Supplementary Information:

Computational study of oxygen adsorption in metal-organic frameworks with exposed cation sites: Effect of framework metal ions

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1. Dispersion Parameters

In the DFT-D method,[1] a dispersion contribution (E_{disp}) is added to the conventional Kohn-Sham DFT energy ($E_{\text{KS-DFT}}$), leading to a dispersion-corrected total energy as given by

$$E_{\text{DFT-D}} = E_{\text{KS-DFT}} + E_{\text{disp}} \tag{1}$$

where E_{disp} is given by

$$E_{\text{disp}} = -S_6 \sum_{i=1}^{N_{at}-1} \sum_{j=i+1}^{N_{at}} \frac{C_6^{ij}}{R_{ij}^6} f_{dmp}(R_{ij}) \tag{2}$$

Here, N_{at} is the number of atoms in the system, C_6^{ij} is the dispersion coefficient for atom pair ij, S_6 is a global scaling factor that only depends on the density functional (DF) used, and R_{ij} is an interatomic distance. The damping function f_{dmp} is given by:

$$f_{dmp}(R_{ij}) = \frac{1}{1 + e^{-d\ (R_{ij}/R_r - 1)}} \tag{3}$$

where R_r is the sum of atomic vdW radii. The atomic C_6 coefficients and vdW radii (R_0) used in this work were taken from the literature,[1] as given in Table S1. Because PBE functional was used in our calculations, S_6 and the damping parameter d were taken 0.75 and 20, respectively.

Table S1. Parameters of C_6 (J nm^6 mol^{-1}) and R_0 (Å) used in this work

Element	**C_6 (in J nm^6 mol^{-1})**	**R_0 (in Å)**
H	0.14	1.001
C	1.75	1.452
O	0.70	1.342
N	1.23	1.397
Cr	10.80	1.562
Mn	10.80	1.562
Fe	10.80	1.562
Co	10.80	1.562
Ni	10.80	1.562
Cu	10.80	1.562

2. Interaction energies of O_2 and N_2 with $M_3(BTC)_2$

Table S2. Comparison of the interaction energies of O_2 and N_2 molecules with $M_3(BTC)_2$ (units: kJ mol^{-1}).

	$Cr_3(BTC)_2$	**$Mn_3(BTC)_2$**	**$Fe_3(BTC)_2$**	**$Ni_3(BTC)_2$**	**$Co_3(BTC)_2$**	**$Cu_3(BTC)_2$**
O_2	-63.5	-85.3	-56.0	-45.2	-40.5	-8.1
N_2	-22.2	-50.1	-66.2	-34.0	-44.6	-18.9

References:

1 S. Grimme, *J. Comput. Chem.*, 2006, **27**, 1787.