Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Electronic Supplementary Information

The Binding Nature of Light Hydrocarbons on Fe/MOF-74 for Gas Separation

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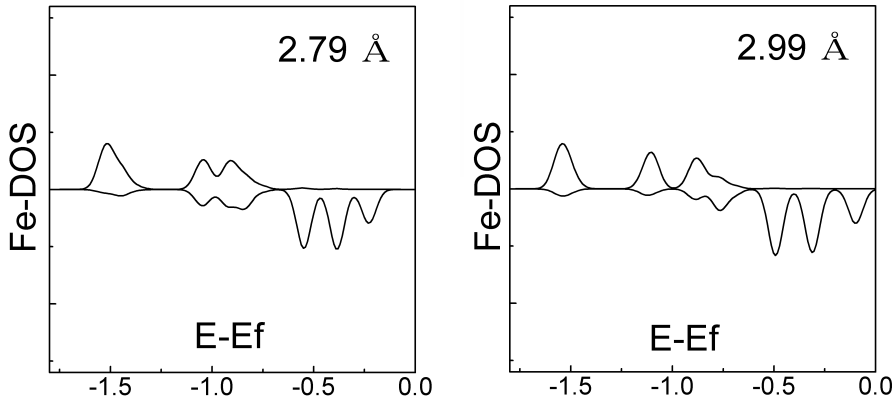

Figure S1. The projected DOS of Fe atom near the Fermi level at the Fe-Fe distance of 2.79 Å and 2.99 Å. The split of the HOMO bands that indicating the Fe-Fe direct interaction is also observed at the experimental Fe-Fe distance of 2.99 Å.

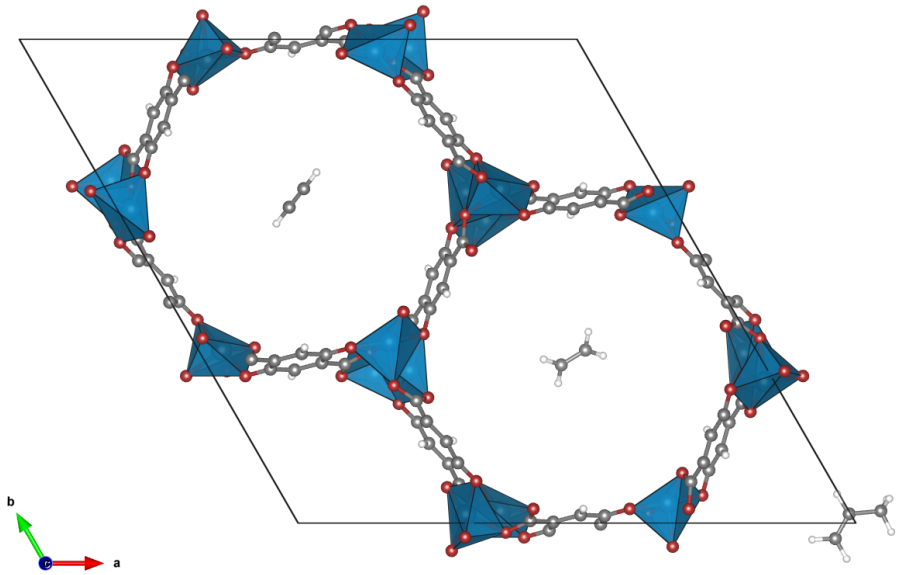

Figure S2. The relative HOMO and LUMO energies of gas molecules in Figure 2a were evaluated by placing each gas molecule at the center of the pores in MOF-74. The distance between gas molecule and MOF framework is 6–7 Å, and the interactions between them were negligible.

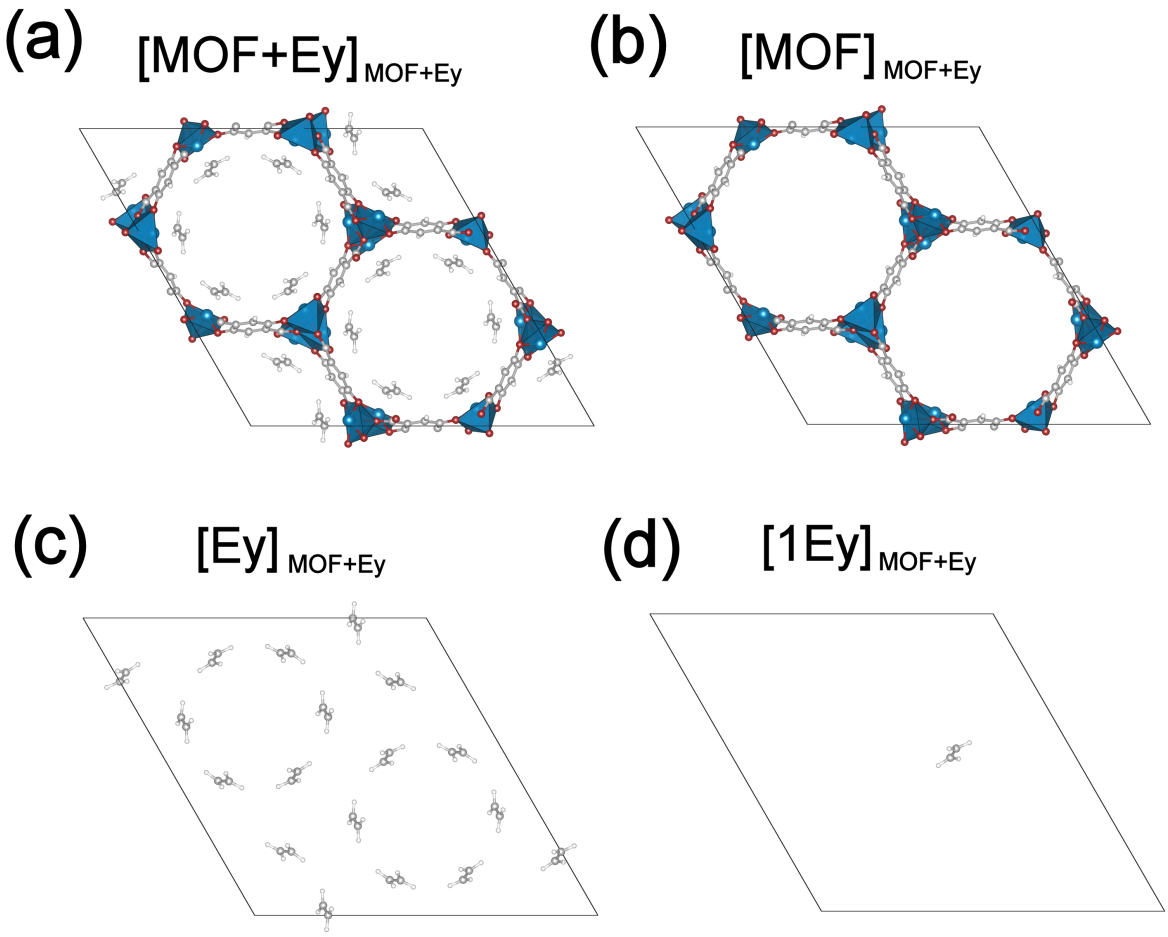

Figure S3. The $[mol]_{geom}$ Notations used in the "Paraffin Adsorption" section. The mutual gas interaction is calculated from the single point energy difference between (c) and (d) per molecule, i.e. E(c)/36 – E(d).

Table S1. The binding energy comparison for different calculation methods. The correlation between experimental value and each case is evaluated with the R^2 value (coefficient of determination).

Adsorbate	Binding Energy (kJ/mol)				
	Experiments (ref. 10)	RPBE+D2 (Figure 5)	RPBE+D2+U	PBE+D2	PBE+D2+U
acetylene	47	46.423	33.889	69.601	59.868
ethylene	45	44.371	36.673	70.649	65.616
propylene	44	48.142	46.794	78.653	77.692
methane	20	14.049	16.730	23.389	30.301
ethane	25	22.480	26.492	36.870	44.079
propane	33	28.088	32.602	46.067	53.266
R^2	1	0.972	0.710	0.945	0.804

Table S2. The intrachain Fe-Fe distance (Fe-Fe), average of Fe-O distance (Fe-O), oxo-bridged intrachain Fe-O-Fe bond angle (Fe-O-Fe) of bare Fe/MOF-74, and their changes after the gas adsorption are presented. All geometries are taken from the ground state magnetic orderings. The changes of C-C distance of gas molecules (ΔC-C(gas)) after the adsorption are also presented.

Adsorbate	Geometry (distance or angle)				
	Fe-Fe (Å)	Fe-O (Å)	Fe-O-Fe (°)		ΔC-C(gas) (Å)
bare	2.794	2.095	83.914	83.942	
	Δ	Δ	Δ	Δ	
acetylene	0.518	0.105	23.205	8.650	0.031
ethylene	0.487	0.088	22.043	8.609	0.034
propylene	0.483	0.084	21.390	8.835	0.032
methane	0.018	-0.002	0.731	0.779	0.000
ethane	0.033	-0.003	1.427	1.380	-0.001
propane	0.022	-0.007	1.032	1.252	-0.002

Table S3. The binding energies calculated from the ground state magnetic orderings, and measured in experiments as illustrated in Figure 5. The intrachain FM/interchan parallel (FM/par), intrachain FM/interchain antiparallel (FM/anti), and intrachain AFM/interchain antiparallel (AFM/anti) ordering cases are also presented. The correlation between experimental value and each case is evaluated with the R^2 value (coefficient of determination).

Adsorbate	Binding Energy (kJ/mol)				
	Experiments (ref. 10)	Ground state (Figure 5)	FM/par	FM/anti	AFM/anti
acetylene	47	46.423	42.954	43.163	54.764
ethylene	45	44.371	41.082	41.144	52.712
propylene	44	48.142	45.324	45.323	56.484
methane	20	14.049	14.061	14.049	15.478
ethane	25	22.480	22.525	22.480	25.024
propane	33	28.088	28.142	28.088	31.485
R^2	1	0.972	0.967	0.968	0.973