - 174 - 918	6.000	106.048
912 - 912 - 915	5.000	119.517
912 - 912 - 912	5.000	120.966
174 - 192 - 75	0.000	71.667
173 - 192 - 75	0.000	74.852

Table S6. Out-of-plane bending force constants (*k*).

Angle	*k* (kcal mol^{-1}/radian^2)
192 - 171 - 192 - 192	0.000
915 - 912 - 902 - 912	0.000
912 - 912 - 902 - 915	0.000
915 - 912 - 912 - 912	0.000

Table S7. Torsion force constants (k), equilibrium phase angles (Φ_0), and integer periodicity (n).

Angle	k (kcal mol^{-1}/radian^2)	Φ_0 (deg)	n
173 - 192 - 170 - 913	5.000	180.0	2
174 - 192 - 170 - 913	5.000	180.0	2
170 - 192 - 173 - 916	5.000	180.0	2
170 - 192 - 174 - 917	5.000	180.0	2
170 - 192 - 174 - 918	5.000	180.0	2
174 - 192 - 173 - 916	5.000	180.0	2
173 - 192 - 174 - 917	5.000	180.0	2
173 - 192 - 174 - 918	5.000	180.0	2
173 - 192 - 171 - 192	5.000	180.0	2
174 - 192 - 171 - 192	5.000	180.0	2
171 - 192 - 173 - 916	5.000	180.0	2
171 - 192 - 174 - 917	5.000	180.0	2
171 - 192 - 174 - 918	5.000	180.0	2
915 - 912 - 912 - 912	4.930	180.0	2
915 - 912 - 912 - 915	0.000	180.0	2
912 - 912 - 912 - 912	4.930	180.0	2
75 - 192 - 174 - 917	5.000	180.0	2
75 - 192 - 174 - 918	5.000	180.0	2
75 - 192 - 173 - 916	5.000	180.0	2
173 - 192 - 75 - 21	5.000	180.0	2
174 - 192 - 75 - 21	5.000	180.0	2
173 - 192 - 75 - 192	5.000	180.0	2
174 - 192 - 75 - 192	5.000	180.0	2

Table S8. Structural properties of NU1T(OBz)-MIX-S cluster.

		DFT	NU1T	Signed Deviation	Percentage Error (%)
	# of bonds	Averaged bond length (Å)			
C(913) – C(902)	8	1.491	1.467	-0.024	1.610
C(913) – O(170)	16	1.270	1.281	0.011	0.866
Zr(192) – O(75)	12	2.315	2.292	-0.023	0.994
Zr(192) – O(170)	16	2.277	2.305	0.028	1.230
Zr(192) – O(171)	12	2.097	2.097	-0.000	0.000
Zr(192) – O(173)	4	2.108	2.096	-0.012	0.569
Zr(192) – O(174)	4	2.322	2.309	-0.013	0.560
O(75) – H(21)	4	0.963	0.958	-0.005	0.519
O(173) – H(916)	4	0.963	0.961	-0.002	0.208
O(173) – H(918)	4	1.624	1.622	-0.002	0.123
O(174) – H(917)	4	0.966	0.960	-0.006	0.621
O(174) – H(918)	4	1.015	1.025	0.010	0.985
	MUD = 0.011				
	# of angles	Averaged bond angle (deg)			
C(912) – C(902) – C(913)	16	120.506	120.390	-0.116	0.096
O(170) – C(913) – O(170)	8	125.647	123.264	-2.383	1.897
C(902) – C(913) – O(170)	16	117.172	118.296	1.124	0.959
Zr(192) – O(170) – C(913)	16	133.600	133.739	0.139	0.104
Zr(192) – O(75) – Zr(192)	12	101.245	104.345	3.100	3.062
Zr(192) – O(171) – Zr(192)	12	117.105	119.462	2.357	2.013
Zr(192) – O(75) – H(21)	12	116.780	114.077	-2.703	2.315
Zr(192) – O(173) – H(916)	4	111.274	110.737	-0.537	0.483
Zr(192) – O(174) – H(917)	4	104.371	103.751	-0.620	0.594
Zr(192) – O(174) – H(918)	4	107.997	107.729	-0.268	0.248
H(917) – O(174) – H(918)	4	106.048	105.911	-0.137	0.129
	MUD = 1.226				

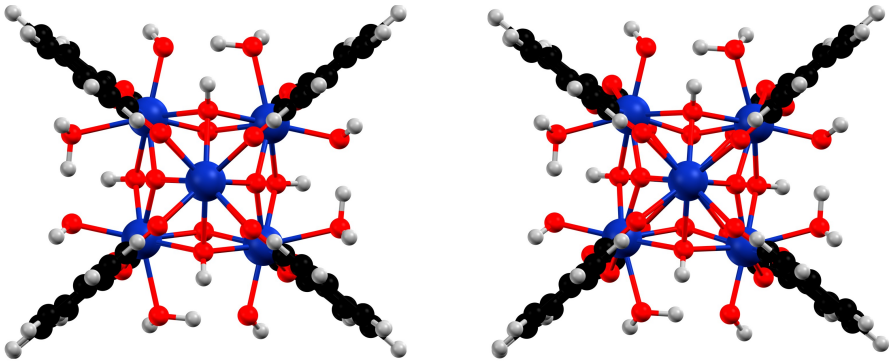

Fig. S2 Optimized structures for the NU1T(OBz)-MIX-S cluster using DFT and the NU1T force field.

ble S9. Full QM total energies (in Hartree).

	NU1T(OBz)	NU1T(OAc)	NU1T(formate)
MIX-S	-4860.426844	-3326.292756	-3011.655954
OH	-4860.299807	-3326.164959	-3011.521561
OH_2	-4860.322633	-3326.187982	-3011.561869
MIX-L	-4860.329538	-3326.196413	-3011.556485
MIX-C	-4860.368265	-3326.232037	-3011.595211
X-E(30)	-4860.371345	-3326.237690	-3011.601701
IX-E(8)	-4860.368384	-3326.234768	-3011.600521

ble S10. QM/MM total energies based on H link atoms (in Hartree).

	Mechanical Embedding	Electronic Embedding					
		BRC	BRC2	BRC3	BRCD	BS	Amber-2
MIX-S	-3011.504897	-3011.647141	-3011.633604	-3011.621557	-3011.670118	-3011.914815	-3011.616266
OH	-3011.367982	-3011.522149	-3011.506616	-3011.492259	-3011.547129	-3011.790405	-3011.488138
OH_2	-3011.409191	-3011.538463	-3011.527725	-3011.519799	-3011.558678	-3011.805009	-3011.512396
MIX-L	-3011.407374	-3011.549607	-3011.536308	-3011.524165	-3011.572337	-3011.817628	-3011.518911
MIX-C	-3011.445091	-3011.587982	-3011.574269	-3011.562045	-3011.611154	-3011.855739	-3011.556831
X-E(30)	-3011.450560	-3011.591815	-3011.578500	-3011.567162	-3011.614584	-3011.859372	-3011.561463
IX-E(8)	-3011.445841	-3011.586880	-3011.573624	-3011.562194	-3011.609607	-3011.854342	-3011.556590

ble S11. QM/MM total energies based on the F* link atoms (in Hartree).

	Mechanical Embedding	Electronic Embedding					
		BRC	BRC2	BRC3	BRCD	BS	Amber-2
MIX-S	-3186.146108	-3190.354069	-3189.247819	-3188.579132	-3191.469994	-3190.851100	-3188.794768
OH	-3186.001758	-3190.222347	-3189.112233	-3188.441647	-3191.342063	-3190.717822	-3188.658284
OH_2	-3186.063291	-3190.259029	-3189.155674	-3188.491053	-3191.372113	-3190.755471	-3188.704526
MIX-L	-3186.047315	-3190.252134	-3189.148788	-3188.480238	-3191.365172	-3190.751708	-3188.695778
MIX-C	-3186.085966	-3190.294524	-3189.187929	-3188.519156	-3191.410790	-3190.791417	-3188.734817
X-E(30)	-3186.094036	-3190.301045	-3189.194843	-3188.526905	-3191.416926	-3190.797820	-3188.742126
IX-E(8)	-3186.088798	-3190.295961	-3189.189726	-3188.521592	-3191.411920	-3190.792556	-3188.736940

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