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Molecular dynamics simulation of stability of metal-organic frameworks against H_2O using the ReaxFF reactive force field

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Supporting Information

S.1 Simulation details

In this work, we used molecular dynamics (MD) simulation to simulate volume changes of metal-organic frameworks (MOFs) such as isoreticular MOF-1 (IRMOF-1) and MOF-74 as a function of H_2O content. Our MD simulations used a time step of 0.001 ps (picosecond) and were performed up to 2000 ps. We maintained the temperature (300 K) using a Berendsen thermostat with a damping constant of 0.001 ps. Also, the pressure (1 atm) is maintained using a Berendsen barostat with a damping constant of 5 ps. (Such MD is denote as NPT). This method leads to independent changes of lattice parameters (a, b, c) of the MOF structures while the lattice angles (α, β, γ) are fixed. To eliminate boundary effects in calculating volume changes of the MOFs, we considered an infinite three-dimensionally periodic simulation boxes, in which we used simulation boxes containing unit cells ($1 \times 1 \times 1$) for IRMOF-1 and a $1 \times 1 \times 3$ supercell for MOF-74. And, the initial structures including MOFs and H_2O molecules are built using a grand-canonical Monte-Carlo simulation[S1] with the universal force field[S2] where the H_2O molecules are randomly distributed in free volume of the MOFs.

To describe the dynamics of MOFs including H_2O molecules, we used the reactive force field (ReaxFF)[S3] known to accurately simulate chemical reactions (bond breaking and formation) in large systems in contrast to classical force fields. The ReaxFF uses a general relationship between bond distance and bond order on one hand and between bond order and bond energy on the other hand that leads to proper dissociation of bonds to separated atoms.[3a] The connectivities between the atoms can be modified during a MD simulation allowing spontaneous bond breaking and bond formation.[3e] And, similar to quantum mechanical (QM) calculations, each element is represented by only one atom type in the ReaxFF. This facilitates the transferability of the

parameters to a different system and avoids the modification of atom types during a chemical reaction.

The nonbonded interactions need to be calculated between every atom pair in order to describe a system with changing connectivity. Thus, the van der Waals energy is calculated between all atom pairs using a distance-corrected Morse potential. A shielded interaction is implemented to avoid the excessive high repulsion between the bonded atom pairs. Similarly, the Coulomb energy is calculated between all atom pairs using a shielded coulomb potential. For each element, the electronegativity, hardness, and shielding parameters are optimized to reproduce the QM derived charges. To account for the polarization effect, the atomic charges are dynamically derived using the electronegativity equalization method where they are calculated at every step in contrast to classical force field using fixed charges. Generally, all parameters of the ReaxFF are developed from QM calculations. For further details about the ReaxFF method see refs. S3a and S3b.

In this work, we used reported ReaxFF parameters[S4] for description of the ZnO-water system. The ReaxFF reproduce experimental and/or QM lattice parameters, heats of formation, and mechanical properties such as bulk modulus and elastic constants for four ZnO crystal structures (wurtzite, zinc blende, rocksalt, and caesium chloride). Also, it successfully predicts water adsorption reactions on ZnO surfaces. By MD simulations with this ReaxFF, we obtained the following lattice parameters for pure MOFs; 26.88 Å for IRMOF-1, 35.25 Å for IRMOF-10, and a = 26.73 Å and c = 6.78 Å for MOF-74. These are comparable to experimental values; 25.67 – 25.89 Å for IRMOF-1,[S5] 34.28 Å for IRMOF-10,[S5c] and a = 25.93 Å and c = 6.84 Å for MOF-74.[S6] The ReaxFF parameters used in this work are shown below. And this force field can be used with

both the standalone ReaxFF program (available from Prof. A. C. T. van Duin of this work on request) and with the open source LAMMPS/ReaxFF software (from Sandia).

```
Reactive MD-force field: Han et al. ZnO/MOF force field
 39          ! Number of general parameters
    50.0000 !Overcoordination parameter
     9.5469 !Overcoordination parameter
    26.5405 !Valency angle conjugation parameter
     1.7224 !Triple bond stabilisation parameter
     6.8702 !Triple bond stabilisation parameter
    60.4850 !C2-correction
     1.0588 !Undercoordination parameter
     4.6000 !Triple bond stabilisation parameter
    12.1176 !Undercoordination parameter
    13.3056 !Undercoordination parameter
   -70.5044 !Triple bond stabilization energy
     0.0000 !Lower Taper-radius
    10.0000 !Upper Taper-radius
     2.8793 !Not used
    33.8667 !Valency undercoordination
     6.0891 !Valency angle/lone pair parameter
     1.0563 !Valency angle
     2.0384 !Valency angle parameter
     6.1431 !Not used
     6.9290 !Double bond/angle parameter
     0.3989 !Double bond/angle parameter: overcoord
     3.9954 !Double bond/angle parameter: overcoord
    -2.4837 !Not used
     5.7796 !Torsion/BO parameter
    10.0000 !Torsion overcoordination
     1.9487 !Torsion overcoordination
    -1.2327 !Conjugation 0 (not used)
```

```
   2.1645 !Conjugation
   1.5591 !vdWaals shielding
   0.1000 !Cutoff for bond order (*100)
   2.1365 !Valency angle conjugation parameter
   0.6991 !Overcoordination parameter
  50.0000 !Overcoordination parameter
   1.8512 !Valency/lone pair parameter
   0.5000 !Not used
  20.0000 !Not used
   5.0000 !Molecular energy (not used)
   0.0000 !Molecular energy (not used)
   2.6962 !Valency angle conjugation parameter
 4      ! Nr of atoms; cov.r; valency;a.m;Rvdw;Evdw;gammaEEM;cov.r2;#
              alfa;gammavdW;valency;Eunder;Eover;chiEEM;etaEEM;n.u.
              cov r3;Elp;Heat inc.;n.u.;n.u.;n.u.;n.u.
              ov/un;val1;n.u.;val3,vval4
C      1.3825    4.0000   12.0000    1.9133    0.1853    0.9000    1.1359    4.0000
       9.7602    2.1346    4.0000   33.2433   79.5548    5.8678    7.0000    0.0000
       1.2104    0.0000  199.0303    8.6991   34.7289   13.3894    0.8563    0.0000
      -2.8983    2.5000    1.0564    4.0000    2.9663    0.0000    0.0000    0.0000
H      0.8930    1.0000    1.0080    1.3550    0.0930    0.8203   -0.1000    1.0000
       8.2230   33.2894    1.0000    0.0000  121.1250    3.7248    9.6093    1.0000
      -0.1000    0.0000   61.6606    3.0408    2.4197    0.0003    1.0698    0.0000
     -19.4571    4.2733    1.0338    1.0000    2.8793    0.0000    0.0000    0.0000
O      1.2450    2.0000   15.9990    2.3890    0.1000    1.0898    1.0548    6.0000
       9.7300   13.8449    4.0000   37.5000  116.0768    8.5000    8.3122    2.0000
       0.9049    0.4056   59.0626    3.5027    0.7640    0.0021    0.9745    0.0000
      -3.5500    2.9000    1.0493    4.0000    2.9225    0.0000    0.0000    0.0000
Zn     1.8862    2.0000   65.3900    1.9200    0.2998    0.4828   -1.6836    2.0000
      11.5134   18.3776    2.0000    0.0078    0.0000    2.0219    5.7915    0.0000
      -1.2000    0.0000  266.4838    5.3430   10.1260    0.7590    0.0000    0.0000
      -3.0614    2.1158    1.0338    6.2998    2.5791    0.0000    0.0000    0.0000
10       ! Nr of bonds; Edis1;LPpen;n.u.;pbe1;pbo5;13corr;pbo6
                        pbe2;pbo3;pbo4;n.u.;pbo1;pbo2;ovcorr
 1   1 158.2004   99.1897   78.0000   -0.7738   -0.4550    1.0000   37.6117    0.4147
```

```
         0.4590   -0.1000    9.1628    1.0000   -0.0777    6.7268    1.0000    0.0000
 1   2 169.4760    0.0000    0.0000   -0.6083    0.0000    1.0000    6.0000    0.7652
         5.2290    1.0000    0.0000    1.0000   -0.0500    6.9136    0.0000    0.0000
 2   2 153.3934    0.0000    0.0000   -0.4600    0.0000    1.0000    6.0000    0.7300
         6.2500    1.0000    0.0000    1.0000   -0.0790    6.0552    0.0000    0.0000
 1   3 158.6946  107.4583   23.3136   -0.4240   -0.1743    1.0000   10.8209    1.0000
         0.5322   -0.3113    7.0000    1.0000   -0.1447    5.2450    0.0000    0.0000
 3   3 142.2858  145.0000   50.8293    0.2506   -0.1000    1.0000   29.7503    0.6051
         0.3451   -0.1055    9.0000    1.0000   -0.1225    5.5000    1.0000    0.0000
 2   3 160.0000    0.0000    0.0000   -0.5725    0.0000    1.0000    6.0000    0.5626
         1.1150    1.0000    0.0000    1.0000   -0.0920    4.2790    0.0000    0.0000
 1   4   0.0000    0.0000    0.0000    0.0000   -0.5000    1.0000   36.0000    0.0082
         1.7973   -0.2500   20.0000    1.0000   -0.2578    6.5219    0.0000    0.0000
 2   4   0.0000    0.0000    0.0000    0.0000   -0.5000    1.0000   50.0000    0.5000
         0.5000   -0.5000   30.0000    1.0000   -0.2000    8.0000    0.0000    0.0000
 3   4 159.9755    0.0000    0.0000   -0.4548   -0.5000    0.0000   35.0000    0.0375
         1.3099   -0.5000   25.0000    1.0000   -0.4787    4.6717    0.0000    0.0000
 4   4  38.4643    0.0000    0.0000   -0.6944   -0.2000    0.0000   16.0000    0.2129
         0.5059   -0.2000   15.0000    1.0000   -0.0814    6.0333    0.0000    0.0000
 7      ! Nr of off-diagonal terms; Ediss;Ro;gamma;rsigma;rpi;rpi2
 1   2   0.1219    1.4000    9.8442    1.1203   -1.0000   -1.0000
 2   3   0.0283    1.2885   10.9190    0.9215   -1.0000   -1.0000
 2   4   0.1059    1.8290    9.7818    0.9598   -1.0000   -1.0000
 1   3   0.1131    1.8523    9.8442    1.2775    1.1342    1.0621
 1   4   0.3000    1.6692   11.1307    0.0100   -1.0000   -1.0000
 2   4   0.0987    1.8227   12.0654    0.1000   -1.0000   -1.0000
 3   4   0.2744    2.1414    9.7703    1.9804   -1.0000   -1.0000
24      ! Nr of angles;at1;at2;at3;Thetao,o;ka;kb;pv1;pv2
 1   1   1  59.0573   30.7029    0.7606    0.0000    0.7180    6.2933    1.1244
 1   1   2  65.7758   14.5234    6.2481    0.0000    0.5665    0.0000    1.6255
 2   1   2  70.2607   25.2202    3.7312    0.0000    0.0050    0.0000    2.7500
 1   2   2   0.0000    0.0000    6.0000    0.0000    0.0000    0.0000    1.0400
 1   2   1   0.0000    3.4110    7.7350    0.0000    0.0000    0.0000    1.0400
 2   2   2   0.0000   27.9213    5.8635    0.0000    0.0000    0.0000    1.0400
 1   1   3  49.6811    7.1713    4.3889    0.0000    0.7171   10.2661    1.0463
```

3	1	3	77.7473	40.1718	2.9802	-25.3063	1.6170	-46.1315	2.2503
2	1	3	65.0000	13.8815	5.0583	0.0000	0.4985	0.0000	1.4900
1	3	1	73.5312	44.7275	0.7354	0.0000	3.0000	0.0000	1.0684
1	3	3	79.4761	36.3701	1.8943	0.0000	0.7351	67.6777	3.0000
3	3	3	80.7324	30.4554	0.9953	0.0000	1.6310	50.0000	1.0783
1	3	2	70.1880	20.9562	0.3864	0.0000	0.0050	0.0000	1.6924
2	3	3	75.6935	50.0000	2.0000	0.0000	1.0000	0.0000	1.1680
2	3	2	85.8000	9.8453	2.2720	0.0000	2.8635	0.0000	1.5800
1	2	3	0.0000	25.0000	3.0000	0.0000	1.0000	0.0000	1.0400
1	2	5	0.0000	0.0019	6.0000	0.0000	0.0000	0.0000	1.0400
3	2	3	0.0000	15.0000	2.8900	0.0000	0.0000	0.0000	2.8774
2	2	3	0.0000	8.5744	3.0000	0.0000	0.0000	0.0000	1.0421
2	3	4	77.5446	9.9016	2.3157	0.0000	0.4543	0.0000	2.3770
3	4	3	10.8790	38.9915	0.7072	0.0000	2.0000	0.0000	2.6162
4	3	4	37.5284	32.3525	0.2657	0.0000	0.4403	0.0000	1.1000
3	4	4	16.9624	30.3241	0.2697	0.0000	2.0000	0.0000	3.0708
3	3	4	60.0000	20.0000	0.5000	0.0000	1.0000	0.0000	2.0000

21 ! Nr of torsions;at1;at2;at3;at4;;V1;V2;V3;V2(BO);vconj;n.u;n

1	1	1	1	-0.2500	11.5822	0.1879	-4.7057	-2.2047	0.0000	0.0000
1	1	1	2	-0.2500	31.2596	0.1709	-4.6391	-1.9002	0.0000	0.0000
2	1	1	2	-0.1770	30.0252	0.4340	-5.0019	-2.0697	0.0000	0.0000
1	1	1	3	-0.7098	22.2951	0.0060	-2.5000	-2.1688	0.0000	0.0000
2	1	1	3	-0.3568	22.6472	0.6045	-4.0088	-1.0000	0.0000	0.0000
3	1	1	3	-0.0528	6.8150	0.7498	-5.0913	-1.0000	0.0000	0.0000
1	1	3	1	2.0007	25.5641	-0.0608	-2.6456	-1.1766	0.0000	0.0000
1	1	3	2	-1.1953	42.1545	-1.0000	-8.0821	-1.0000	0.0000	0.0000
2	1	3	1	-0.9284	34.3952	0.7285	-2.5440	-2.4641	0.0000	0.0000
2	1	3	2	-2.5000	79.6980	1.0000	-3.5697	-2.7501	0.0000	0.0000
1	1	3	3	-0.0179	5.0603	-0.1894	-2.5000	-2.0399	0.0000	0.0000
2	1	3	3	-0.5583	80.0000	1.0000	-4.4000	-3.0000	0.0000	0.0000
3	1	3	1	-2.5000	76.0427	-0.0141	-3.7586	-2.9000	0.0000	0.0000
3	1	3	2	0.0345	78.9586	-0.6810	-4.1777	-3.0000	0.0000	0.0000
3	1	3	3	-2.5000	66.3525	0.3986	-3.0293	-3.0000	0.0000	0.0000
1	3	3	1	2.5000	-0.5332	1.0000	-3.5096	-2.9000	0.0000	0.0000
1	3	3	2	-2.5000	3.3219	0.7180	-5.2021	-2.9330	0.0000	0.0000

```
2   3   3   2    2.2500   -6.2288    1.0000   -2.6189   -1.0000    0.0000    0.0000
1   3   3   3    0.0531  -17.3983    1.0000   -2.5000   -2.1584    0.0000    0.0000
2   3   3   3    0.4723  -12.4144   -1.0000   -2.5000   -1.0000    0.0000    0.0000
3   3   3   3   -2.5000  -25.0000    1.0000   -2.5000   -1.0000    0.0000    0.0000
1      ! Nr of hydrogen bonds;at1;at2;at3;Rhb;Dehb;vhb1
3   2   3    2.1200   -3.5800    1.4500   19.5000
```

S.2 MD snapshots of IRMOF-10

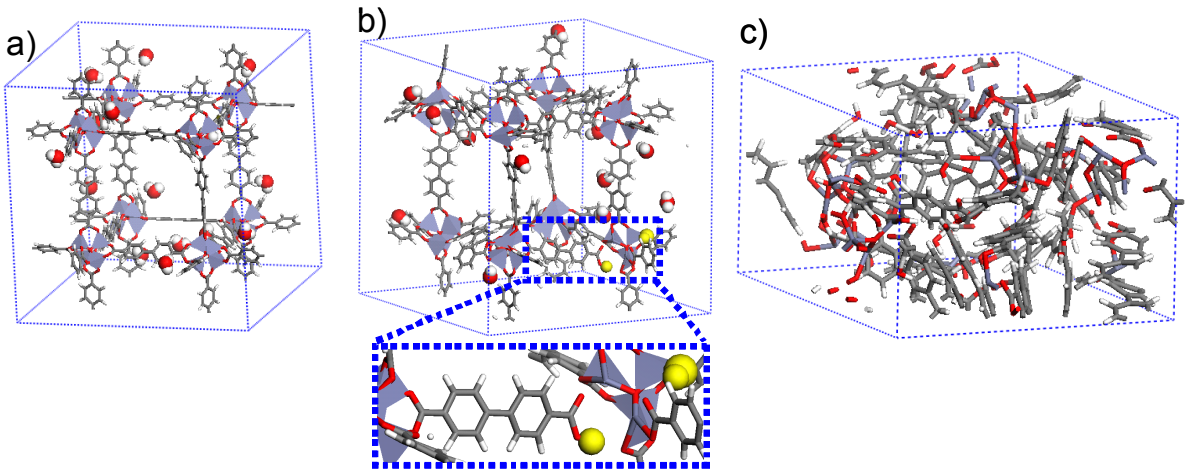

Figure S1. MD snapshots of IRMOF-10 with 16 H_2O molecules (3.5 wt% H_2O) at 0 ps (initial structure) (a), 20 ps (b), and 2000 ps (c). In Fig. b, the yellow atoms indicate OH (bonded to Zn cation of the SBU) and H (bonded to the organic linker) atoms dissociated from H_2O.

S.2 References

S1. Using the Cerius2 software (Version 4.10, Accelrys Inc., San Diego)

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