Supporting information for

ReaxFF Molecular Dynamics Simulations of Water Stability of Interpenetrated Metal-Organic Frameworks

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Lattice parameters of MOFs

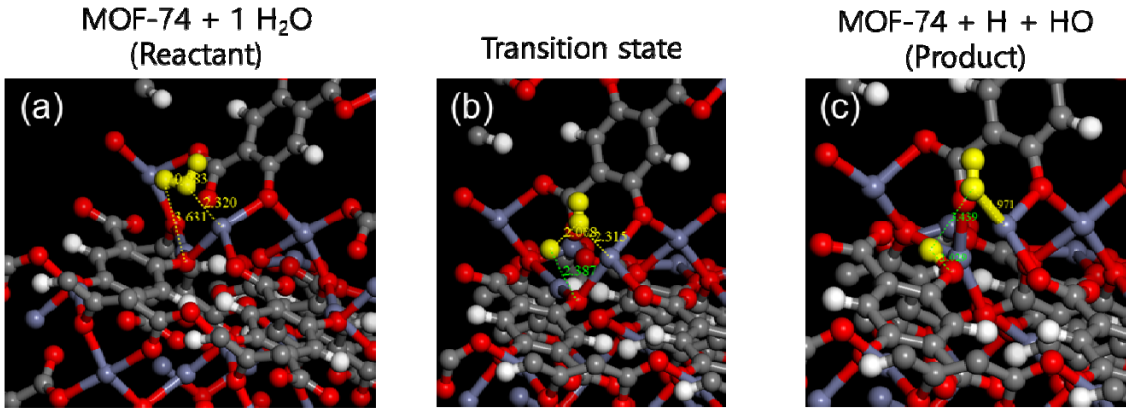
Table S1. Lattice parameters of IRMOF-9, IRMOF-10, IRMOF-13, IRMOF-14, and SUMOF-4 used in this work. These are from Ref. S1 and S2.

Structure	Lattice parameter (*Å*)
IRMOF-9	a = 17.15, b = 23.32, c = 25.25
IRMOF-10	$a = b$ = 24.82, c = 56.73
IRMOF-13	a = 18.38, b = 17.30, c = 17.96
IRMOF-14	$a = b = c$ = 34.28
SUMOF-4	$a = b = c$ = 34.38

[Ref. S1] Eddaoudi, M.; Kim, J.; Rosi, N.; Vodak, D.; Wachter, J.; O'Keeffe, M.; Yaghi, O. M. *Science* **2002**, *295*, 469.

[Ref. S2] Yao, Q.; Su, J.; Cheung, O.; Liu, Q.; Hedin, N.; Zou, X. *J. Mater. Chem.* **2012**, *22*, 10345.

Water dissociation reaction in Zn-MOF-74: ReaxFF versus DFT



(d)

Method	Energy barrier (kcal/mol)	Energy difference (kcal/mol)
DFT[29]	25.1	-23.1
ReaxFF	22.5	-21.0

Figure S1. ReaxFF versus DFT for a water dissociation reaction in Zn-MOF-74. (a-c) the water dissociation reaction pathway predicted by the ReaxFF. (d) comparison of ReaxFF and DFT energies for the reaction. Here, the DFT values are from Ref. 29.

Effects of Zn-O_{ligand} strength on the water stability of MOFs

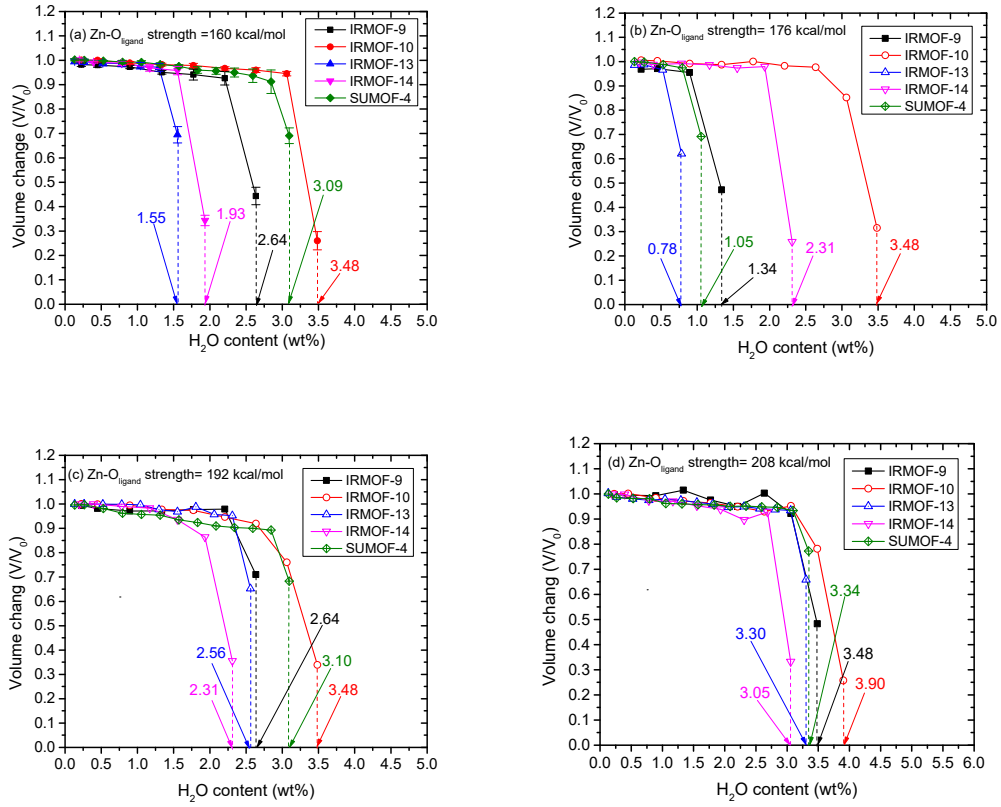


Figure S2. Simulated volume change of IRMOF-9, IRMOF-10, IRMOF-13, IRMOF-14 and SUMOF-4 as a function of water contents at 300 K and 1 atm. Here, (a), (b), (c) and (d) correspond to the Zn-O_{ligand} bond strength of 160 kcal/mol (default value), 176 kcal/mol (10 % increase of the default value), 192 kcal/mol (20 % increase), and 208 kcal/mol (30 % increase), respectively. Note that the original ReaxFF parameter for the $E_{Zn-O_{ligand}}$ optimized from first-principles calculations is 160 kcal/mol (default value).[42]

The ReaxFF parameters used in this work

```
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
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```
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
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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
```