Supporting Information

Effect of Spin State on the Dihydrogen Binding Strength to Transition Metal Centers in Metal-organic Frameworks

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Fig. S1. The perspective side view (a) and top view (b) of the Mn-MOF. The small cube shown in (a) is the basic building block of the MOF and is thus used in our calculations with appropriate hydrogen passivation (see panel c). The magenta, gray, yellow, green, and cyan balls represent Mn, N, C, Cl, and H atoms, respectively. The molecule in (c) consists of four Mn atoms coordinated by eight tetrazolate rings occupying the eight octants and a Cl atom sitting in the center.

Calculation details. Our *ab initio* calculations were based on the PBE exchangecorrelation functional. The PBE functional is known to consistently underestimate the van der Waals interactions, which contribute a portion of the binding energy. Therefore, more accurate calculations should give slightly larger binding than what we obtained here. This should not affect our analysis and conclusion because the main objective of this study is to design new MOF systems that could bind H_2 stronger than the Mn-MOF.

We employed plane-wave basis set with a cutoff energy of 400 eV and the allelectron-like projector augmented wave potentials. A supercell approach is adopted, in which we put the molecule at the center of a vacuum cube of $(20 \times 20 \times 20 \text{ Å})$ being arranged periodically.



Fig. S2. Charge density plots of the d_{z^2} (left) and $d_{x^2-y^2}$ (right) orbitals, suggesting maximal orbital overlap of H₂ σ with d_{z^2} but minimal overlap with $d_{x^2-y^2}$. As can be seen from this plot, one TM center could bind only one H₂. This is because of a steric effect. After the first H₂ bound to TM d_{z^2} , the space left is not enough for further binding of another H₂ due to the surrounding tetrazolate rings. This is also what was observed in the experiment.



Fig. S3. Spin-dependent local density of states for Sc *d* and H *s* in Sc-MOF. Dashed lines separate the occupied and unoccupied states. The upper panel is for the case before H₂ adsorption, and the lower panel is for the case after H₂ adsorption. We have aligned the energy of the upper and lower panels by aligning the electrostatic potentials in the vacuum region. For Sc here and Ti in Fig. S4, we did not directly identify which levels are the d_{z^2} levels. Rather, we made sure that none of the occupied levels belong to d_{z^2} .



Fig. S4. Same as in Fig. S3 for Ti *d* and H *s* in Ti-MOF.



Fig. S5. Same as in Fig. S3 for V *d* and H *s* in V-MOF. Arrows indicate the positions of the spin-up d_{z^2} levels.



Fig. S6. Same as in Fig. S5 for Cr d and H s in Cr-MOF.



Fig. S7. Same as in Fig. S5 for Mn *d* and H *s* in Mn-MOF. Both spin-up and spin-down d_{z^2} levels are now indicated by the arrows. Figures S3 to S7 were generated by using the same smearing energy of 0.01 eV. For visual clarity, however, a larger smearing energy of 0.05 eV was used in Fig. 2(a).

Stability of the early TM MOFs. A simple rendering of the relative stability is to calculate the substitution energy of the MOF with respect to the Mn-MOF. Namely,

 $\Delta E = [E(TM-MOF) - 4 \times E(TM) - E(Mn-MOF) + 4 \times E(Mn)]/4,$

where E(TM-MOF) and E(Mn-MOF) are the total energies of the TM-MOF and the Mn-MOF, E(TM) and E(Mn) are the total energies of isolated TM and Mn atoms, respectively. The factor of 4 enters because we have 4 TM atoms per molecule. Negative number indicates exothermic process due to substituting Mn in the Mn-MOF by other TM atoms.

ΔE	Sc	Ti	V	Cr	Mn
eV	-2.79	-2.67	-1.92	-0.54	0.00