Supplementary Information

Tunable Electronic and Magnetic Properties of Planar and Corrugated Phases of Two-dimensional Metal-Organic Frameworks

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The linear response theory (LRT)

The Hubbard U can be calculated directly by the response function as follows,

$$\chi_{IJ} = \frac{\partial E}{\partial n_I \partial n_J} = -\frac{\partial n_I}{\partial \alpha_J}$$. In the LRT approach, χ_{IJ} is obtained from the response of d state

occupations (n) to a small localized perturbation potential shift α. An occupation-dependent

energy functional is required for the self-consistent solution of the Kohn-Sham equations. The

effective interaction parameter U of site I can then be calculated as follows:

$$U = \frac{\partial n_{I,0}}{\partial (n_I)} - \frac{\partial n_I}{\partial (n_I)} = [\chi_0^{-1} - \chi^{-1}]_I$$
,

where χ_0^{-1} and χ^{-1} represent the Kohn-Sham and the non-interacting inverse density respons

e functions of the system with respect to the localized potential shift, respectively. The self-co

nsistent determination of U was performed with VASP. (http://grandcentral.apam.columbia.ed

u:5555/tutorials/dft_procedures/linear_response_u/index.html).

Spin Hamiltonian

The exchange interaction can be conveniently studied by mapping the total energies of the

systems with different magnetic orderings to the Ising model with J_1, J_2, and J_3, respectively:

$$H_{spin} = -\sum_{i,j} J_1 S_i \cdot S_j - \sum_{i,k} J_2 S_i \cdot S_k - \sum_{i,l} J_3 S_i \cdot S_l$$

where S_i is the magnetic moment at the Ni site and (i, j), (i, k), and (i, l) the nearest, next-nearest,

and next-next-nearest Ni atoms, respectively. By mapping the DFT energies to the Hamiltonian,

J can be calculated from the following equations:

$$E_{FM} = E_0 - (4J_1 + 2J_2 + 4J_3)S^2$$

$$E_{AFM} = E_0 - (2J_1 - 2J_2 - 4J_3)S^2$$

$$E_{FIM1} = E_0 - (-2J_2 + 4J_3)S^2$$

$$E_{FIM2} = E_0 - (4J_1 - 2J_2 - 4J_3)S^2$$

Biaxial strain

Biaxial strain stretching is defined as $\varepsilon = (a-a_0)/a_0 \times 100\%$, where a and a_0 are the lattice constants of the strain structure and the plane structure, respectively.
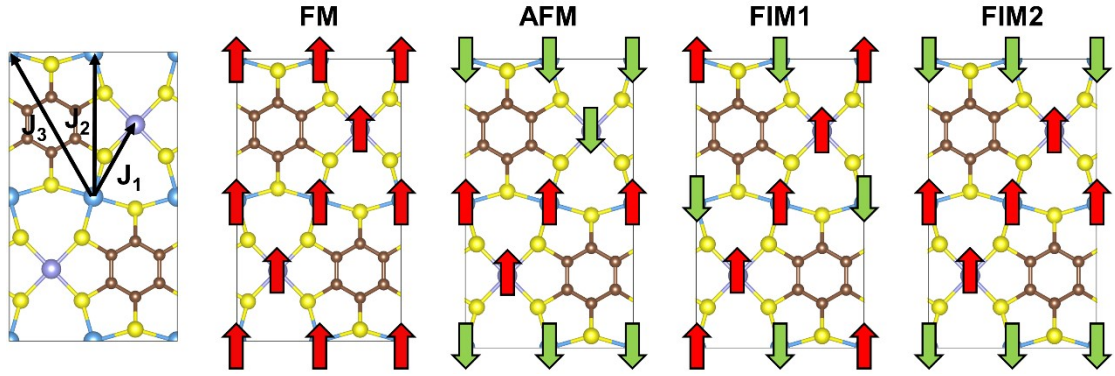

Fig. S1 The collinear magnetic models and the ferromagnetic (FM), the antiferromagnetic (AFM), and two ferrimagnetic (FIM) states for calculating the magnetic ground state of c-Ni_3HTB and p-Ni_3HTB. Three magnetic exchange coupling constants (J_1, J_2, and J_3) are shown.
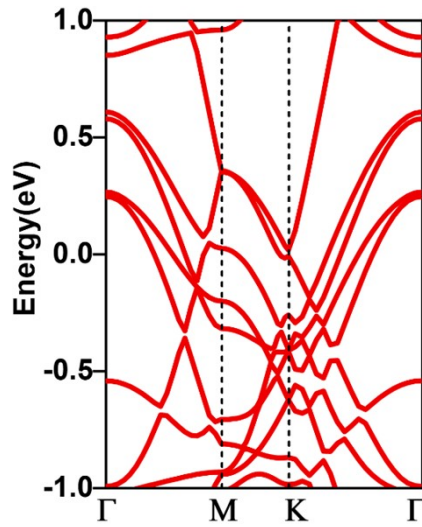

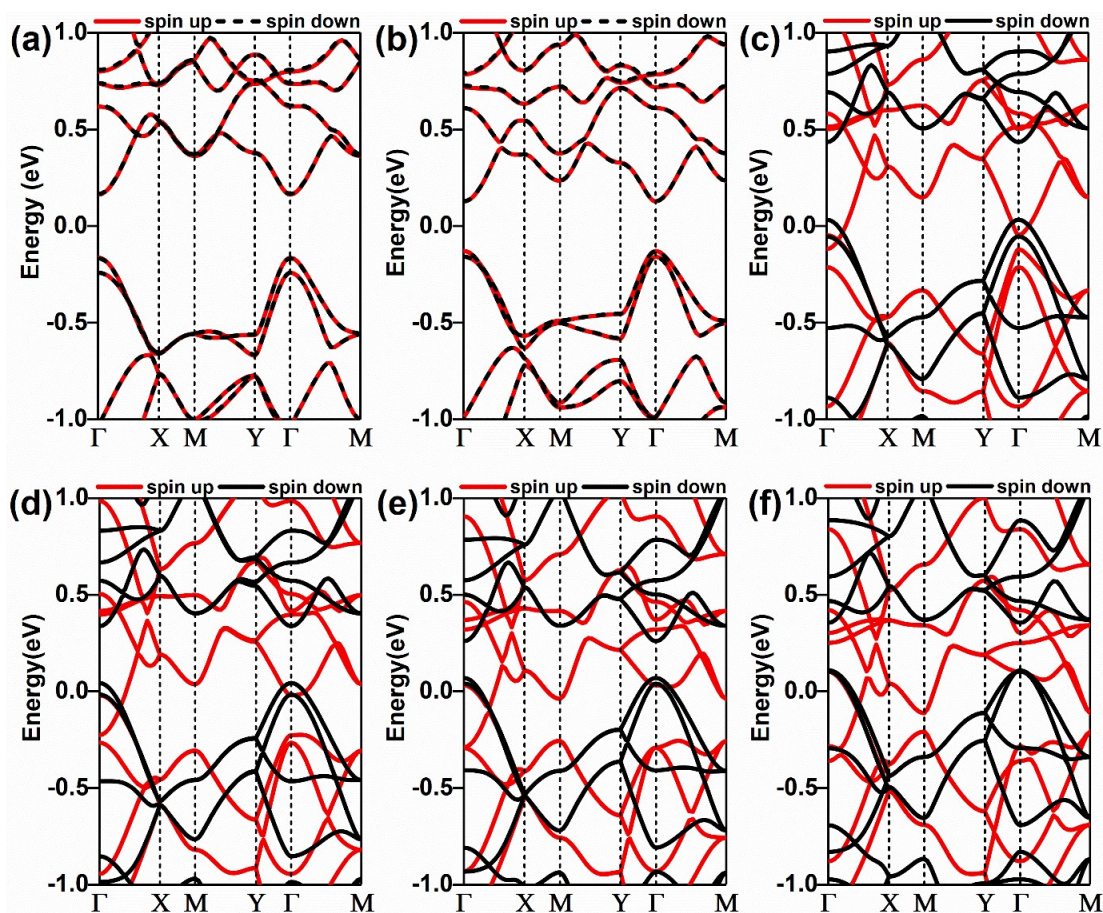**Fig. S2** Band structures of p-Ni_3HTB with spin-orbital couplings (SOC).

Fig. S3 Band structures of c-Ni$_3$HTB by applying biaxial strain from 0 to 5%. Spin-up and spin-down is marked with red and black lines.
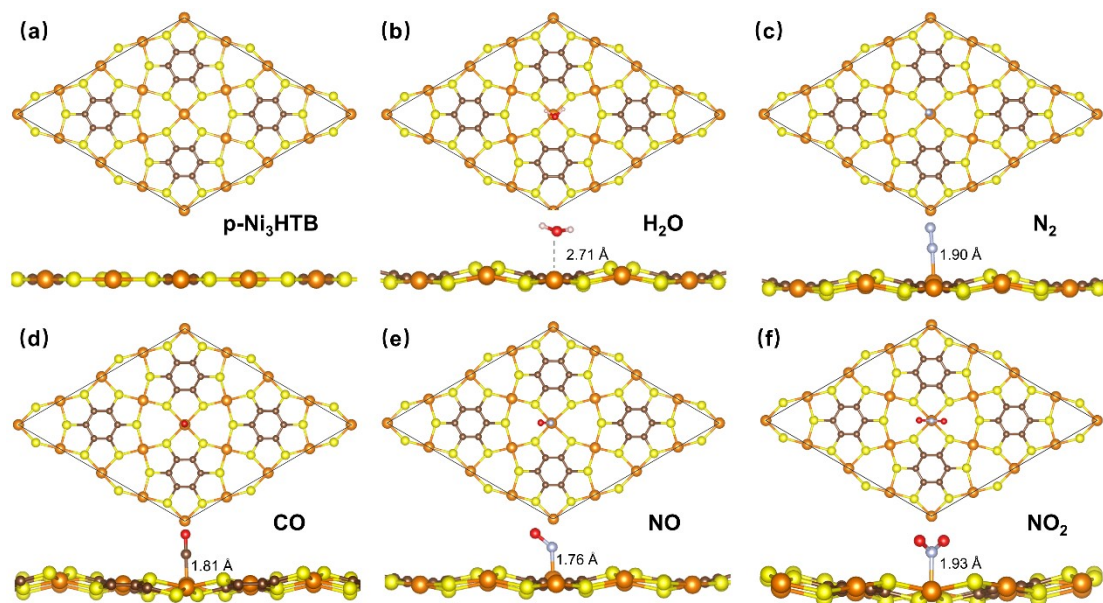

Fig. S4 Top and side views of the (a) $2\times2\times1$ p-Ni$_3$HTB supercell, the most stable adsorption of (b) H$_2$O, (c) N$_2$, (d) CO, (e) NO, (f) NO$_2$ molecules on $2\times2\times1$ p-Ni$_3$HTB supercell.
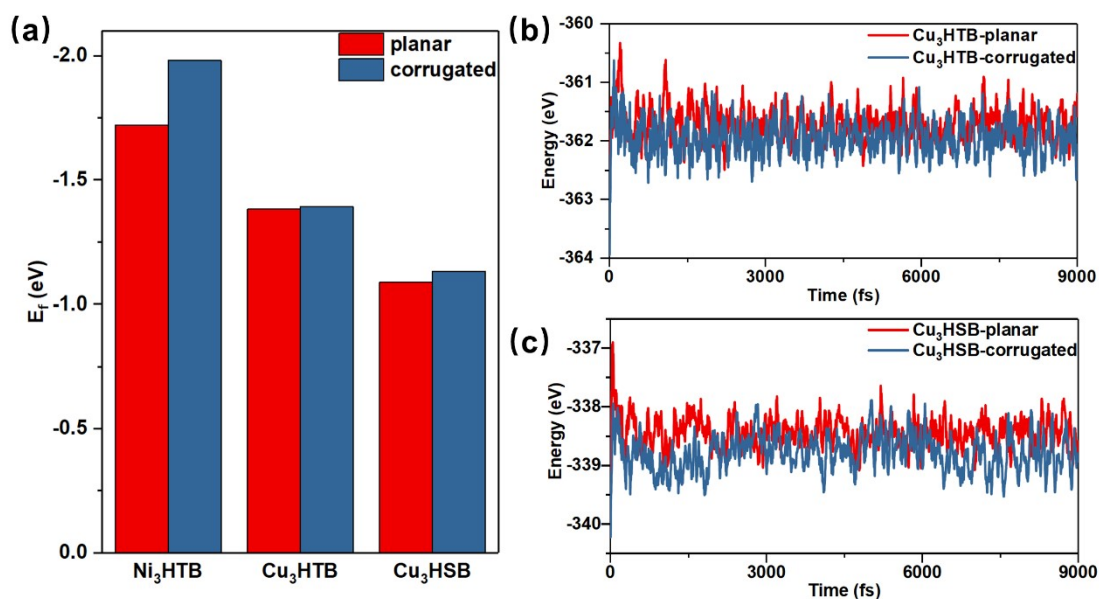
Fig. S5 (a) The formation energies of the corrugated and planar phases of Ni_3HTB, Cu_3HTB, and Cu_3HSB. The total potential energy of MOFs as a function of simulation time for (b) c-Cu_3HTB and p-Cu_3HTB (c) c-Cu_3HSB and p-Cu_3HSB by using ab-initio molecular dynamics (300K) in 9 ps.
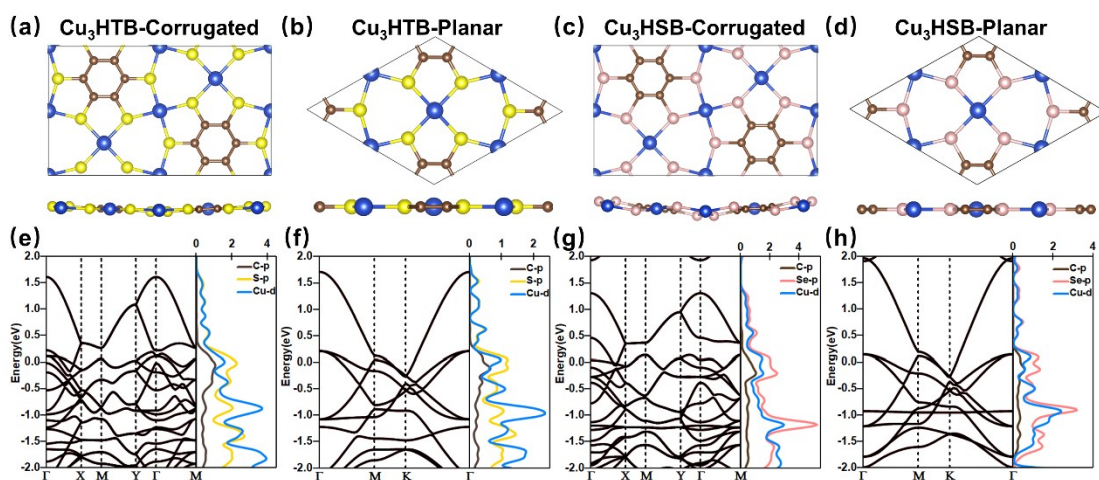

Fig. S6 Top and side views of (a) c-Cu_3HTB, (b) p-Cu_3HTB, (c) c-Cu_3HSB, and (d) p-Cu_3HSB. Band structures and PDOS of (e) c-Cu_3HTB, (f) p-Cu_3HTB, (g) c-Cu_3HSB, and (h) p-Cu_3HSB, respectively.
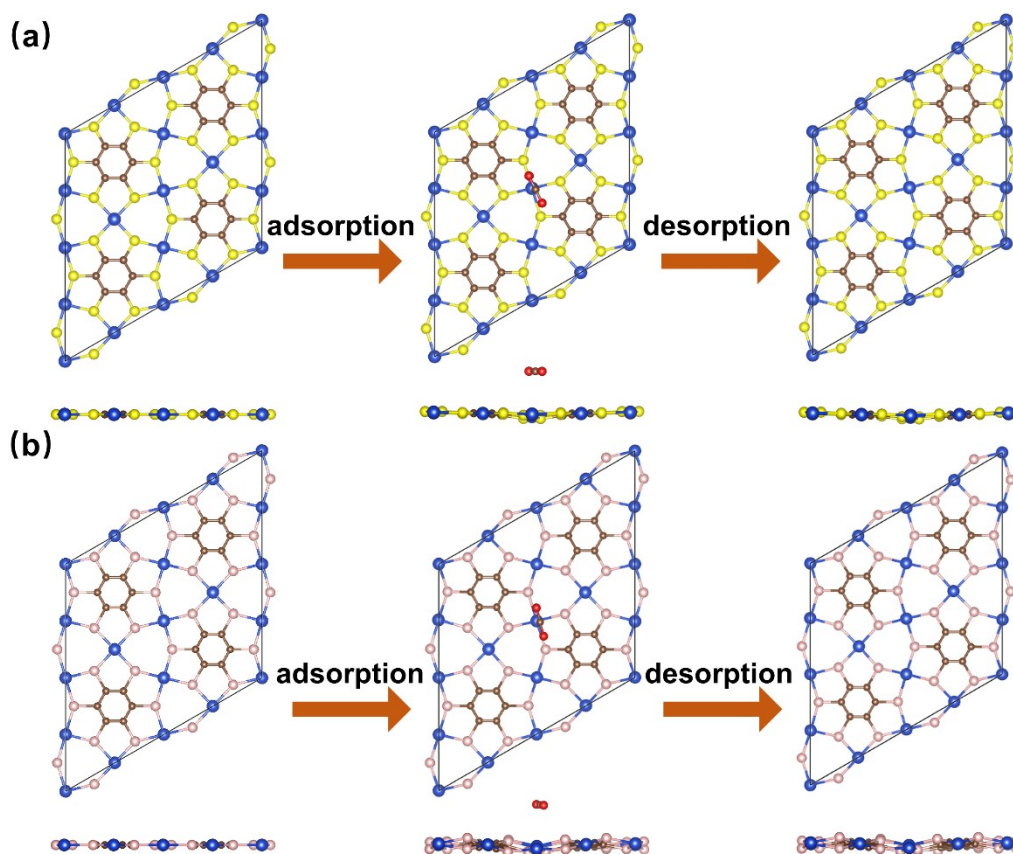
Fig. S7 Top and side views of the CO_2 molecular adsorbed and desorbed on the p-Cu$_3$HTB and p-Cu$_3$HSB.

Geometrical Information

c-Ni$_3$HTB

1.0

8.4029483795	0.0000000000	0.0000000000
0.0000000000	14.4239816666	0.0000000000
0.0000000000	0.0000000000	15.0000000000

S   C   Ni

12   12   6

Direct

0.067528002	0.141133003	0.452179019
0.932471998	0.858866997	0.452179019
0.567528002	0.858866997	0.452179019
0.432471998	0.141133003	0.452179019
0.932783026	0.640995975	0.477553018
0.067217003	0.359003992	0.477553018
0.432782997	0.359003992	0.477553018
0.567216974	0.640995975	0.477553018
0.750000000	0.458644010	0.408065001
0.250000000	0.541356023	0.408065001
0.250000000	0.958574025	0.520890999

0.750000000	0.041426000	0.520890999
0.893459012	0.201673002	0.468546009
0.106541003	0.798327048	0.468546009
0.393458983	0.798327048	0.468546009
0.606540988	0.201673002	0.468546009
0.106558005	0.701637017	0.460422993
0.893441988	0.298372999	0.460422993
0.606558012	0.298372999	0.460422993
0.393442016	0.701637017	0.460422993
0.750000000	0.345937004	0.447185008
0.250000000	0.654062996	0.447185008
0.250000000	0.845931021	0.481578000
0.750000000	0.154069012	0.481578000
0.250000000	0.250102994	0.465418021
0.750000000	0.749897006	0.465418021
0.000000000	0.500000000	0.438084984
0.500000000	0.500000000	0.438084984
-0.000000000	-0.000000000	0.491055012
0.500000000	-0.000000000	0.491055012

p-Ni$_3$HTB
1.0

8.5580167770	0.0000000000	0.0000000000
-4.2790312318	7.4114698717	0.0000000000
0.0000000000	0.0000000000	15.0000000000

S   C   Ni
6   6   3
Direct

0.789305005	0.578597004	0.500000000
0.210695008	0.421403005	0.500000000
0.421407009	0.210700007	0.500000000
0.578593015	0.789300050	0.500000000
0.789298006	0.210705990	0.500000000
0.210701999	0.789294003	0.500000000
0.905306028	0.810608064	0.500000000
0.094694003	0.189392009	0.500000000
0.189393007	0.094694002	0.500000000
0.810607030	0.905305998	0.500000000
0.905301984	0.094697002	0.500000000
0.094698031	0.905303039	0.500000000
0.500000000	0.000000000	0.500000000
-0.000000000	0.500000004	0.500000000
0.500000000	0.500000004	0.500000000