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


# Supporting information:

## Multi-scale computational investigation of Ag-doped two-dimensional Zn-based MOF for storage and release of small NO and CO bioactive molecules

Shabnam Naderlou[a,*] Morteza Vahedpour[a], Douglas M. Franz[b]

[a.] *Department of Chemistry, University of Zanjan (ZNU), P.O. Box 38791-45371, Zanjan, Iran*

[b.] *Department of Chemistry, University of South Florida, 4202 East Fowler Avenue, CHE205, Tempa, FL 33620-5250, USA*

* Corresponding author.
*E-mail address*: sh.naderlou@znu.ac.ir and sh.naderloo68@gmail.com.

**Table S1** Structural properties of MOFs

| Term | symmetry | a | b | c | $\alpha$ | $\beta$ | $\gamma$ | Pore dimeter | AV ($cm^3.g^{-1}$) | NAV ($cm^3.g^{-1}$) | ASA ($m^2.g^{-1}$) | NASA ($m^2.g^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| (Zn)MOF-470 | P -3 1 c | 16.7057 | 16.7057 | 14.3418 | 90 | 90 | 120 | 14.89123 | 3.223 | 0 | 13825.3 | 0 |
| Ag-(Zn)MOF-470 | P -3 1 c | 16.7057 | 16.7057 | 14.3418 | 90 | 90 | 120 | 13.45286 | 2.569 | 0 | 13308.8 | 0 |

**Table S2** Morse potential non-bonded parameters for interactions of $H_2$, NO, CO, Ag and $H_2O$ with MOF atoms (see the Figure S1 for the definition rules of atom types).

| Term | $D/k_B$ (K) | α ($Å^{-1}$) | r (Å) | Term | $D/k_B$ (K) | α ($Å^{-1}$) | r (Å) |
|---|---|---|---|---|---|---|---|
| N_no-C1 | 92.15 | 1.12 | 4.07 | C_co-C1 | 178.91 | 1.47 | 3.8 |
| N_no-C2 | 78.49 | 2.09 | 3.2 | C_co-C2 | 78.33 | 1.88 | 3.78 |
| N_no-C3 | 86.07 | 1.28 | 3.79 | C_co-C3 | 54.53 | 1.46 | 4.12 |
| N_no-C4 | 102.12 | 1.32 | 3.69 | C_co-C4 | 168.36 | 1.41 | 3.81 |
| N_no-C5 | 96.01 | 1.28 | 3.8 | C_co-C5 | 73.94 | 1.55 | 3.95 |
| N_no-C8 | 53.43 | 2.87 | 3.13 | C_co-C8 | 95.65 | 1.76 | 3.72 |
| N_no-C9 | 81.45 | 1.43 | 3.62 | C_co-C9 | 185.13 | 1.69 | 3.5 |
| N_no-H3 | 15.51 | 2.31 | 3.14 | C_co-H3 | 23.59 | 1.52 | 3.68 |
| N_no-H4 | 60.61 | 1.43 | 3.39 | C_co-H4 | 28.35 | 2.07 | 3.21 |
| N_no-H9 | 45.95 | 1.58 | 3.45 | C_co-H9 | 23.81 | 1.11 | 4 |
| N_no-O2 | 120.58 | 1.63 | 3.28 | C_co-O2 | 107.08 | 1.2 | 4.01 |
| N_no-O3 | 58.68 | 1.09 | 4.36 | C_co-O3 | 35.14 | 1.52 | 4.02 |
| N_no-Zn2 | 80.77 | 2.05 | 2.85 | C_co-Zn2 | 31.16 | 1.59 | 4.1 |
| O_no-C1 | 63.4 | 1.51 | 4.12 | O_co-C1 | 181 | 1.57 | 3.71 |
| O_no-C2 | 41.38 | 2.17 | 3.8 | O_co-C2 | 147.85 | 1.38 | 3.98 |
| O_no-C3 | 64.47 | 1.7 | 4 | O_co-C3 | 112.43 | 1.68 | 3.81 |
| O_no-C4 | 60.51 | 1.6 | 4.14 | O_co-C4 | 53.64 | 1.62 | 4.13 |
| O_no-C5 | 64.03 | 1.55 | 4.2 | O_co-C5 | 76.16 | 1.78 | 3.84 |
| O_no-C8 | 183.43 | 1.28 | 4.08 | O_co-C8 | 61.41 | 1.65 | 4.04 |
| O_no-C9 | 146.46 | 1.62 | 3.8 | O_co-C9 | 50.94 | 1.59 | 4.23 |
| O_no-H3 | 47.9 | 1.23 | 3.79 | O_co-H3 | 27.88 | 1.5 | 3.76 |
| O_no-H4 | 10.08 | 1.34 | 4.15 | O_co-H4 | 21.81 | 2.04 | 3.34 |
| O_no-H9 | 18.79 | 1.27 | 4.13 | O_co-H9 | 6.66 | 1.2 | 4.48 |
| O_no-O2 | 230.37 | 1.77 | 3.35 | O_co-O2 | 37.18 | 1.76 | 3.89 |
| O_no-O3 | 68.18 | 2.19 | 3.46 | O_co-O3 | 73.1 | 1.55 | 3.95 |
| O_no-Zn2 | 6.95 | 1.34 | 4.28 | O_co-Zn2 | 132.83 | 1.55 | 3.71 |
| N_no-N_no [b] | 120.18 | 1.1 | 3.97 | C_co-C_co [b] | 69.04 | 1.37 | 3.89 |
| N_no-O_no [b] | 104.46 | 1.36 | 3.91 | C_co-O_co [b] | 59.92 | 1.61 | 3.84 |
| O_no-O_no [b] | 113.99 | 1.36 | 3.71 | O_co-O_co [b] | 48.61 | 2 | 3.38 |
| H_h2-C1 | 24.84 | 1.87 | 3.75 | Ag-N_no | 567.94 | 2.48 | 2.67 |
| H_h2-C2 | 29.98 | 1.7 | 3.74 | Ag-O_no | 694.17 | 1.45 | 3.47 |
| H_h2-C3 | 31.73 | 1.6 | 3.7 | Ag-C_co | 456.87 | 2.799 | 2.69 |
| H_h2-C4 | 30.19 | 1.76 | 3.63 | Ag-O_co | 529.26 | 1.48 | 3.46 |
| H_h2-C5 | 24.84 | 1.75 | 3.75 | Ag-C1 | 31.54 | 1.34 | 4.37 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| H_h2-C8 | 57.65 | 2.13 | 3.5 | Ag-C2 | 64.77 | 1.51 | 3.85 |
| H_h2-C9 | 35.86 | 2.21 | 3.6 | Ag-C3 | 86.09 | 1.74 | 3.42 |
| H_h2-H3 | 8.7 | 2.03 | 3.54 | Ag-C4 | 50.64 | 1.73 | 3.6 |
| H_h2-H4 | 8.7 | 1.91 | 3.54 | Ag-C5 | 104.94 | 1.38 | 3.87 |
| H_h2-H9 | 8.2 | 1.94 | 3.63 | Ag-C8 | 115.69 | 1.49 | 3.69 |
| H_h2-O2 | 29.52 | 2.07 | 3.83 | Ag-C9 | 59.81 | 1.92 | 3.41 |
| H_h2-O3 | 74.64 | 1.87 | 3.53 | Ag-H3 | 41.37 | 2.1 | 2.96 |
| H_h2-Zn2 | 16.22 | 1.84 | 3.82 | Ag-H4 | 31.54 | 1.34 | 4.37 |
| H_h2-H_h2 [a] | 11.85 | 1.5 | 3.55 | Ag-H9 | 53.37 | 1.55 | 3.42 |
| H_w-C1 | 12.4 | 1.86 | 3.54 | Ag-O2 | 86.62 | 1.49 | 3.63 |
| H_w-C2 | 19.94 | 1.65 | 3.42 | Ag-O3 | 74.19 | 1.97 | 3.28 |
| H_w-C3 | 28.56 | 1.55 | 3.33 | Ag-Zn2 | 77.11 | 2.37 | 3.48 |
| H_w-C4 | 27.49 | 1.65 | 3.48 | Ag-Ag | 72.67 | 2.33 | 3.31 |
| H_w-C5 | 35.04 | 1.85 | 3.22 | Ag-H_w [b] | 47.69 | 2.06 | 2.85 |
| H_w-C8 | 12.73 | 2.5 | 2.99 | Ag-O_w [b] | 42.67 | 2.38 | 3.06 |
| H_w-C9 | 19.73 | 2.37 | 2.94 | | | | |
| H_w-H3 | 9.88 | 1.65 | 3.92 | | | | |
| H_w-H4 | 9.88 | 1.65 | 3.92 | | | | |
| H_w-H9 | 15.88 | 1.01 | 4.11 | | | | |
| H_w-O2 | 148.32 | 1.57 | 2.7 | | | | |
| H_w-O3 | 5.82 | 1.26 | 3.21 | | | | |
| H_w-Zn2 | 110.98 | 1.43 | 3.32 | | | | |
| O_w-C1 | 50.32 | 1.64 | 3.71 | | | | |
| O_w-C2 | 100.32 | 1.84 | 3.41 | | | | |
| O_w-C3 | 240.32 | 1.24 | 3.21 | | | | |
| O_w-C4 | 240.32 | 1.24 | 3.21 | | | | |
| O_w-C5 | 180.32 | 1.24 | 3.71 | | | | |
| O_w-C8 | 73.42 | 1.22 | 3.32 | | | | |
| O_w-C9 | 65.61 | 1.41 | 3.63 | | | | |
| O_w-H3 | 40.07 | 1.65 | 3.52 | | | | |
| O_w-H4 | 40.07 | 1.65 | 3.52 | | | | |
| O_w-H9 | 50.21 | 1.15 | 3.21 | | | | |
| O_w-O2 | 158.87 | 1.43 | 3.58 | | | | |
| O_w-O3 | 110.85 | 2.02 | 3.22 | | | | |
| O_w-Zn2 | 92.26 | 2.23 | 2.89 | | | | |
| O_w-H_w [b] | 25.55 | 1.87 | 2.76 | | | | |
| O_w-O_w [b] | 146.17 | 1.73 | 2.96 | | | | |
| H_w-H_w [b] | 59.87 | 1.31 | 3.31 | | | | |
| N_no-H_w [b] | 47.68 | 1.91 | 2.74 | | | | |
| O_no-H_w [b] | 60.29 | 1.85 | 2.76 | | | | |
| O_no-O_w [b] | 62.08 | 1.56 | 4.11 | | | | |
| N_no-O_w [b] | 74.08 | 1.48 | 3.54 | | | | |

a. Force field parameters for H_h2-H_h2 were taken from the study of Ghosh et. al (1)
b. All of the fist-principles calculations for dimer molecules were carried out using CCSD(T)/ aug-cc-pVQZ method.

1.Ghosh S, Singh JK. Int J Hydrog Energy. 2019;44(3).

**Table S3** Comparison of diffusion coefficients of NO and CO in (Zn)MOF-470 and Ag-(Zn)MOF-470 computed from short (1000 ps) and long (2500 ps) simulation runs in the fixed mode of Ag atoms (D in $10^{-9}$ $m^2s^{-1}$) and related β values at 310K and 1 bar.

| MD time | NO | | Ag-fix-NO | | CO | | Ag-fixed-CO | |
|---|---|---|---|---|---|---|---|---|
| | $\beta$ | D | $\beta$ | D | $\beta$ | D | $\beta$ | D |
| Short-run | 0.99 | 6.90 | 1.00 | 1.81 | 0.98 | 9.49 | .0.96 | 2.17 |
| Long-run | 0.93 | 6.90 | 0.91 | 1.75 | 0.94 | 9.51 | 0.98 | 2.15 |

**Table S4** The binding energies from first-principles calculations and Morse potential fitting for Ag, $H_2$, NO, Co, and $H_2O$ with four cluster models( Frag-1, 2, 3, and 4 refers to the models of a, b, e, and d of Figure 2).

| E ($kcal.mol^{-1}$) | First-Principles | | | | Morse Potential | | | |
|---|---|---|---|---|---|---|---|---|
| | Frag-1 | Frag-2 | Frag-3 | Frag-4 | Frag-1 | Frag-2 | Frag-3 | Frag-4 |
| Ag | -3.61 | -4.03 | - | -5.62 | -3.95 | -4.26 | - | -5.34 |
| H2 | -0.701 | -0.853 | -0.923 | -2.00 | -0.713 | -0.850 | -0.928 | -2.06 |
| NO | -1.71 | -1.26 | -0.47 | -4.96 | -1.66 | -1.03 | -0.42 | -4.93 |
| CO | -1.01 | -1.35 | -1.56 | -3.8 | -1.06 | -1.39 | -1.27 | -3.5 |

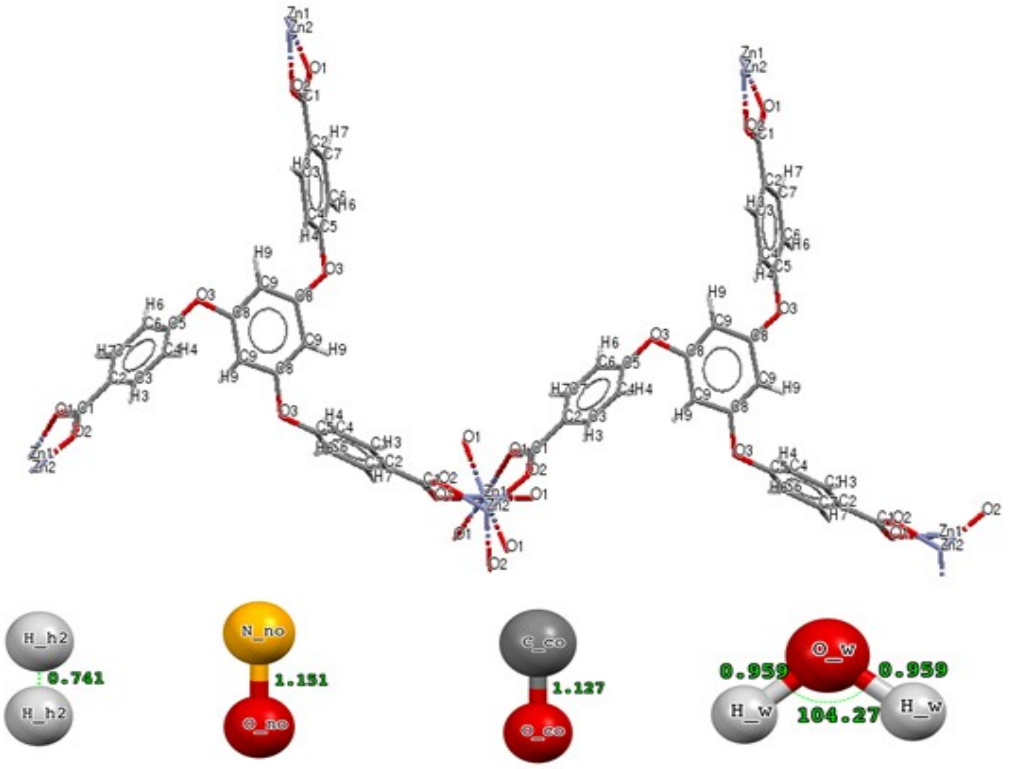


**Figure S1** The structures of $H_2$, NO, CO, and $H_2O$ molecules and (Zn)BTTB with label of atom types used for non-bonded interactions.

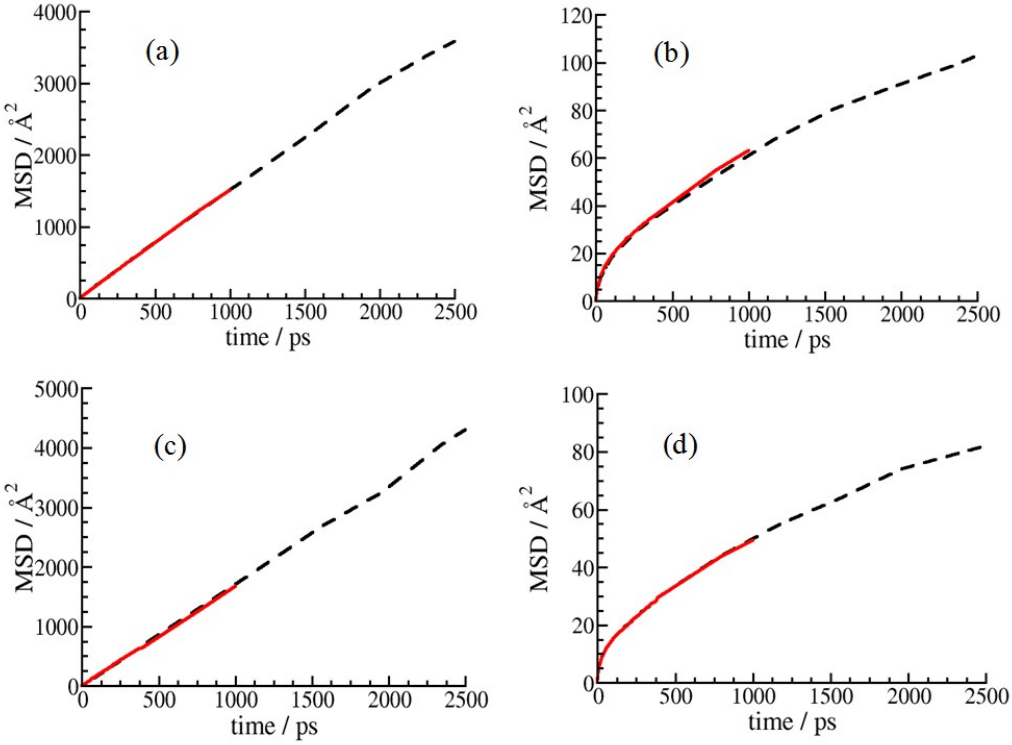


**Figure S2** Comparison of the MSD of NO (a,b) and CO (c,d) in (Zn)MOF-470 and Ag-(Zn)MOF-470 computed from short (1000 ps) and long (2500 ps) simulation runs. The dashed and the solid lines correspond to the long and short runs, respectively.

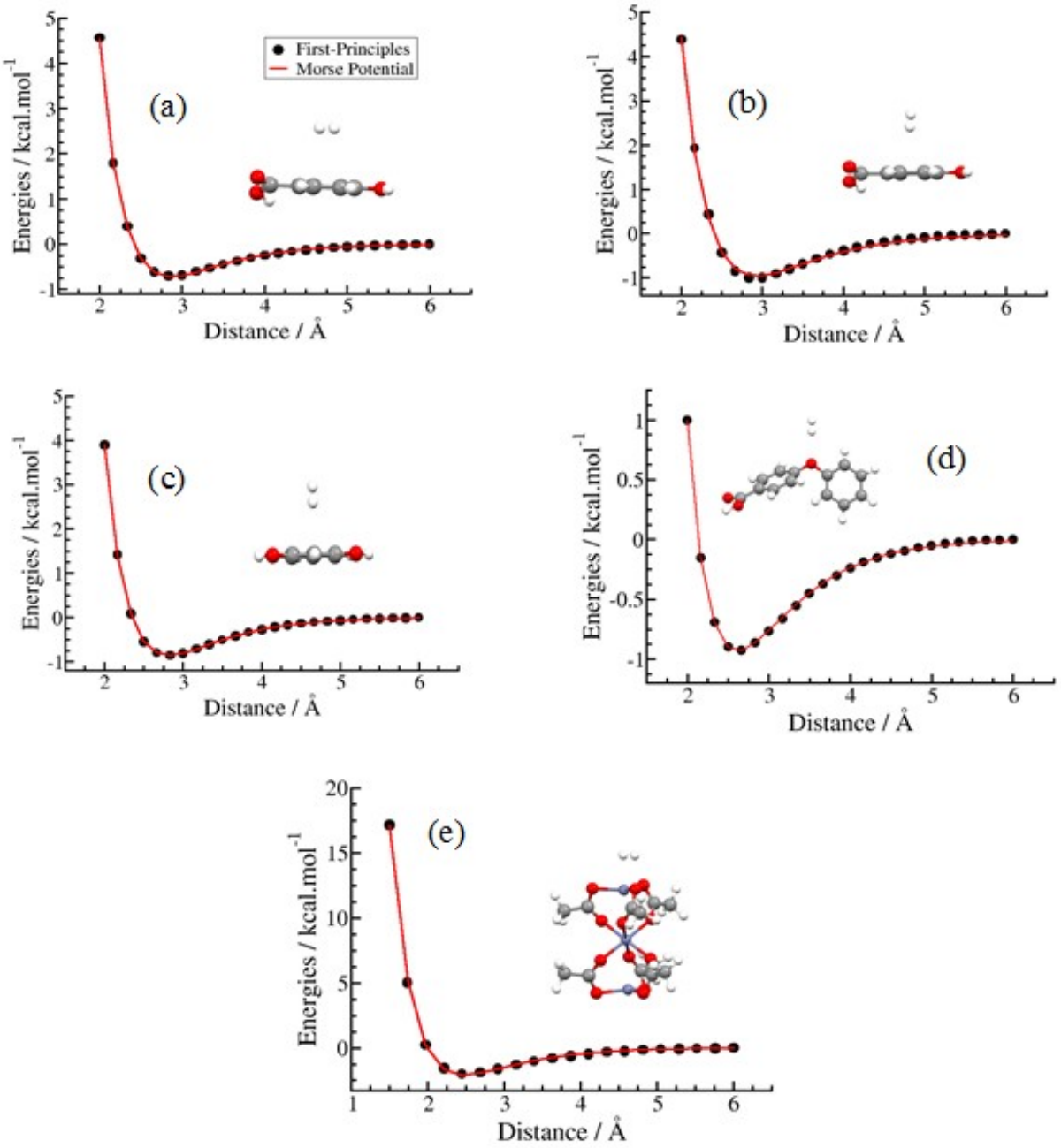


**Figure S3** Potential energies of $H_2$ with fragments of MOF structure derived from the first-principles calculations and force field fitting: (a) parallel to the plane of frag-1, (b) vertical to theplane frag-1, (c) vertical to the plane of frag-2, (d) vertical to the plane of frag-3, and (e) parallel to the plane of frag-4.

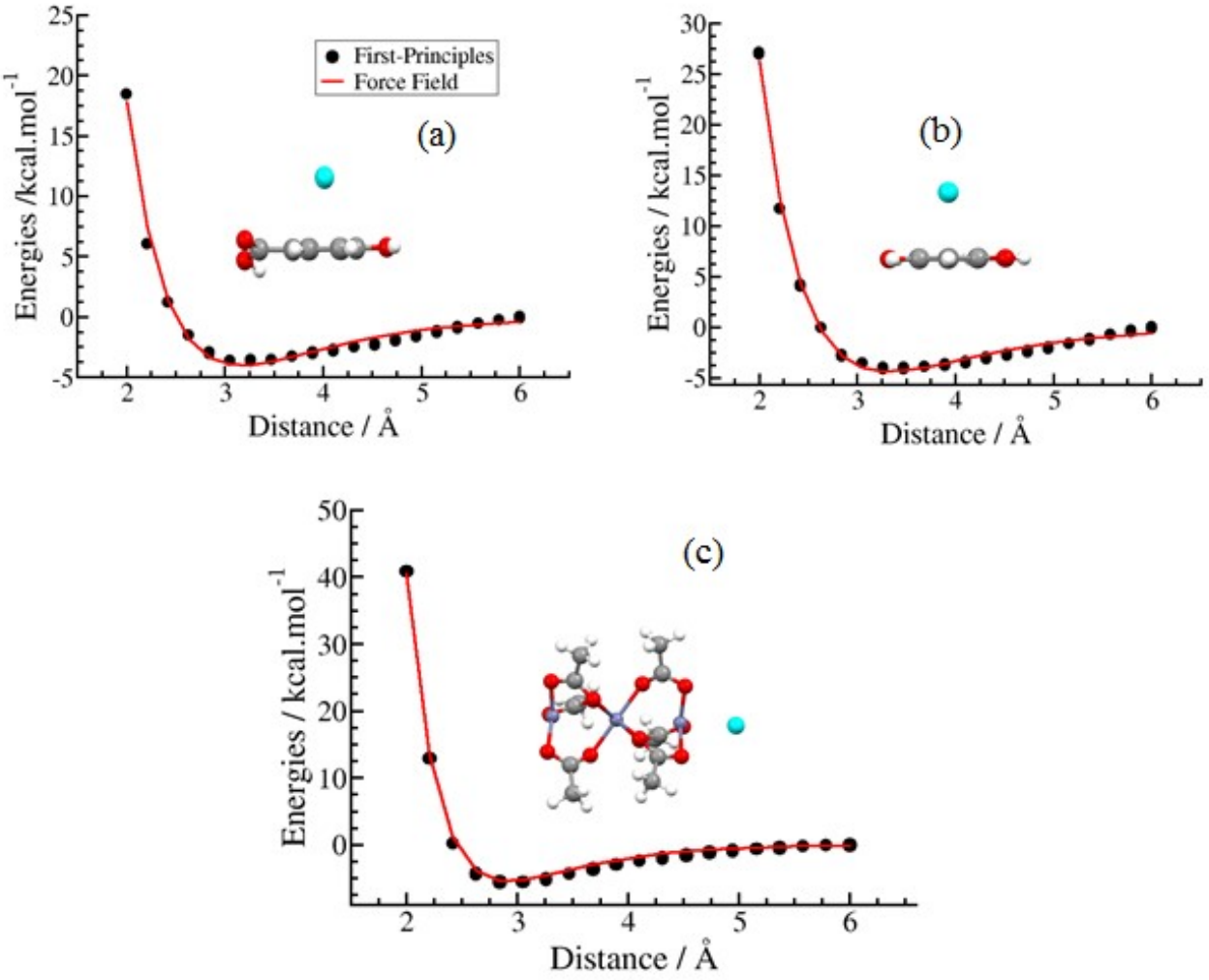


**Figure S4** Potential energies of Ag with fragments of MOF structure derived from the first-principles calculations and force field fitting: (a) frag-1, (b) frag-2 and (c) frag-4.

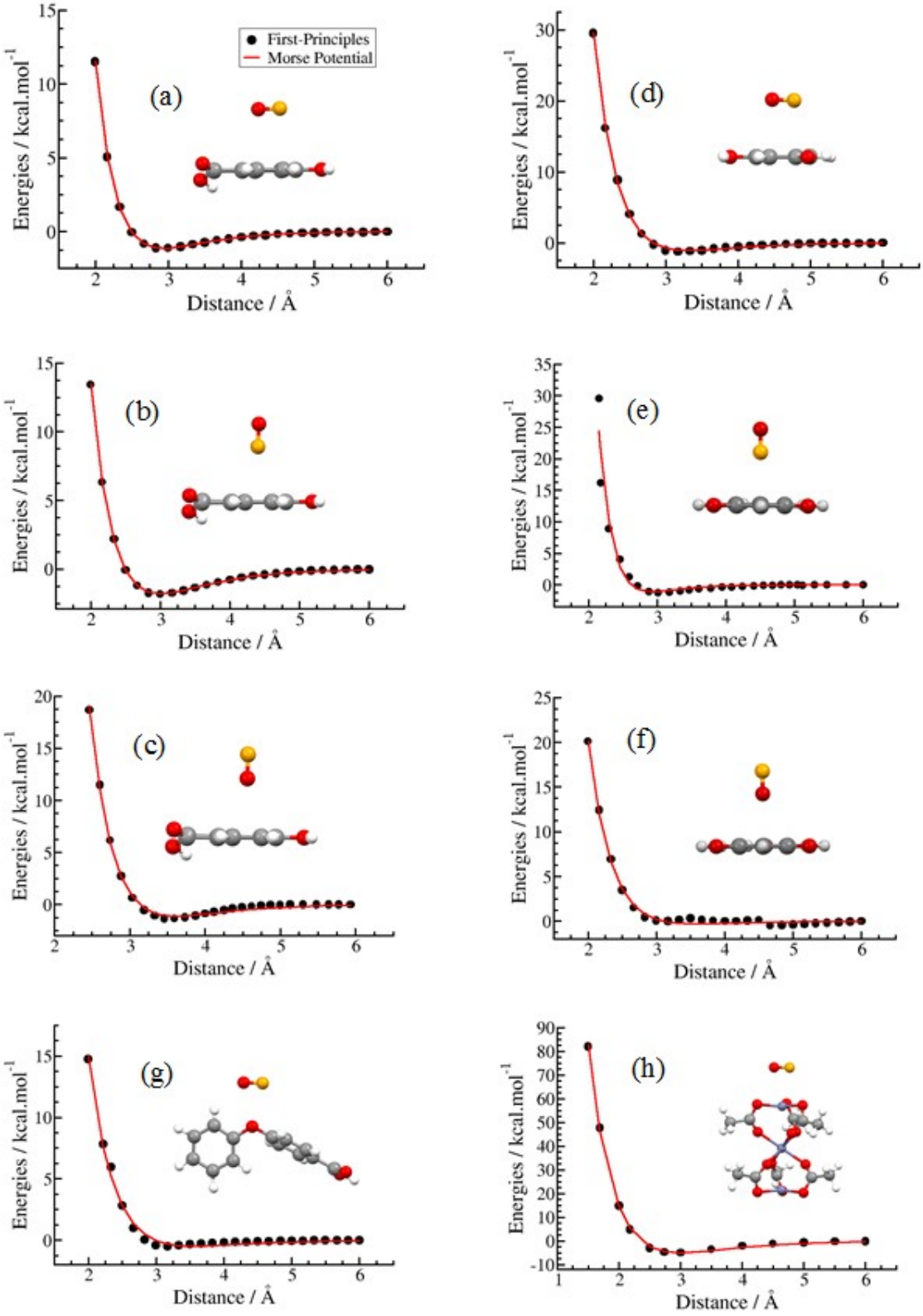


**Figure S5** Potential energies of NO with fragments of MOF structure derived from the first-principles calculations and force field fitting: (a) parallel to the plane of frag-1, (b) vertical N-side to the plane frag-1, (c) vertical O-side to the plane of frag-1, (d) parallel to the plane of frag-2, (e) vertical N-side to the plane frag-2, (f) vertical O-side to the plane of frag-2, (g) parallel to the plane of frag-3, and (h) parallel to the plane of frag-4.

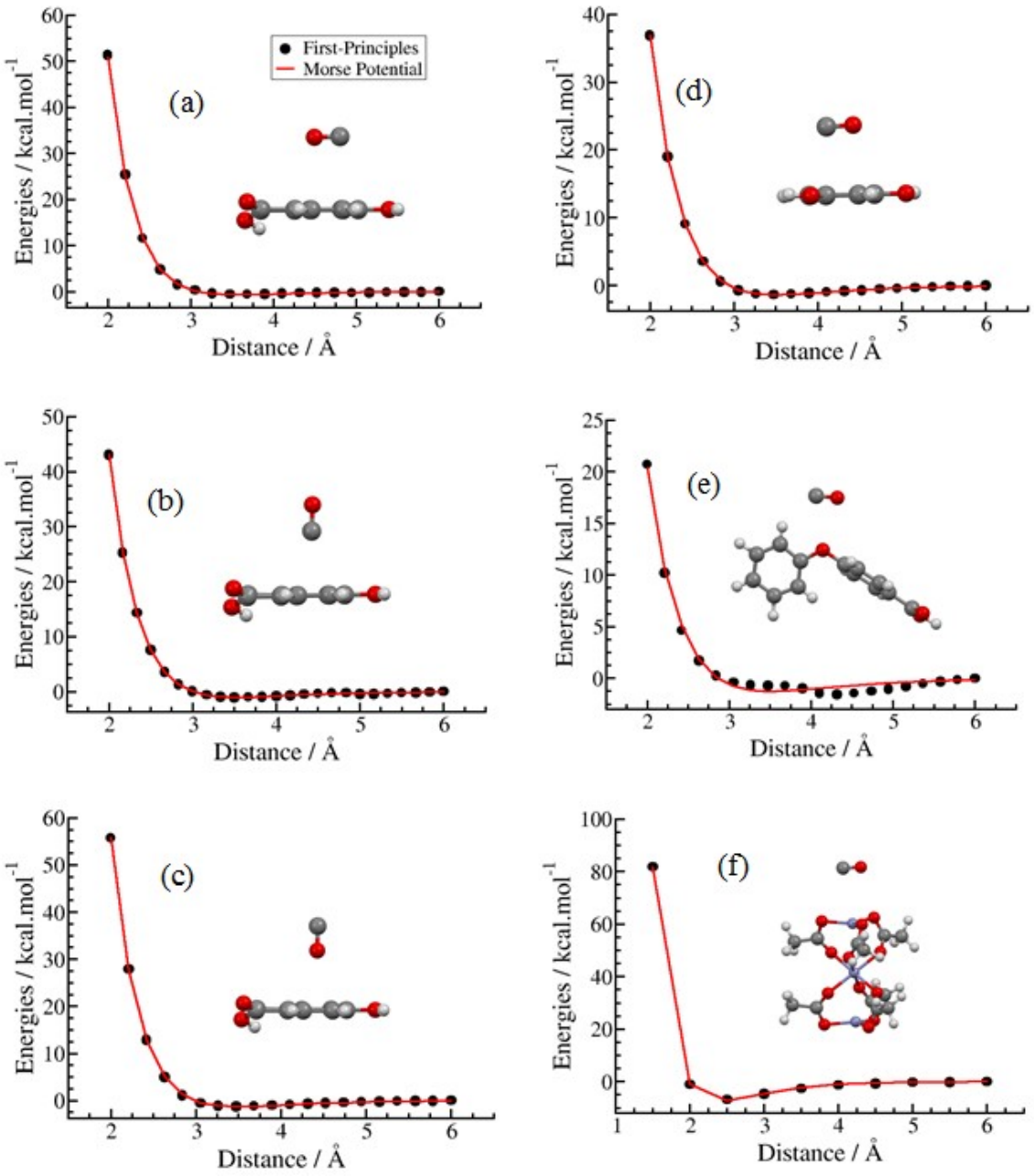


**Figure S6** Potential energies of CO with fragments of MOF structure derived from the first-principles calculations and force field fitting: (a) parallel to the plane of frag-1, (b) vertical C-side to the plane frag-1, (c) vertical O-side to the plane of frag-1, (d) parallel to the plane of frag-2, (e) parallel to the plane of frag-3, and (f) parallel to the plane of frag-4.

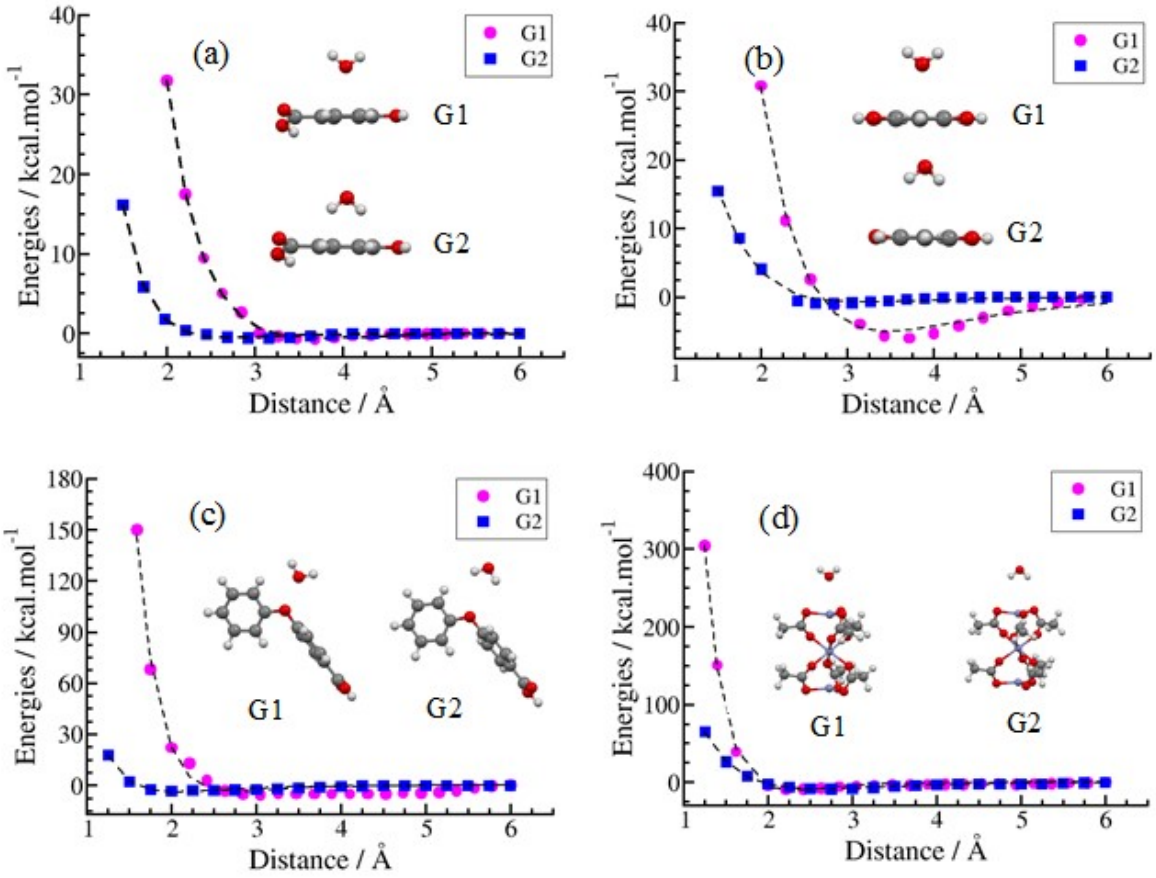


**Figure S7** Potential energies of $H_2O$ with fragments of MOF structure derived from the first-principles calculations and force field fitting: (a) G1 and G2 configurations of $H_2O$ with frag-1, (b) G1 and G2 configurations of $H_2O$ with frag-2, (c) G1 and G2 configurations of $H_2O$ with frag-3, (d) G1 and G2 configurations of $H_2O$ with frag-4.

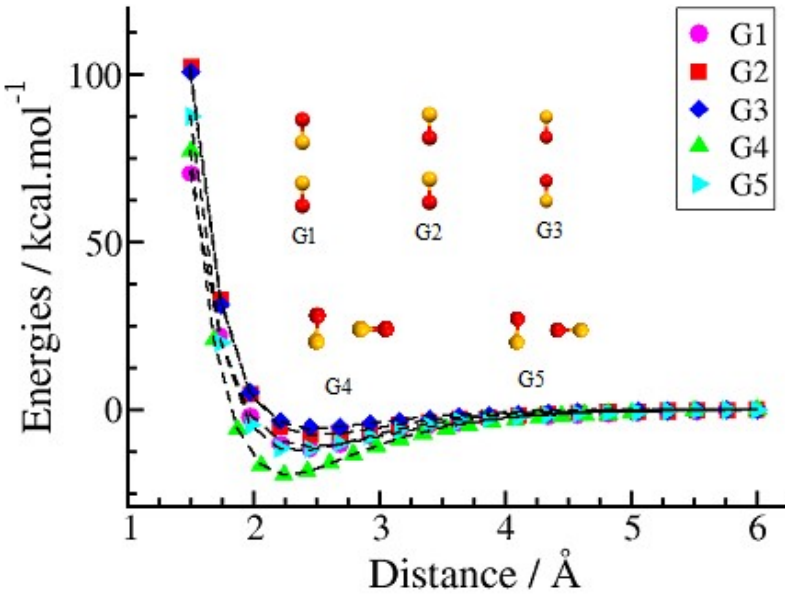


**Figure S8** Potential energies of five possible configurations of NO-NO dimer (G1, G2, G3, G4, and G5) derived from the first-principles calculations and force field fitting.

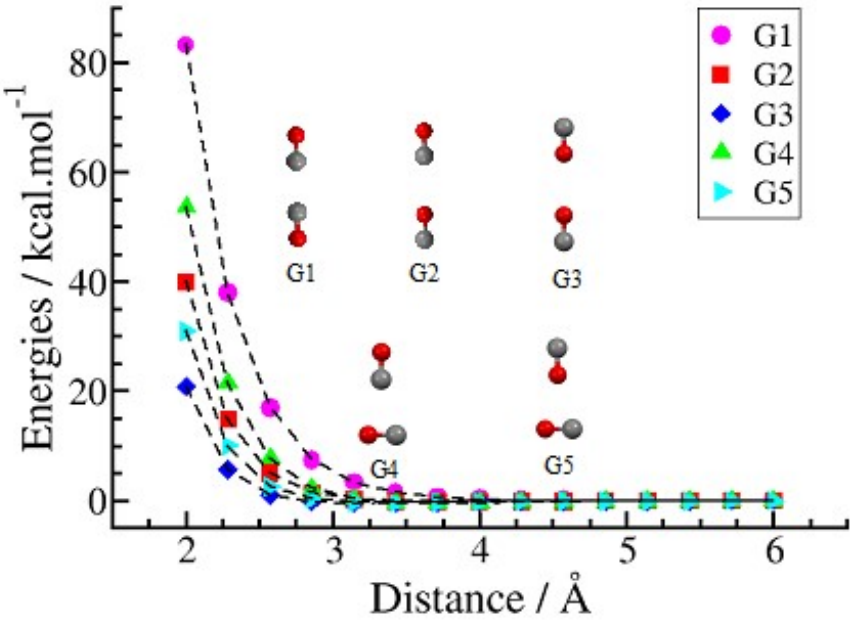


**Figure S9** Potential energies of five possible configurations of CO-CO dimer (G1, G2, G3, G4, and G5) derived from the first-principles calculations and force field fitting.

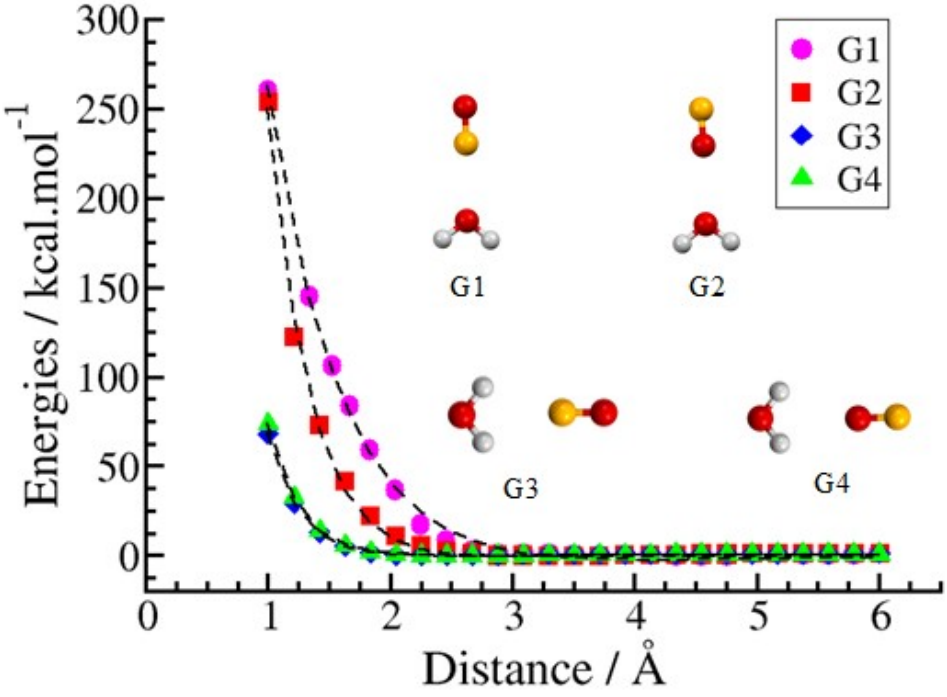


**Figure S10** Potential energies of four possible configurations of NO-$H_2O$ dimer (G1, G2, G3, and G4) derived from the first-principles calculations and force field fitting.

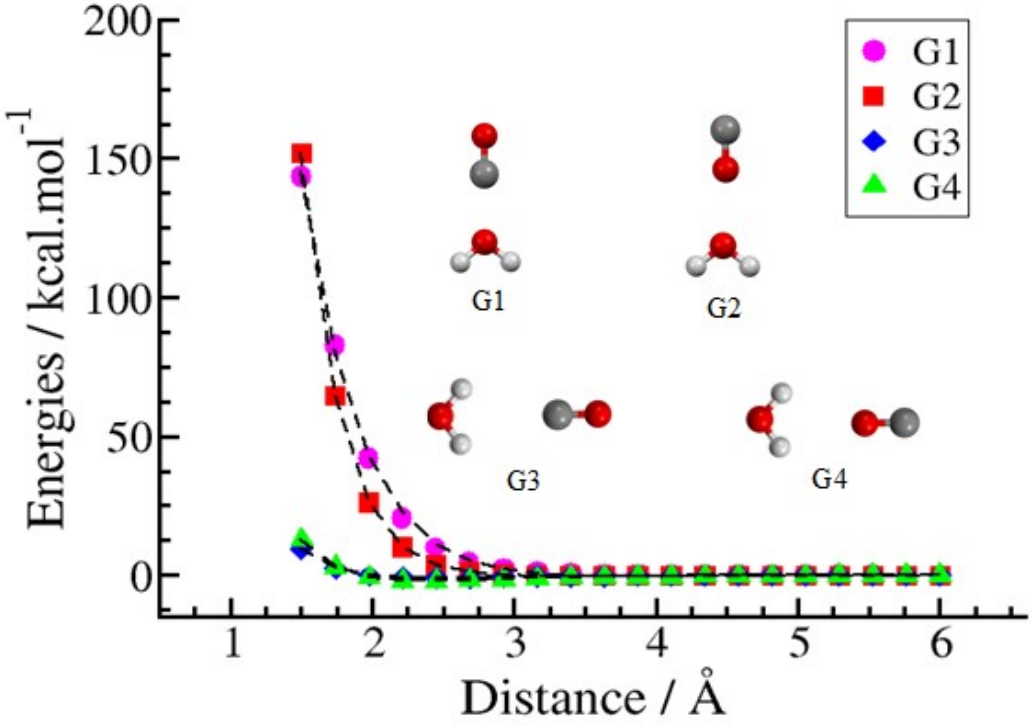


**Figure S11** Potential energies of four possible configurations of CO-$H_2O$ dimer (G1, G2, G3, and G4) derived from the first-principles calculations and force field fitting.

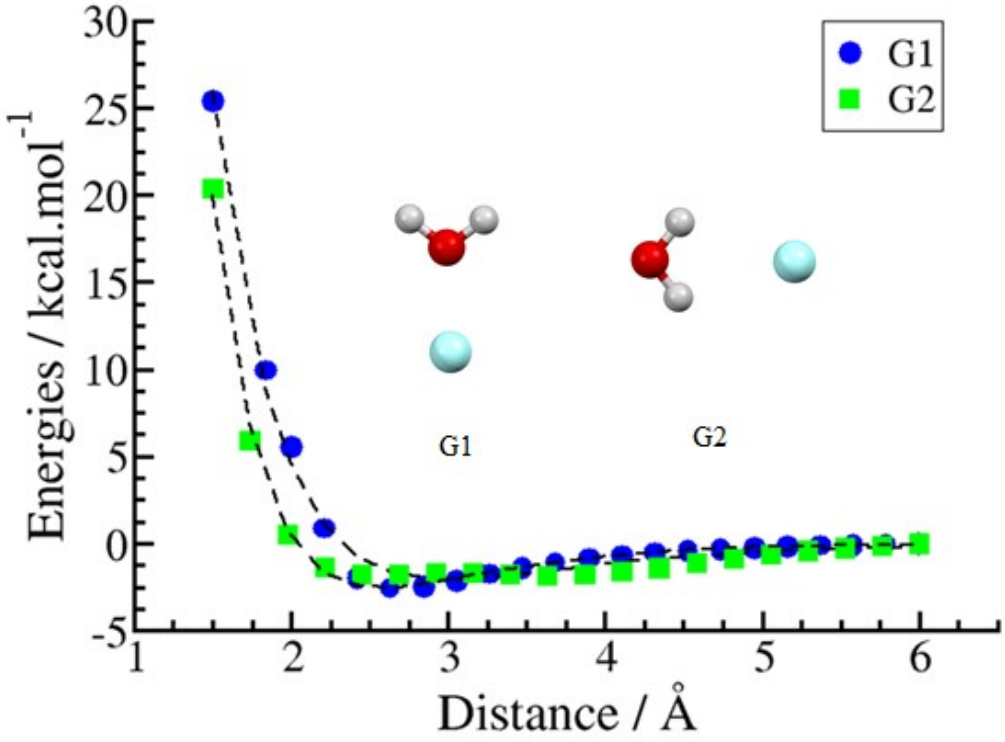


**Figure S12** Potential energies of two configurations of Ag-$H_2O$ dimer (G1, G2) derived from the first-principles calculations and force field fitting.

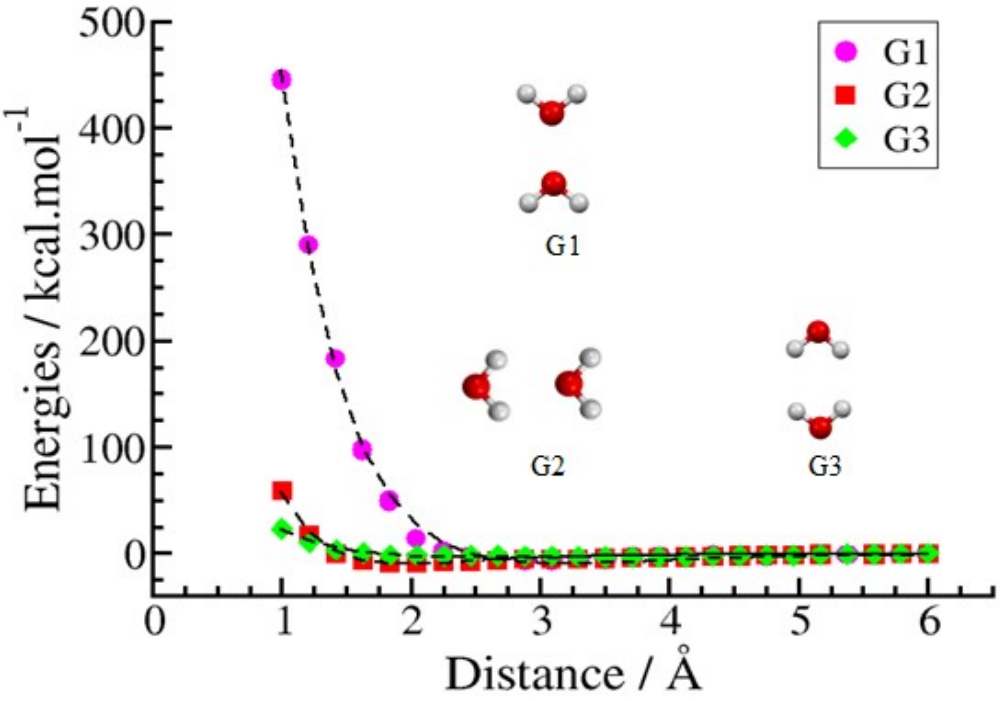


**Figure S13** Potential energies of three configurations of $H_2O$-$H_2O$ dimer (G1, G2, and G3) derived from the first-principles calculations and force field fitting

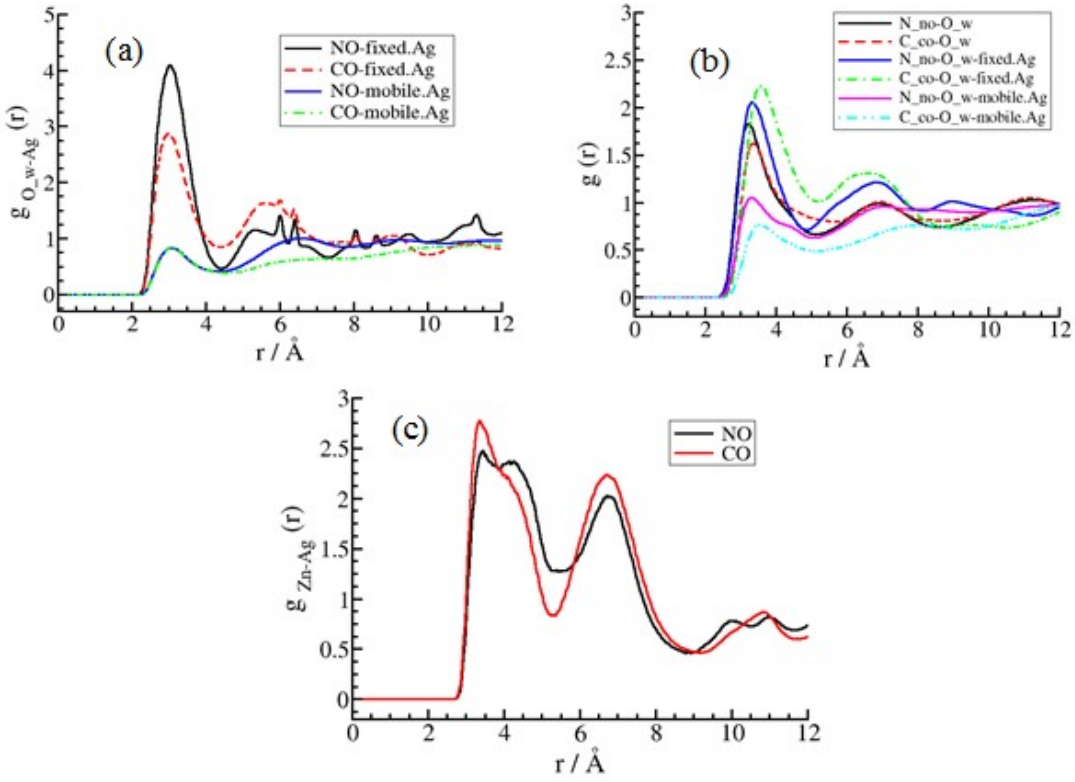


**Figure S14** The RDFs from the simulations between (a) O_w and Ag atoms in the fixed and mobile modes, (b) N_no and C_co with O_w in (Zn)MOF-470 and Ag-(Zn)MOF-470 structures, and (c) Zn2 and mobile Ag atoms for NO and CO guest molecules.