

Electronic Supplementary Information

Comprehensive DFT Investigation of Small-Molecule Adsorption on the Paradigm M-MOF-74 Family of Metal-Organic Frameworks

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Table S1. Selected structural parameters of adsorbed molecules on M-MOF-74.^a

Metal	H ₂ S		NH ₃		NO ₂		SO ₂	
	Interacting Atoms	Bond ^a length	Interacting Atoms	Bond ^a length	Interacting Atoms	Bond ^a length	Interacting Atoms	Bond ^a length
Mg	Mg-S	2.856	Mg-N	2.276	Mg-O	2.276	Mg-O	2.236
Ti	Ti-S	2.796	Ti-N	2.369	Ti-O	2.002	Ti-O	2.058
V	V-S	2.682	V-N	2.246	V-O	1.930	V-O	2.270
Cr	Cr-S	3.054	Cr-N	2.508	Cr-O	2.290	Cr-O	2.699
Mn	Mn-S	2.845	Mn-N	2.349	Mn-O	2.448	Mn-O	2.381
Fe	Fe-S	2.782	Fe-N	2.300	Fe-O	2.102	Fe-O	2.183
Co	Co-S	2.961	Co-N	2.328	Co-O	2.518	Co-O	2.613
Ni	Ni-S	2.637	Ni-N	2.164	Ni-O	2.230	Ni-O	2.264
Cu	Cu-S	3.005	Cu-N	2.400	Cu-O	3.803	Cu-O	3.806
Zn	Zn-S	2.809	Zn-N	2.243	Zn-O	2.349	Zn-O	2.372

^aBond lengths in Å, obtained with DFT+U (PBE-D3/PW).

Spin configuration

Permutation of up and down spins in the six cations of the primitive unit cell results in 64 possible spin configurations. The arrangement of up and down high-spin configurations of atoms in the primitive unit cell leads to intra- and inter-chain ferromagnetic or antiferromagnetic interactions in M-MOF-74. Fig. S1a and S1b show the arrangement of atoms in the primitive unit cell of M-MOF-74 and the way in which six cations make up intra- and inter-channels of M-MOF-74. Every two ions are part of an inter-chain and every three cations along the c-crystallographic axis line up an hexagonal channel. The metals 1, 3 and 5 are part of the same rod, while 2, 4 and 6 are part of another metallic rod along the c direction, which leads to intra-chain interaction along two groups of atoms along the c direction.

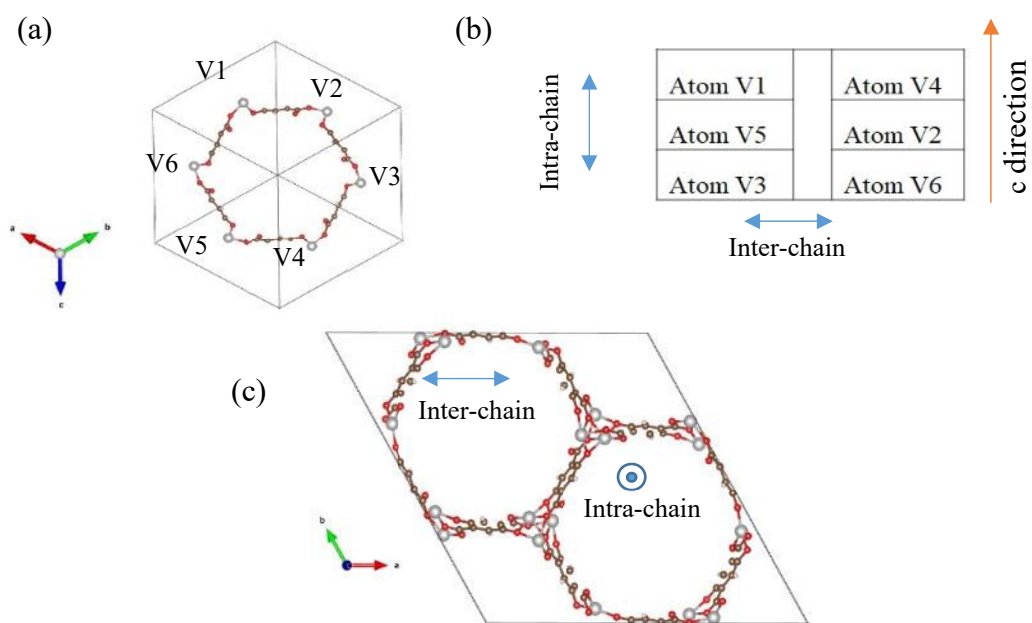


Figure S1. Arrangement of metal centers and magnetic interactions in M-MOF-74. (a) Primitive unit cell. (b) Illustration of inter- and intra-chain magnetic coupling in the primitive cell. (c) Inter- and intra-chain magnetic coupling in the conventional unit cell representation of M-MOF-74. V, grey; C, brown; O, red; H, white.

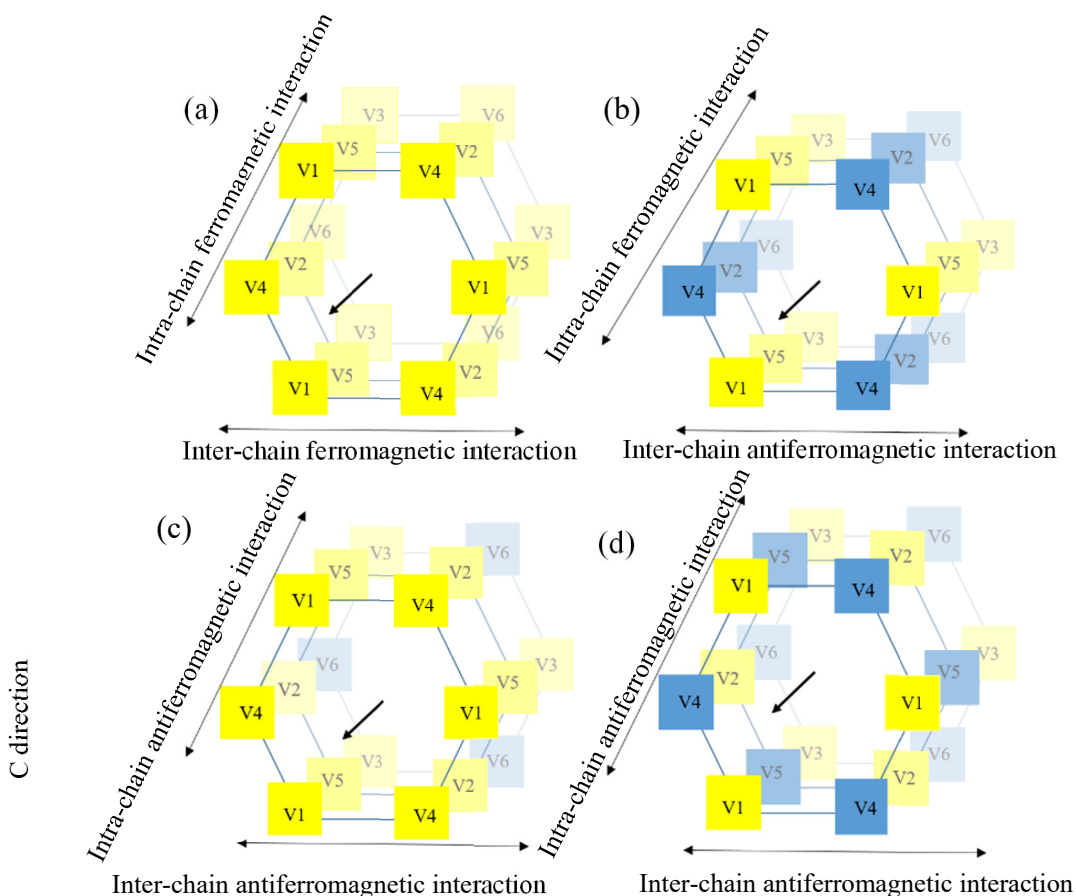


Figure S2. Arrangement of metal centers in M-MOF-74 and type of interactions along and between rods. Yellow and blue represent atoms with up and down high-spin, respectively.

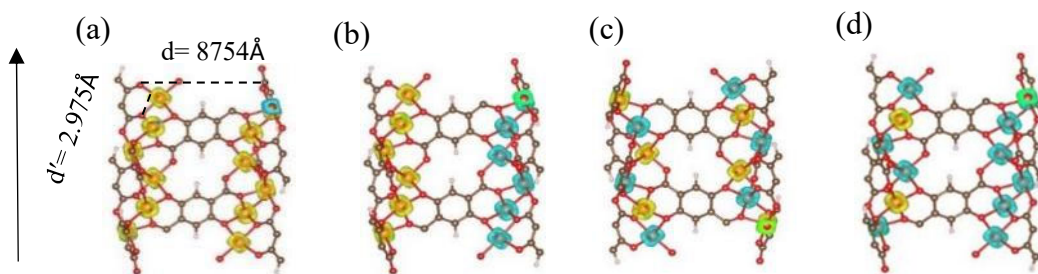


Figure S3. Spin density of V atoms in the portion of the V-MOF-74 structure along the c direction. (a), (b), (c) and (d) correspond FM, AFM1, AFM2 and AFM3 states, respectively. d and d' are the metal-to-metal distance in a chain and along a chain, respectively. Blue and yellow contours represent the negative and positive spin densities with an isosurface value of 0.05 e/\AA^3 for V atoms. Calculated with DFT (PBE-D3/PW). V, grey; C, brown; O, red; H, white.

Table S2. Properties of V-MOF-74 with different electronic configurations.^a

N	V1	V2	V3	V4	V5	V6	ΔE^a
1	↑ ↑ ↑	↑ ↑ ↑	↑ ↑ ↑	↑ ↑ ↑	↑ ↑ ↑	↑ ↑ ↑	0.0
2	↓ ↓ ↓	↓ ↓ ↓	↓ ↓ ↓	↓ ↓ ↓	↓ ↓ ↓	↓ ↓ ↓	0.0
3	↑ ↑ ↑	↓ ↓ ↓	↑ ↑ ↑	↓ ↓ ↓	↑ ↑ ↑	↓ ↓ ↓	0.1
4	↓ ↓ ↓	↑ ↑ ↑	↓ ↓ ↓	↑ ↑ ↑	↓ ↓ ↓	↑ ↑ ↑	0.1
5	↑ ↑ ↑	↑ ↑ ↑	↑ ↑ ↑	↓ ↓ ↓	↓ ↓ ↓	↓ ↓ ↓	3.5
6	↓ ↓ ↓	↑ ↑ ↑	↑ ↑ ↑	↑ ↑ ↑	↓ ↓ ↓	↓ ↓ ↓	3.5
7	↓ ↓ ↓	↓ ↓ ↓	↑ ↑ ↑	↑ ↑ ↑	↑ ↑ ↑	↓ ↓ ↓	3.5
8	↓ ↓ ↓	↓ ↓ ↓	↓ ↓ ↓	↑ ↑ ↑	↑ ↑ ↑	↑ ↑ ↑	3.5
9	↑ ↑ ↑	↓ ↓ ↓	↓ ↓ ↓	↓ ↓ ↓	↑ ↑ ↑	↑ ↑ ↑	3.5
10	↑ ↑ ↑	↑ ↑ ↑	↓ ↓ ↓	↓ ↓ ↓	↓ ↓ ↓	↑ ↑ ↑	3.5
11	↑ ↑ ↑	↓ ↓ ↓	↑ ↑ ↑	↑ ↑ ↑	↓ ↓ ↓	↓ ↓ ↓	3.5
12	↓ ↓ ↓	↑ ↑ ↑	↓ ↓ ↓	↑ ↑ ↑	↑ ↑ ↑	↓ ↓ ↓	3.5
13	↓ ↓ ↓	↓ ↓ ↓	↑ ↑ ↑	↓ ↓ ↓	↑ ↑ ↑	↑ ↑ ↑	3.5
14	↑ ↑ ↑	↓ ↓ ↓	↓ ↓ ↓	↑ ↑ ↑	↓ ↓ ↓	↑ ↑ ↑	3.5
15	↑ ↑ ↑	↑ ↑ ↑	↓ ↓ ↓	↓ ↓ ↓	↑ ↑ ↑	↓ ↓ ↓	3.5
16	↓ ↓ ↓	↑ ↑ ↑	↑ ↑ ↑	↓ ↓ ↓	↓ ↓ ↓	↑ ↑ ↑	3.5
17	↓ ↓ ↓	↑ ↑ ↑	↓ ↓ ↓	↓ ↓ ↓	↑ ↑ ↑	↑ ↑ ↑	3.5
18	↑ ↑ ↑	↓ ↓ ↓	↑ ↑ ↑	↓ ↓ ↓	↓ ↓ ↓	↑ ↑ ↑	3.5
19	↑ ↑ ↑	↑ ↑ ↑	↓ ↓ ↓	↑ ↑ ↑	↓ ↓ ↓	↓ ↓ ↓	3.5
20	↓ ↓ ↓	↑ ↑ ↑	↑ ↑ ↑	↓ ↓ ↓	↑ ↑ ↑	↓ ↓ ↓	3.5
21	↓ ↓ ↓	↓ ↓ ↓	↑ ↑ ↑	↑ ↑ ↑	↓ ↓ ↓	↑ ↑ ↑	3.5
22	↑ ↑ ↑	↓ ↓ ↓	↓ ↓ ↓	↑ ↑ ↑	↑ ↑ ↑	↓ ↓ ↓	3.5
23	↓ ↓ ↓	↓ ↓ ↓	↑ ↑ ↑	↑ ↑ ↑	↑ ↑ ↑	↑ ↑ ↑	3.5
24	↑ ↑ ↑	↓ ↓ ↓	↓ ↓ ↓	↑ ↑ ↑	↑ ↑ ↑	↑ ↑ ↑	3.5
25	↑ ↑ ↑	↑ ↑ ↑	↓ ↓ ↓	↓ ↓ ↓	↑ ↑ ↑	↑ ↑ ↑	3.5
26	↑ ↑ ↑	↑ ↑ ↑	↑ ↑ ↑	↓ ↓ ↓	↓ ↓ ↓	↑ ↑ ↑	3.5
27	↑ ↑ ↑	↑ ↑ ↑	↑ ↑ ↑	↑ ↑ ↑	↓ ↓ ↓	↓ ↓ ↓	3.5
28	↓ ↓ ↓	↑ ↑ ↑	↑ ↑ ↑	↑ ↑ ↑	↑ ↑ ↑	↓ ↓ ↓	3.5
29	↓ ↓ ↓	↑ ↑ ↑	↑ ↑ ↑	↓ ↓ ↓	↑ ↑ ↑	↑ ↑ ↑	3.5
30	↑ ↑ ↑	↓ ↓ ↓	↑ ↑ ↑	↑ ↑ ↑	↓ ↓ ↓	↑ ↑ ↑	3.5
31	↑ ↑ ↑	↑ ↑ ↑	↓ ↓ ↓	↑ ↑ ↑	↑ ↑ ↑	↓ ↓ ↓	3.5
32	↑ ↑ ↑	↑ ↑ ↑	↓ ↓ ↓	↑ ↑ ↑	↑ ↑ ↑	↓ ↓ ↓	3.5
33	↓ ↓ ↓	↑ ↑ ↑	↑ ↑ ↑	↓ ↓ ↓	↓ ↓ ↓	↓ ↓ ↓	3.5
34	↓ ↓ ↓	↓ ↓ ↓	↑ ↑ ↑	↑ ↑ ↑	↓ ↓ ↓	↓ ↓ ↓	3.5
35	↓ ↓ ↓	↓ ↓ ↓	↓ ↓ ↓	↑ ↑ ↑	↑ ↑ ↑	↓ ↓ ↓	3.5
36	↓ ↓ ↓	↓ ↓ ↓	↓ ↓ ↓	↓ ↓ ↓	↑ ↑ ↑	↑ ↑ ↑	3.5

close in energy to the FM state. States 5 to 40 involve intra- and inter-chain antiferromagnetic coupling (Fig. S2c) in a so-called AFM2 configuration, with an energy difference of 3.5 kcal/mol relative to the FM state for V-MOF-74. States 41 to 64 involve intra- and inter chain antiferromagnetic interactions in a so-called AFM3 configuration, with some high-spin atoms along the c direction (Fig. S2d), and an energy difference of 1.8 kcal/mol with the FM state for V-MOF-74. Figure S3 shows the spin density of a portion of V-MOF-74 along the c direction. Due to symmetry, there are only 4 distinct electronic states (or groups of states) in M-MOF-74, and we only examine states 1, 3, 5 and 59, herein referred to as FM, AFM1, AFM2 and AFM3, respectively, as representative states of these 4 groups. Results are presented here for V-MOF-74, for which spin configuration energy differences are most pronounced; FM, AFM1, AFM2 and AFM3 states lie much closer in energy for the other M-MOF-74s, as evident from the smaller energy deviations presented in Table 3.

Table S3. Binding energies of adsorbates on different spin configurations of M-MOF-74.^a

E ^a	Adsorbates	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
E ₁ ^b	H ₂ S	14.7	17.2	9.0	12.5	12.9	9.6	14.8	8.3
	SO ₂	20.5	20.2	9.0	11.2	7.8	8.9	12.3	7.8
	NH ₃	22.6	27.2	13.2	19.9	20.6	16.6	24.0	13.2
	NO ₂	41.0	30.3	9.0	12.7	20.9	8.0	13.1	5.8
E ₂ ^c	H ₂ S	14.7	20.0	9.0	12.6	12.7	9.6	14.6	8.4
	SO ₂	17.5	22.5	9.0	12.2	7.8	8.9	12.0	8.5
	NH ₃	22.6	30.0	13.3	20.0	20.1	16.6	23.7	13.3
	NO ₂	41.0	32.5	10.5	11.2	21.0	7.1	12.9	6.4
E ₃ ^d	H ₂ S	14.7	16.8	9.0	12.5	12.9	9.6	14.5	9.0
	SO ₂	20.5	20.4	9.1	12.6	7.8	9.0	12.1	8.5
	NH ₃	22.6	27.1	13.3	19.9	20.3	16.7	23.6	13.9
	NO ₂	41.0	30.3	10.6	13.7	21.0	7.3	12.9	6.7
E ₄ ^e	H ₂ S	14.7	16.9	9.0	12.6	12.9	9.6	14.4	9.0
	SO ₂	20.5	20.4	9.1	12.2	7.8	9.0	11.9	8.5
	NH ₃	22.6	26.9	13.3	20.0	20.3	16.7	23.6	13.8
	NO ₂	41.0	30.1	10.6	14.0	21.0	7.3	12.8	3.8

^aCalculated in kcal/mol with DFT+U (PBE-D3/PW).

^bBinding energies of adsorbates on AFM1 spin configuration of M-MOF-74.

^cBinding energies of adsorbates on AFM2 spin configuration of M-MOF-74.

^dBinding energies of adsorbates on AFM3 spin configuration of M-MOF-74.

^eBinding energies of adsorbates on FM spin configuration of M-MOF-74.

Table S4. Binding energies of adsorbates on M-MOF-74.^a

Adsorbates	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
H ₂ S	17.1	17.7	8.5	11.9	11.2	9.3	14.0	7.6
SO ₂	19.0	30.4	19.7	15.6	10.9	11.9	11.6	8.3
NH ₃	29.1	29.1	14.2	18.9	24.1	14.8	23.0	10.9
NO ₂	45.7	43.2	24.3	24.0	31.1	23.7	16.8	6.1

^aCalculated in kcal/mol with DFT (PBE-D3/PW).

d-band model

The density of states (DOS) projected onto the d-states that interact with the adsorbate can be analyzed using the d-DOS moments such as center, filling, and width of the d-bands.¹ This model has been used successfully to investigate the reactivity/adsorption of the CO₂ molecule on different metal catalysts.² In this model, the adsorbate-metal interaction strength is determined by the coupling of the adsorbate bands/orbitals to the transition metal's d-bands/orbitals, which is directly associated with the d-band center (ϵ_d)

$$\epsilon_d = \frac{\int_{-\infty}^{+\infty} n_d(\epsilon)\epsilon d\epsilon}{\int_{-\infty}^{+\infty} n_d(\epsilon)d\epsilon} \quad (\text{S1})$$

where $n_d(\epsilon)$ is the projected density of states (PDOS). The d band is further characterized by the degree of filling (f_d) and its width (W_d)¹

$$f_d = \frac{\int_{-\infty}^{E_f} n_d(\epsilon)d\epsilon}{\int_{-\infty}^{+\infty} n_d(\epsilon)d\epsilon} \quad (\text{S2})$$

$$W_d = \sqrt{\frac{\int_{-\infty}^{+\infty} n_d(\epsilon)\epsilon^2 d\epsilon}{\int_{-\infty}^{+\infty} n_d(\epsilon)d\epsilon}} \quad (\text{S3})$$

Only d states near the Fermi level are taken into account as they influence the strength of the interaction. The correlation between d-band moments and the binding energy of the adsorbates on transition metals was investigated using Pearson's product moments (Figure S4). It is found that the binding energy exhibits a positive correlation with the center and width of the d bands, but an inverse relationship with the filling. Furthermore, the center of the d band is positively correlated with their width, while showing an inverse correlation with their filling. As the number of d-electrons increases, the filling of the d band also increases, causing the d-band center to shift closer to the Fermi level. This leads to weaker interaction between the adsorbate and the transition metal.

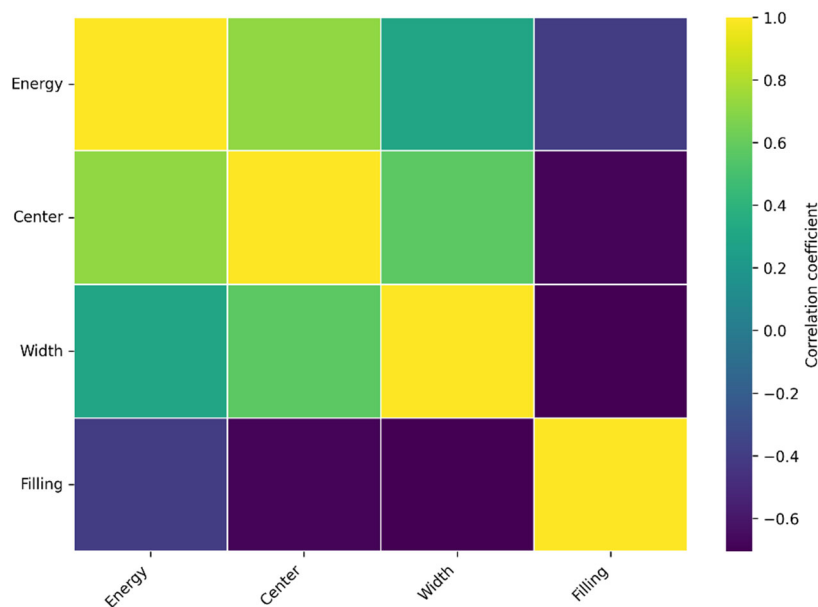


Figure S4. Pearson's pairwise product moment correlation heat map among binding energy, center, filling and width of d-band.

The simplest model of transition metal adsorption includes only the d-band center as an effective indicator of the variations in binding energy/ability. The d-band center is closely linked to the d-band edge of valence bands (below the Fermi level), which impacts the position and occupancy of the conduction bands (above the Fermi level).¹ Figure S5 shows adsorbate binding energies vs the center of transition metal d-bands in M-MOF-74. In M-MOF-74, Ti and V feature d-band centers at -0.1 eV and -0.7 eV, respectively, the closest d-band centers to the Fermi level among the metals in M-MOF-74. The substantial distribution of d bands near the Fermi level contributes to a higher-lying d-band center, thereby enhancing the reactivity of Ti-MOF-74 and V-MOF-74 towards adsorbates. In contrast, d bands centered far from the Fermi level in metals like Cu (-8.5 eV) lead to low binding energies for all adsorbates.

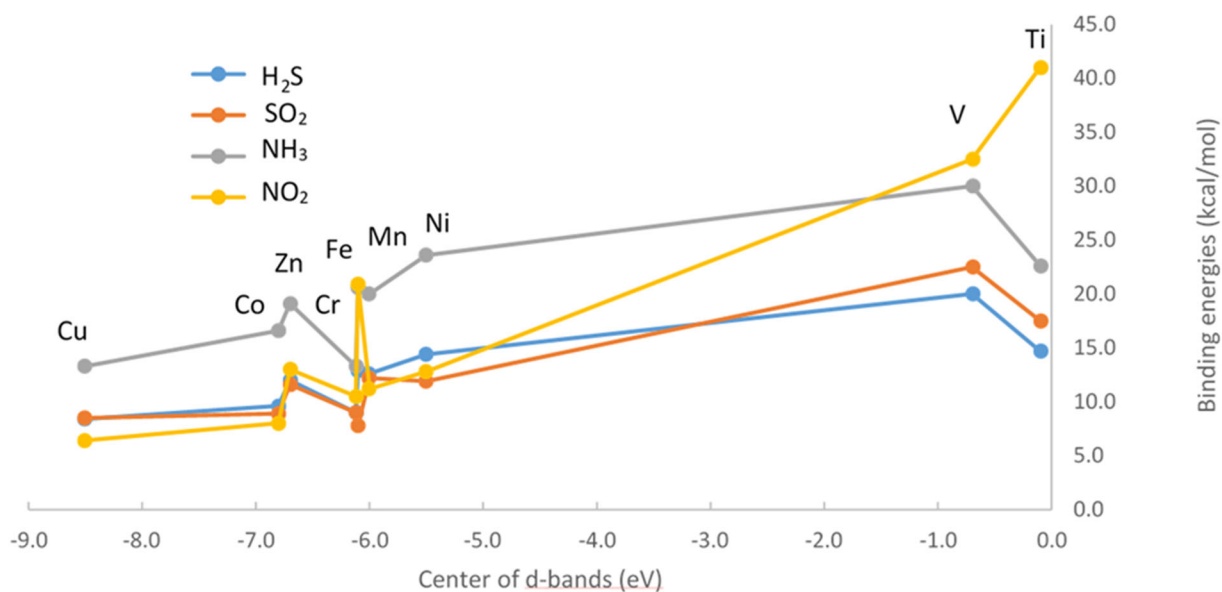


Figure S5. Binding energy of adsorbates on M-MOF-74 vs transition metal d-band center location with respect to the Fermi level. Energies (kcal/mol) calculated with DFT (PBE-D3/PW).

References

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- 2 Z. Li, S. Wang, W. S. Chin, L. E. Achenie and H. Xin, *J. Mater. Chem. A*, 2017, **5**, 24131–24138.