Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information

A Density Functional Theory Study on the Stability of Pt Clusters in MOF-808

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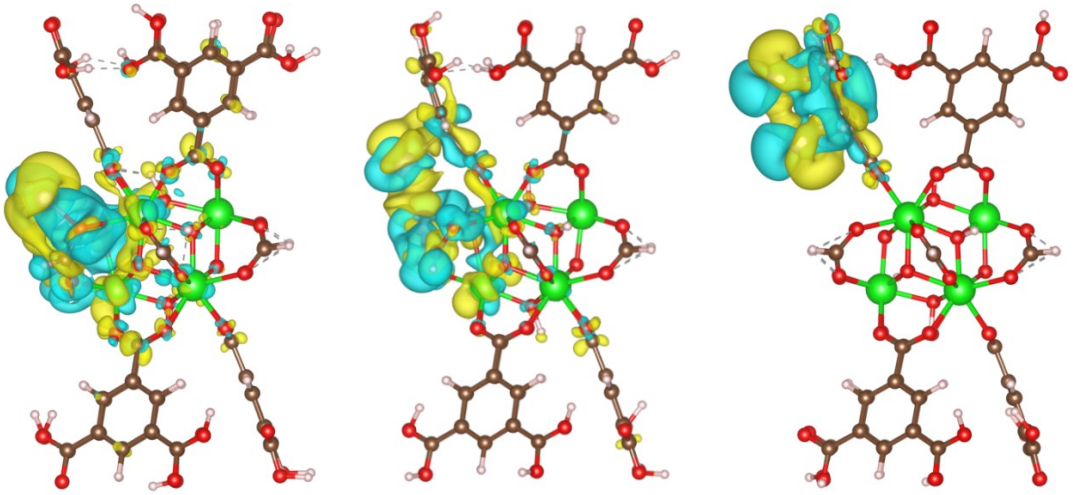
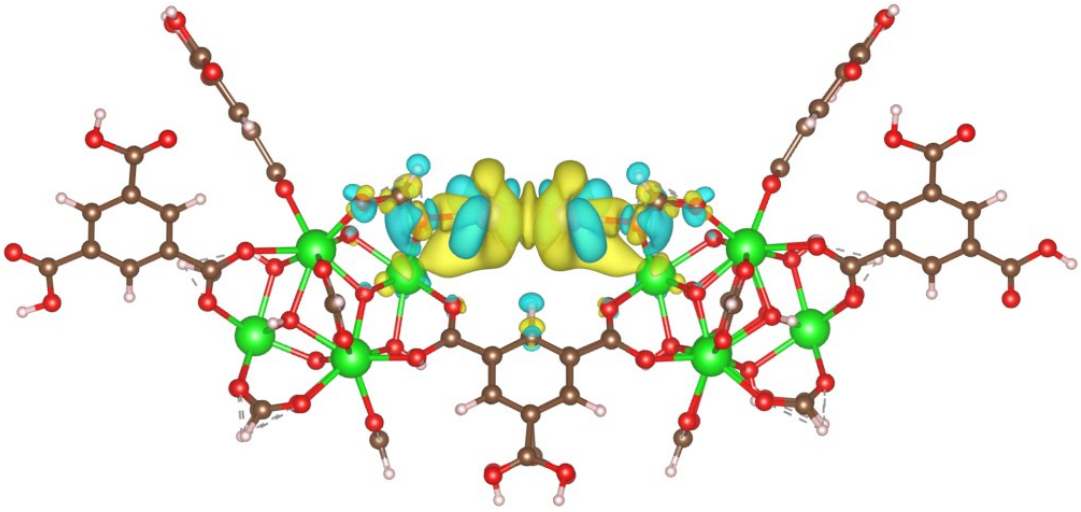
The plots of calculated charge density difference for the adsorbed Pt_2 dimer at the Zr_6 node, the interface, the linker and between two Zr_6 nodes. The AIMD simulation movie of Pt_8@MOF-808 at 300 K with a total simulation time of 5 ps.



MOF-node-Pt_2 MOF-interface-Pt_2 MOF-linker-Pt_2

Fig. S1 The charge density difference of the Pt_2-adsorbed in the node, interface and linker of MOF-808. The yellow and blue isosurfaces represent charge accumulation and depletion in the space, respectively.



Between two nodes-Pt_2

Fig. S2 The charge density difference of the Pt_2-adsorbed in the between two nodes of MOF-808. The yellow and blue isosurfaces represent charge accumulation and depletion in the space, respectively.

The ionization potential (I_1) and electron affinity (I_0) are calculated using the following equation:

$$I_1 = E(Pt_n^+) - E(Pt_n) \quad (1)$$

where $E(Pt_n^+)$ is the energy of the Pt_n cluster after losing an electron; $E(Pt_n)$ is the energy of the Pt_n cluster.

$$I_0 = E(MOF) - E(MOF^-) \quad (2)$$

where E(MOF) is the energy of the MOF-808; $E(MOF^-)$ is the energy of MOF-808 after gaining an electron.

Table S1 The ionization potential (I_1) of the Pt_n clusters and the electron affinity (I_0) of MOF-808 (all in kJ/mol).

	I_1	I_0
MOF-808		584.36
Pt_1	787.45	
Pt_2	787.47	
Pt_3	692.51	
Pt_4	643.67	
Pt_5	615.99	
Pt_6	611.02	
Pt_7	601.65	
Pt_8	605.26	
Pt_{13}	571.77	
Pt_{18}	572.67	
Pt_{23}	565.72	

Table S2 The electronic energy of MOF and MOF^- in the vacuum. (all in a.u.) and the electron affinity energy of the MOF-808 (kJ/mol).

mof-808/VAC	E(MOF)	$E(MOF^-)$	I_0
mof-808	-1536.56025005037	-1536.78281514807	584.36

Table S3 The electronic energy of Pt_n clusters in the vacuum. The electronic energy of Pt_n^+ clusters in the vacuum (all in a.u.) and the ionization potential of the Pt cluster (kJ/mol).

Pt_n/VAC	E(Pt)	Pt_n^+/VAC	E(Pt_n^+)	I_1
Pt_1	-119.963590840172	Pt_1^+	-119.663673960915	787.45
Pt_2	-240.08951464712	Pt_2^+	-239.78959033354	787.47
Pt_3	-360.212064376942	Pt_3^+	-359.948304746257	692.51
$Pt_{4\text{-}1}$	-480.325703795423	Pt_{4-1}^+	-480.099813160402	593.09
$Pt_{4\text{-}2}$	-480.321652493376	Pt_{4-2}^+	-480.0764965087	643.67
$Pt_{5\text{-}1}$	-600.453971821286	Pt_{5-1}^+	-600.21935960092	615.99
$Pt_{5\text{-}2}$	-600.451244345277	Pt_{5-2}^+	-600.211795511267	628.69
$Pt_{6\text{-}1}$	-720.582027760151	Pt_{6-1}^+	-720.357045648047	590.71
$Pt_{6\text{-}2}$	-720.58476974514	Pt_{6-2}^+	-720.352048067708	611.02
Pt_7	-840.722289923652	Pt_7^+	-840.493139597147	601.65
Pt_8	-960.874618786053	Pt_8^+	-960.644093426868	605.26
Pt_{13}	-1561.6601689263	Pt_{13}^+	-1561.44239874205	571.77
Pt_{18}	-2162.42670043567	Pt_{18}^+	-2162.2085870904	572.67
Pt_{23}	-2763.28204561824	Pt_{23}^+	-2763.06657802024	565.72

Table S4 The electronic energy (all in a.u.) of the encapsulated Pt_n (n=1~7) clusters at the Zr_6 node of MOF-808-1. E(MOF′) is the electronic energy of the deformed MOF surface after the Pt_n cluster adsorption. E(Pt_n′) is the electronic energy of the deformed Pt_n.

MOF/Pt_n	E(MOF/Pt_n)	E(Pt_n′)	E(MOF′)
mof-808	-1536.56025005037		
mof-808-node-1pt	-1656.72019296133		-1536.48039624562
mof-808-node-2pt	-1776.82093169005	-240.086126157376	-1536.47110988423
mof-808-node-3pt	-1896.96260087933	-360.206035100783	-1536.43728622196
mof-808-node-4pt	-2017.11658537781	-480.307136167297	-1536.45767222395
mof-808-node-5pt	-2137.27747986258	-600.438137021519	-1536.39914644172
mof-808-node-6pt	-2257.44098397014	-720.571365767296	-1536.31441876909
mof-808-node-7pt	-2377.5954618907	-840.707380733742	-1536.4221435303

Table S5 The electronic energies (all in a.u.) of the encapsulated Pt_n (n=1~7) clusters at the interface of MOF-808-1. E(MOF′) is the electronic energy of the deformed MOF surface after the Pt_n cluster adsorption. E(Pt_n′) is the electronic energy of the deformed Pt_n.

MOF/Pt_n	E(MOF/Pt_n)	E(Pt′)	E(MOF′)
mof-808-interface-1pt	-1656.6452973771		-1536.52923114408
mof-808-interface-2pt	-1776.7977624238	-240.083920651277	-1536.48072385572
mof-808-interface-3pt	-1896.9582790487	-360.205413535118	-1536.48803938455
mof-808-interface-4pt	-2017.09136348107	-480.307932587999	-1536.49198329916
mof-808-interface-5pt	-2137.25073271441	-600.426863175441	-1536.44901924817
mof-808-interface-6pt	-2257.39594263005	-720.565527620343	-1536.45112210482
mof-808-interface-7pt	-2377.59243329908	-840.68719208215	-1536.43205365109

Table S6 The electronic energies (all in a.u.) of the encapsulated Pt_n (n=1~7) clusters at the linker of MOF-808-1. E(MOF′) is the electronic energy of the deformed MOF surface after the Pt_n cluster adsorption. E(Pt_n′) is the electronic energy of the deformed Pt_n.

MOF/Pt_n	E(MOF/Pt_n)	E(Pt′)	E(MOF′)
mof-808-linker-1pt	-1656.63135760777		-1536.54409176056
mof-808-linker-2pt	-1776.75645382756	-240.076098852879	-1536.5223334351
mof-808-linker-3pt	-1896.90954037513	-360.195358208145	-1536.4672395255
mof-808-linker-4pt	-2017.13467748703	-480.309374483908	-1536.50573314103
mof-808-linker-5pt	-2137.26483232606	-600.42463678265	-1536.4935986088
mof-808-linker-6pt	-2257.36666902563	-720.54749863956	-1536.41582489787
mof-808-linker-7pt	-2377.5224460521	-840.680211773397	-1536.41947085894

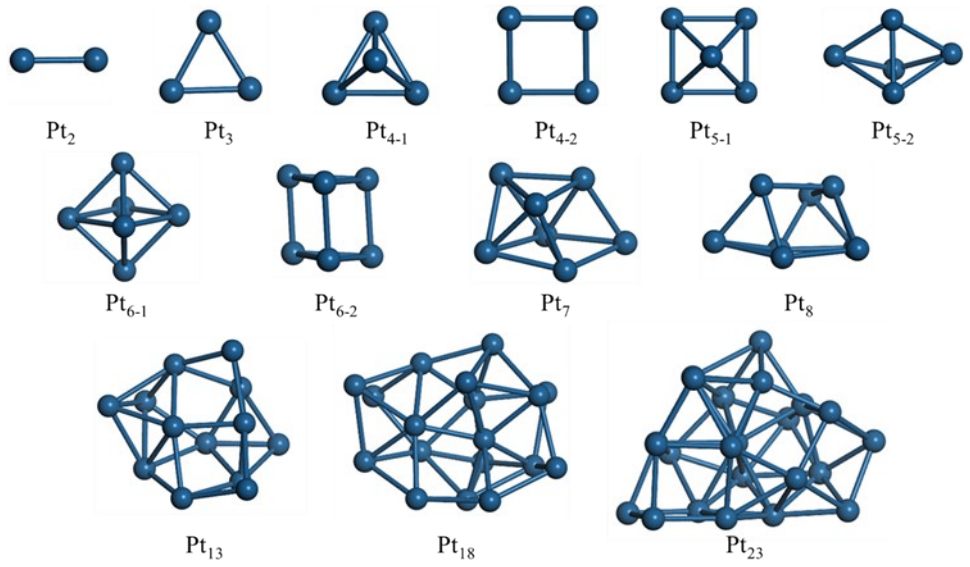


Fig. S3 Optimized structures of Pt_n (n=2~8, 13, 18, 23) clusters.

Table S7 Comparison of calculated Bader charges, q, (|e|), for of the adsorbed Pt_n clusters using PBE functional and DFT+U method.

		q
mof-808-node-1pt	PBE	0.78
	DFT+U	0.83
mof-808-node-4pt	PBE	1.44
	DFT+U	1.67
mof-808-node-7pt	PBE	1.96
	DFT+U	2.05
mof-808-interface-1pt	PBE	0.65
	DFT+U	0.70
mof-808-interface-4pt	PBE	1.19
	DFT+U	1.39
mof-808-interface-7pt	PBE	1.52
	DFT+U	2.23
mof-808-linker-1pt	PBE	0.35
	DFT+U	0.41
mof-808-linker-4pt	PBE	1.15
	DFT+U	1.26
mof-808-linker-7pt	PBE	1.59
	DFT+U	1.72

Table S8 DFT+U calculated adsorption energies E_{ads}, binding energies E_b/MOF, and nucleation energies E_{nuc}/MOF (all in kJ/mol) of the supported Ptn clusters.

		E_{ads}	E_b	E_{nuc}
mof-808-node-1pt	PBE	-516		
	DFT+U	-568		
mof-808-node-4pt	PBE	-605	+219	+16
	DFT+U	-899	+180	-85
mof-808-node-7pt	PBE	-821	+221	
	DFT+U	-1013	+435	
mof-808-interface-1pt	PBE	-319		
	DFT+U	-342		
mof-808-interface-4pt	PBE	-359	-501	-126
	DFT+U	-638	-466	-244
mof-808-interface-7pt	PBE	-813	-1146	
	DFT+U	-871	-1011	
mof-808-linker-1pt	PBE	-282		
	DFT+U	-307		
mof-808-linker-4pt	PBE	-653	-761	-403
	DFT+U	-659	-476	-152
mof-808-linker-7pt	PBE	-629	-1219	
	DFT+U	-689	-1075	

Table S9 DFT calculated adsorption energies E_{ads}, binding energies E_b/MOF, and nucleation energies E_{nuc}/MOF (all in kJ/mol) of the supported Pt_n clusters in different spin states (M = 2S + 1, S = 0, 1, 2).

	Spin states, M	E_{ads}	E_b	E_{nuc}
mof-808-node-1pt	1	-521.83		
	3	-499.50		
	5	-		
mof-808-node-4pt	1	-699.32	193.28	42.76
	3	-647.27	298.31	70.80
	5	-654.12	182.74	43.46
mof-808-node-7pt	1	-802.73	317.75	
	3	-778.45	494.52	
	5	-754.61	288.95	
mof-808-interface-1pt	1	-317.57		
	3	-274.45		
	5	-		
mof-808-interface-4pt	1	-575.54	-499.98	-235.17
	3	-553.09	-507.72	-257.30
	5	-535.12	-503.69	-237.66
mof-808-interface-7pt	1	-845.39	-1154.74	
	3	-848.98	-1151.38	
	5	-803.24	-1169.19	
mof-808-linker-1pt	1	-189.94		
	3	-222.94		
	5	-		
mof-808-linker-4pt	1	-694.31	-1129.26	-327.29
	3	-644.81	-805.46	-244.02
	5	-653.32	-943.00	-279.56
mof-808-linker-7pt	1	-666.60	-1869.35	
	3	-643.99	-1306.92	
	5	-623.63	-1551.50	

Table S10 DFT+U calculated the electronic energies (all in a.u.) of the encapsulated Pt_n clusters

	E
mof-808	-1536.451564
mof-808-node-1pt	-1656.631743
mof-808-node-3pt	-1896.890819
mof-808-node-4pt	-2017.103591
mof-808-node-7pt	-2377.547104
mof-808-interface-1pt	-1656.545325
mof-808-interface-3pt	-1896.817485
mof-808-interface-4pt	-2017.004189
mof-808-interface-7pt	-2377.493024
mof-808-linker-1pt	-1656.531959
mof-808-linker-3pt	-1896.87388
mof-808-linker-4pt	-2017.012272
mof-808-linker-7pt	-2377.423843

Table S11 The electronic energy of the Pt_n (n = 1, 4, 7) clusters in different spin states (M = 2S + 1, S = 0, 1, 2).

Pt_n	M=1	M=3	M=5
Pt_1	-119.963589088992	-119.981528508877	-119.774195277264
Pt_4	-480.309389978602	-480.32695236927	-480.322288420969
Pt_7	-840.709618225322	-840.717582208264	-840.724328060214

Table S12 The electronic energies (all in a.u.) in different spin states for MOF encapsulates Pt_n cluster (M = 2S + 1, S = 0, 1, 2).

	1	3	5
mof-808	-1536.560756	-1536.561275	-1536.562783
mof-808-node-1pt	-1656.723095	-1656.73305	-1656.723039
mof-808-node-4pt	-2017.136498	-2017.134757	-2017.134208
mof-808-node-7pt	-2377.576111	-2377.575348	-2377.574523
mof-808-interface-1pt	-1656.645298	-1656.647333	-1656.646347
mof-808-interface-4pt	-2017.089352	-2017.098882	-2017.088882
mof-808-interface-7pt	-2377.59236	-2377.602209	-2377.593045
mof-808-linker-1pt	-1656.596687	-1656.627717	-1656.615772
mof-808-linker-4pt	-2017.134588	-2017.133819	-2017.133904
mof-808-linker-7pt	-2377.524264	-2377.524136	-2377.524633

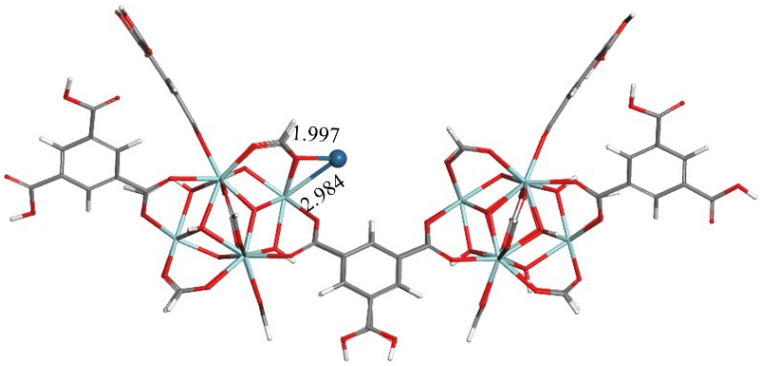


Fig. S4 DFT optimized structures of Pt_1 between two nodes of MOF-808-2.

Table S13 The electronic energies (all in a.u.) of the encapsulated Pt_n (n=1~23) clusters at between two Zr_6 nodes of MOF-808-2.

MOF/Pt_n	E
mof-808-2-node	-2344.33987279822
mof-808-2-node-Pt	-2464.40538987569
mof-808-2-node-2Pt	-2584.49903670424
mof-808-2-node-3Pt_A	-2704.61610615639
mof-808-2-node-3Pt_B	-2704.65974320159
mof-808-2-node-3Pt_C	-2704.66634694679
mof-808-2-node-4Pt_A	-2824.76632953271
mof-808-2-node-4Pt_B	-2824.78473281163
mof-808-2-node-4Pt_C	-2824.79290646846
mof-808-2-node-4Pt_D	-2824.80108584613
mof-808-2-node-5Pt_A	-2944.9033540187
mof-808-2-node-5Pt_B	-2944.91610071418
mof-808-2-node-5Pt_C	-2944.93029532579
mof-808-2-node-6Pt_A	-3065.02520615236
mof-808-2-node-6Pt_B	-3065.03354669536
mof-808-2-node-6Pt_C	-3065.04684064878
mof-808-2-node-6Pt_D	-3065.07369593572
mof-808-2-node-7Pt	-3185.17916628083
mof-808-2-node-8Pt_A	-3305.31723704916
mof-808-2-node-8Pt_B	-3305.340318485
mof-808-2-node-8Pt_C	-3305.38050987244
mof-808-2-node-13Pt	-3906.08021312889
mof-808-2-node-18Pt	-4506.86913076478
mof-808-2-node-23Pt	-5107.73275128186

Table S14 The electronic energies (all in a.u.) of CO over the encapsulated Pt_n (n=1~23) clusters at between two Zr_6 nodes of MOF-808-2.

	E		E
CO	-21.667504248118	Pt-CO	-141.79532698204
Pt_4-linker-Pt	-2944.8508885765	Pt_4-linker-Pt-CO	-2966.63555583887
Pt_4-node-Pt	-2944.86619448083	Pt_4-node-Pt-CO	-2966.65888151519
mof-2-node-Pt_5	-2944.91610210743	mof-2-node-Pt_5-CO	-2966.68871118325
Pt_6-linker-Pt	-3185.11953147143	Pt_6-linker-Pt-CO	-3206.90256836548
Pt_6-node-Pt	-3185.13727967754	Pt_6-node-Pt-CO	-3206.92946877465
mof-2-node-Pt_7	-3185.17916628083	mof-2-node-Pt_7-CO	-3206.96147079585

Table S15 DFT calculated adsorption energies E_{ads}, binding energies E_b/MOF, and nucleation energies E_{nuc}/MOF (all in kJ/mol) of the supported Pt_n (n=2~7) clusters at the node, interface, linker of MOF-808.

	E_{ads}			$E_{b/MOF}$			$E_{nuc/MOF}$		
	node	interface	linker	node	interface	linker	node	interface	linker
Pt_2	–449	–389	–280	+155	–177	–142	+155	–177	–142
Pt_3	–499	–488	–360	+203	–375	–356	+48	–198	–215
Pt_4	–605	–539	–653	+219	–501	–761	+16	–126	–403
Pt_5	–698	–628	–665	+216	–696	–916	–3	–195	–155
Pt_6	–784	–666	–589	+207	–854	–997	–8	–157	–80
Pt_7	–821	–813	–629	+221	–1146	–1219	–15	–292	–222