Supporting Information

Computational Investigation of Multifunctional MOFs for Adsorption and Membrane-based Separation of CF_4/CH_4, CH_4/H_2, CH_4/N_2, and N_2/H_2 Mixtures

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Table S1. Simulation conditions.

Mixture	Adsorption (desorption) pressure (bar)	Total simulation cycles
CF_4/CH_4 (50/50)	1 (0.1)	20,000
CH_4/H_2 (50/50)	10 (1)	20,000
CH_4/N_2 (50/50)	10 (1)	50,000
N_2/H_2 (70/30)	1 (0.1)	≥40,000

Table S2. Interaction parameters of the sorbates.

Molecule	σ (Å)	ε/k_B (K)	q (e)
CF_4 (single-site)	4.66	134.0	0
CH_4 (single-site)	3.73	148.0	0
H_2 (single-site)	2.96	34.2	0
N_N_2	3.31	36.0	-0.482
COM_N_2	0	0	0.964

COM = center of mass

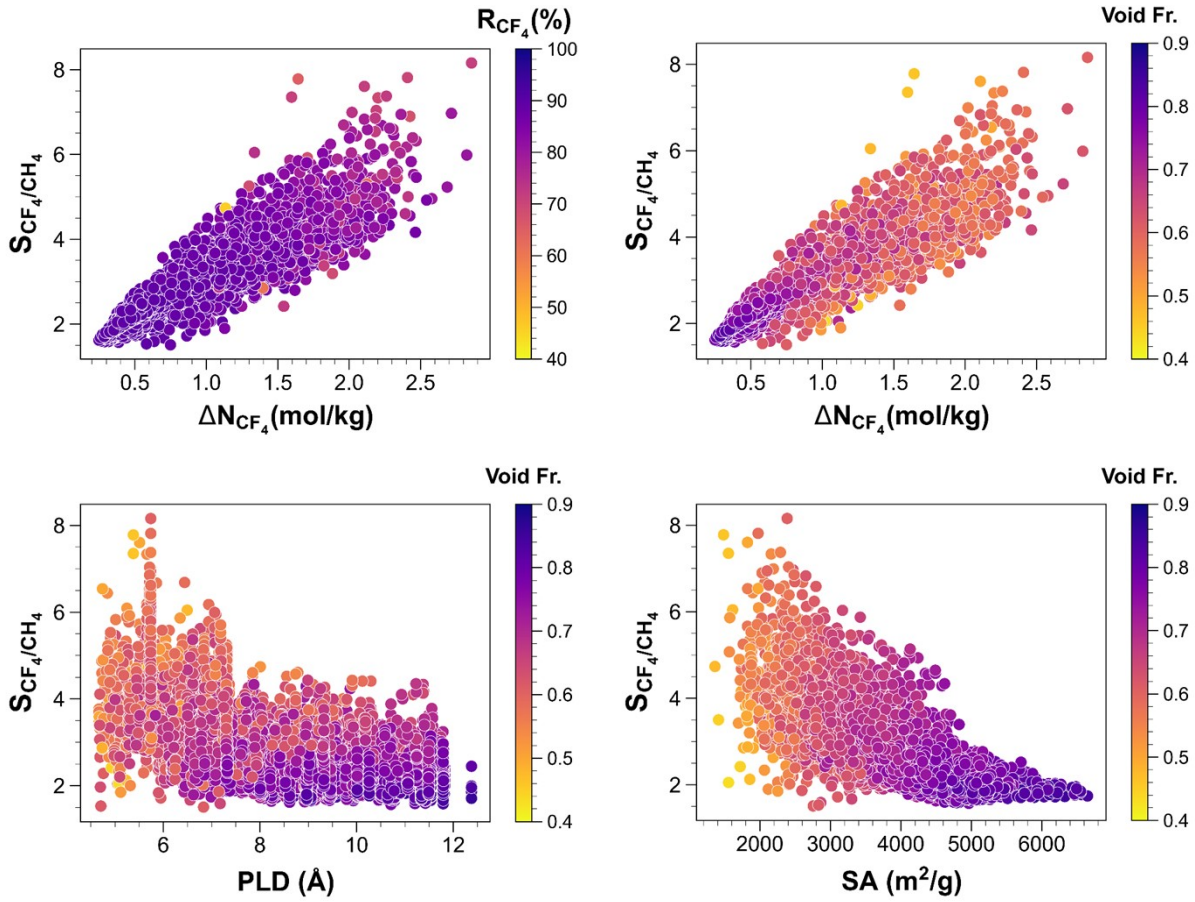


Figure S1. CF_4/CH_4 separation performance metrics of MTV MOFs along with their textural properties.

Table S3. Top 20 MOF adsorbents determined for the CF_4/CH_4 separation.

Structure	Functional Group	$S_{ads,CF_4/CH_4}$	ΔN_{CF_4} (mol/kg)	R_{CF_4} (%)	GCD (Å)	PLD (Å)	LCD (Å)	SA (m^2/g)	Void Fr.	Pore Vol. (cm^3/g)	OSPS
pMOF_10	bare	8.2	2.9	71.6	6.39	5.74	6.38	2387.4	0.605	0.703	279.1
pMOF_26	bare	7.0	2.7	79.8	7.01	5.74	6.51	2470.3	0.625	0.758	268.7
pMOF_8	bare	6.0	2.8	80.6	6.47	5.74	6.47	2898.5	0.624	0.805	261.2
cuf_3865	F−F	7.8	2.4	70.2	6.35	5.74	6.34	1975.4	0.584	0.580	257.7
cuf_6620	F−F	6.9	2.4	78.8	6.50	5.74	6.50	2101.8	0.598	0.616	255.0
cuf_9854	F−NH_2	6.5	2.3	81.1	6.90	5.71	6.90	2357.3	0.598	0.678	249.7
cuf_5531	NH_2−OCH_3	7.4	2.3	72.1	7.63	5.74	7.60	2292.0	0.553	0.696	249.3
cuf_8405	NH_2−OCH_3	6.7	2.2	80.5	8.15	6.44	7.77	2606.7	0.585	0.782	248.8
cuf_6621	F−NH_2	6.3	2.5	76.2	6.50	5.74	6.50	2082.9	0.587	0.609	248.2
cuf_10812	F−NH_2	6.6	2.3	78.7	6.50	5.74	6.50	2126.4	0.584	0.616	248.0
cuf_800	F−OCH_3	6.4	2.4	75.7	7.23	5.72	7.07	2601.6	0.606	0.730	247.6
cuf_2789	NH_2−NH_2	5.2	2.7	80.8	7.90	5.66	7.90	3724.8	0.657	0.941	247.4
cuf_2854	F−NH_2	5.8	2.4	81.9	7.62	5.66	6.50	2896.6	0.638	0.823	247.2
cuf_5547	NH_2−OCH_3	6.6	2.3	76.8	7.03	5.74	6.75	2342.8	0.563	0.711	246.5
cuf_8442	OCH_3−OCH_3	7.6	2.1	71.5	6.64	5.51	6.64	1824.7	0.496	0.583	246.0
pMOF_492	bare	5.5	2.5	83.2	7.33	5.01	6.55	3289.8	0.632	0.836	245.4
cuf_584	OCH_3−NH_2−NH_2	6.2	2.4	76.4	7.52	6.94	7.52	2350.6	0.581	0.720	244.3
cuf_3866	F−NH_2	6.9	2.4	67.6	6.25	5.74	6.20	2030.1	0.573	0.574	244.2
cuf_5869	NH_2−NH_2	6.6	2.1	80.3	7.80	5.74	7.38	2795.7	0.612	0.854	243.9
cuf_3149	F−NH_2−OCH_3	4.9	2.5	85.4	6.61	5.53	6.61	3067.1	0.595	0.753	243.8

GCD = global cavity diameter, PLD = pore limiting diameter, LCD = largest cavity diameter, SA = surface area, Void Fr. = void fraction, Pore Vol. = pore volume, OSPS = overall separation performance score

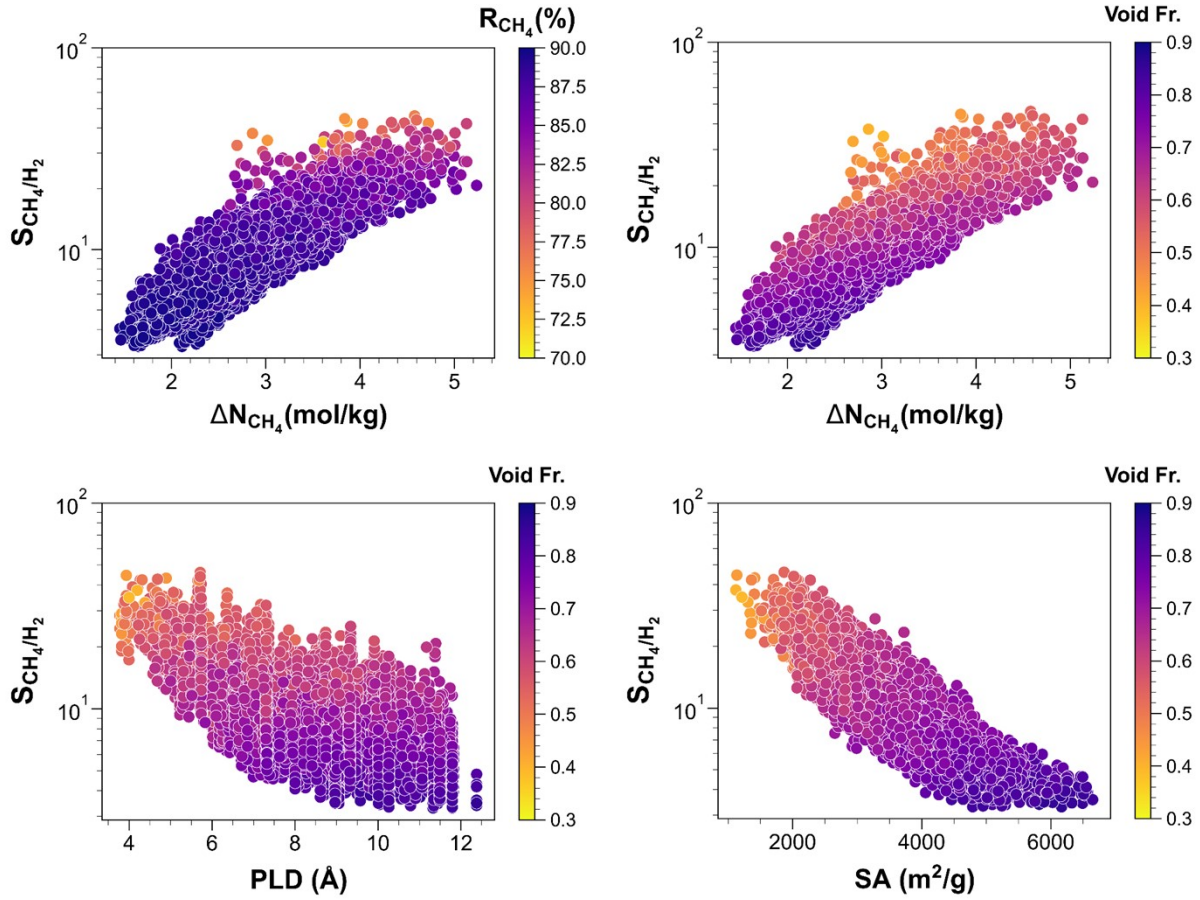


Figure S2. CH_4/H_2 separation performance metrics of MTV MOFs in tandem with their structural properties.

Table S4. Structural properties of 20 best performing MOF adsorbents for the CH_4/H_2 separation.

Structure	Functional Group	GCD (Å)	PLD (Å)	LCD (Å)	SA (m^2/g)	Void Fr.	Pore Vol. (cm^3/g)	OSPS
cuf_2878	NH_2−NH_2	6.15	5.66	6.15	2274.3	0.565	0.645	278.8
cuf_824	NH_2−OCH_3	6.14	5.72	6.14	1868.0	0.536	0.567	272.2
cuf_818	F−OCH_3	6.23	5.72	6.23	2018.3	0.550	0.578	269.5
cuf_586	NH_2−OCH_3	6.50	5.72	6.50	2140.3	0.559	0.641	267.1
cuf_110	OCH_3−OCH_3	6.16	4.27	6.16	2083.5	0.534	0.611	265.7
cuf_3153	NH_2−OCH_3	6.38	4.31	6.38	1705.1	0.501	0.541	264.8
cuf_1627	F−OCH_3	5.89	4.21	5.81	2171.4	0.548	0.610	264.0
cuf_2872	F−NH_2	6.22	5.66	6.20	2462.7	0.577	0.653	263.2
cuf_7134	NH_2−OCH_3	6.29	4.69	6.22	2058.8	0.533	0.557	263.2
cuf_1633	NH_2−OCH_3	5.89	4.09	5.89	1969.1	0.529	0.593	260.8
cuf_3160	F−OCH_3	6.74	4.56	6.52	1770.5	0.512	0.549	260.3
cuf_3866	F−NH_2	6.25	5.74	6.20	2030.1	0.573	0.574	258.9
cuf_2640	NH_2−NH_2	6.68	5.66	6.68	2543.9	0.581	0.712	257.4
cuf_810	NH_2−OCH_3−OCH_3	7.42	6.37	7.42	1868.6	0.514	0.564	257.4
cuf_2160	NH_2−OCH_3	6.38	4.81	6.38	2321.2	0.559	0.679	257.2
cuf_533	F−OCH_3	6.79	5.72	6.19	2357.1	0.578	0.655	256.3
cuf_811	F−OCH_3−OCH_3	7.42	6.37	7.42	1988.3	0.529	0.576	254.6
cuf_3143	OCH_3−OCH_3	5.44	3.94	5.43	1136.1	0.437	0.455	253.6
cuf_812	OCH_3−OCH_3	5.99	5.69	5.99	1363.3	0.474	0.485	253.0
cuf_9626	NH_2−NH_2	5.89	4.49	5.89	2175.5	0.570	0.631	253.0

GCD = global cavity diameter, PLD = pore limiting diameter, LCD = largest cavity diameter, SA = surface area, Void Fr. = void fraction, Pore Vol. = pore volume, OSPS = overall separation performance score

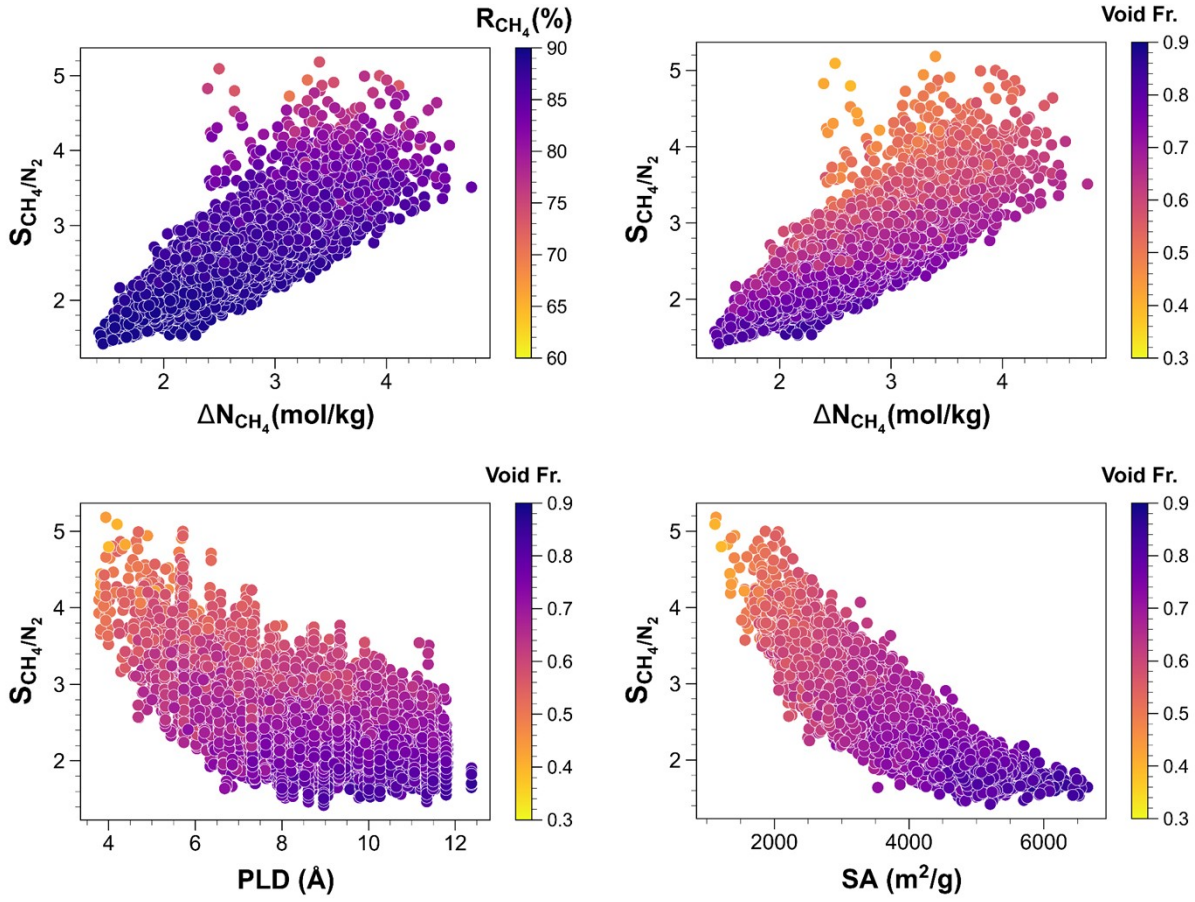


Figure S3. CH_4/N_2 separation performance metrics and structural features of MTV MOFs.

Table S5. Structural properties of 20 best MOF adsorbents identified for the CH_4/N_2 separation.

Structure	Functional Group	GCD (Å)	PLD (Å)	LCD (Å)	SA (m^2/g)	Void Fr.	Pore Vol. (cm^3/g)	OSPS
cuf_2878	NH_2−NH_2	6.15	5.66	6.15	2274.3	0.565	0.645	270.4
cuf_1627	F−OCH_3	5.89	4.21	5.81	2171.4	0.548	0.610	268.2
cuf_586	NH_2−OCH_3	6.50	5.72	6.50	2140.3	0.559	0.641	266.9
cuf_810	NH_2−OCH_3−OCH_3	7.42	6.37	7.42	1868.6	0.514	0.564	265.4
cuf_1633	NH_2−OCH_3	5.89	4.09	5.89	1969.1	0.529	0.593	265.0
cuf_811	F−OCH_3−OCH_3	7.42	6.37	7.42	1988.3	0.529	0.576	264.8
cuf_735	NH_2−OCH_3	7.90	5.71	7.90	3277.6	0.636	0.851	264.1
cuf_818	F−OCH_3	6.23	5.72	6.23	2018.3	0.550	0.578	263.9
pMOF_44	bare	5.89	4.97	5.88	2823.0	0.619	0.754	263.0
cuf_2872	F−NH_2	6.22	5.66	6.20	2462.7	0.577	0.653	262.7
cuf_7134	NH_2−OCH_3	6.29	4.69	6.22	2058.8	0.533	0.557	262.1
cuf_809	NH_2−OCH_3	7.02	5.71	6.86	2557.3	0.592	0.722	261.6
pMOF_513	bare	11.56	11.39	11.56	2477.5	0.650	0.937	261.6
cuf_824	NH_2−OCH_3	6.14	5.72	6.14	1868.0	0.536	0.567	261.5
cuf_110	OCH_3−OCH_3	6.16	4.27	6.16	2083.5	0.534	0.611	261.5
cuf_2640	NH_2−NH_2	6.68	5.66	6.68	2543.9	0.581	0.712	261.5
cuf_7812	NH_2−NH_2−NH_2	6.73	5.04	6.73	2855.9	0.582	0.719	261.4
pMOF_41	bare	6.90	5.71	6.88	3074.3	0.635	0.836	261.2
cuf_533	F−OCH_3	6.79	5.72	6.19	2357.1	0.578	0.655	260.3
cuf_340	F−OCH_3	6.22	4.39	6.22	2648.5	0.606	0.727	260.2

GCD = global cavity diameter, PLD = pore limiting diameter, LCD = largest cavity diameter, SA = surface area, Void Fr. = void fraction, Pore Vol. = pore volume, OSPS = overall separation performance score

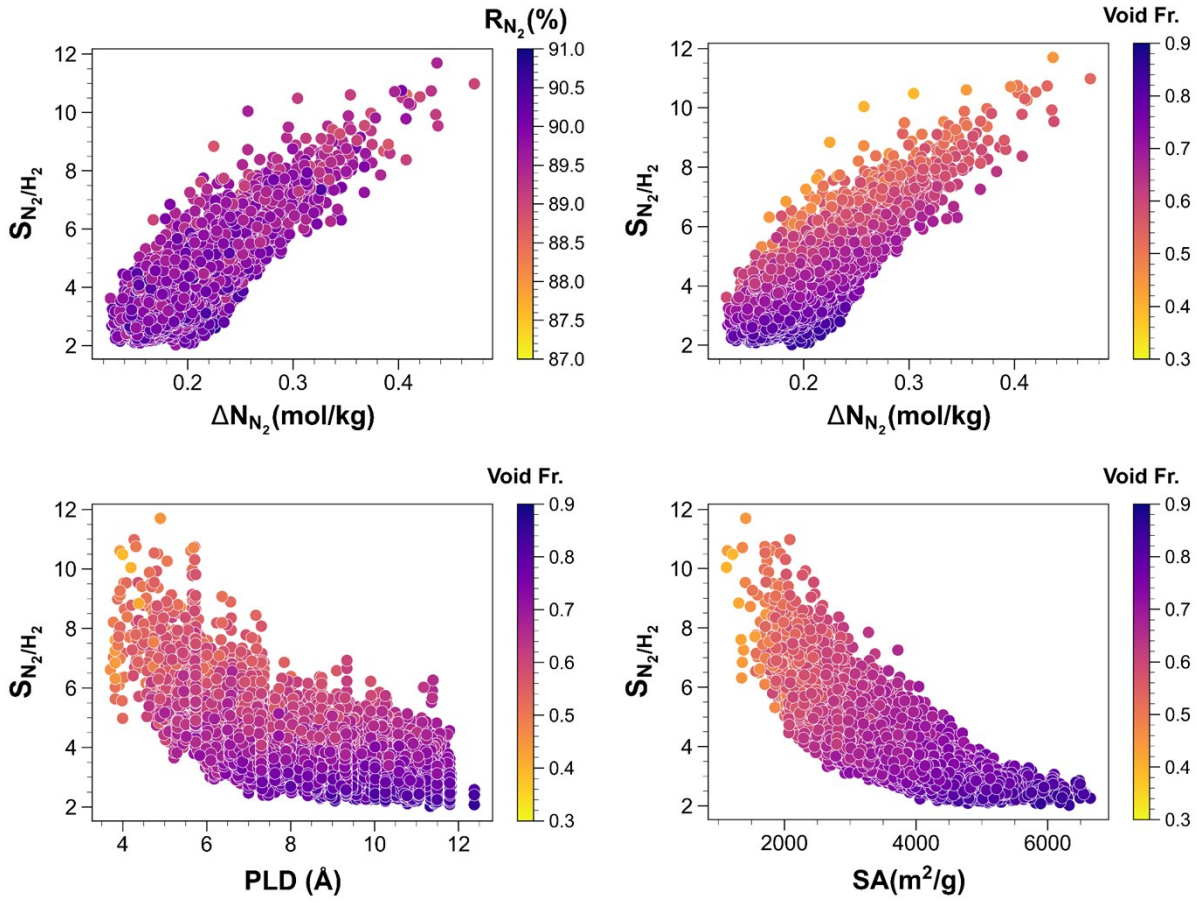


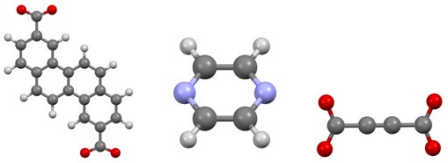
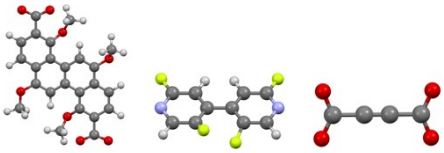
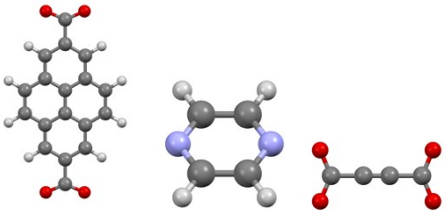
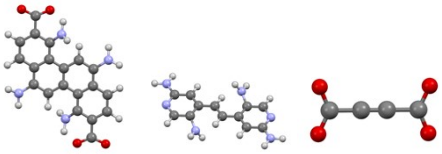
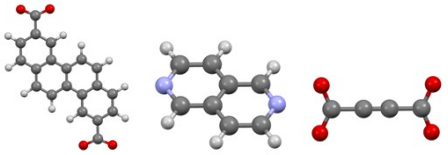
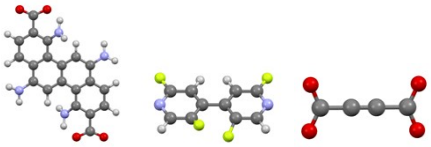
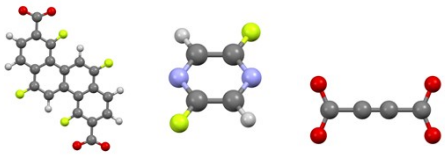
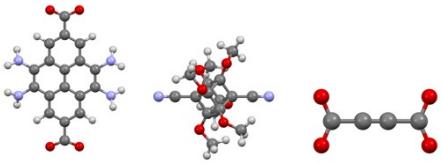
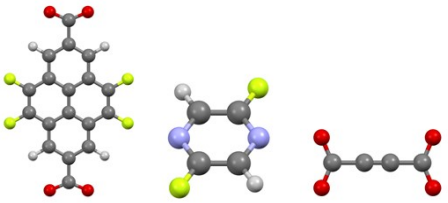
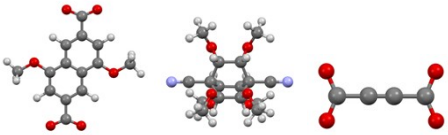
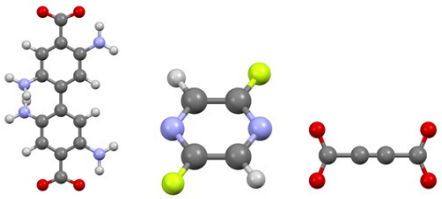
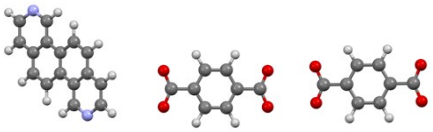
Figure S4. N_2/H_2 separation performance metrics and structural properties of MTV MOFs.

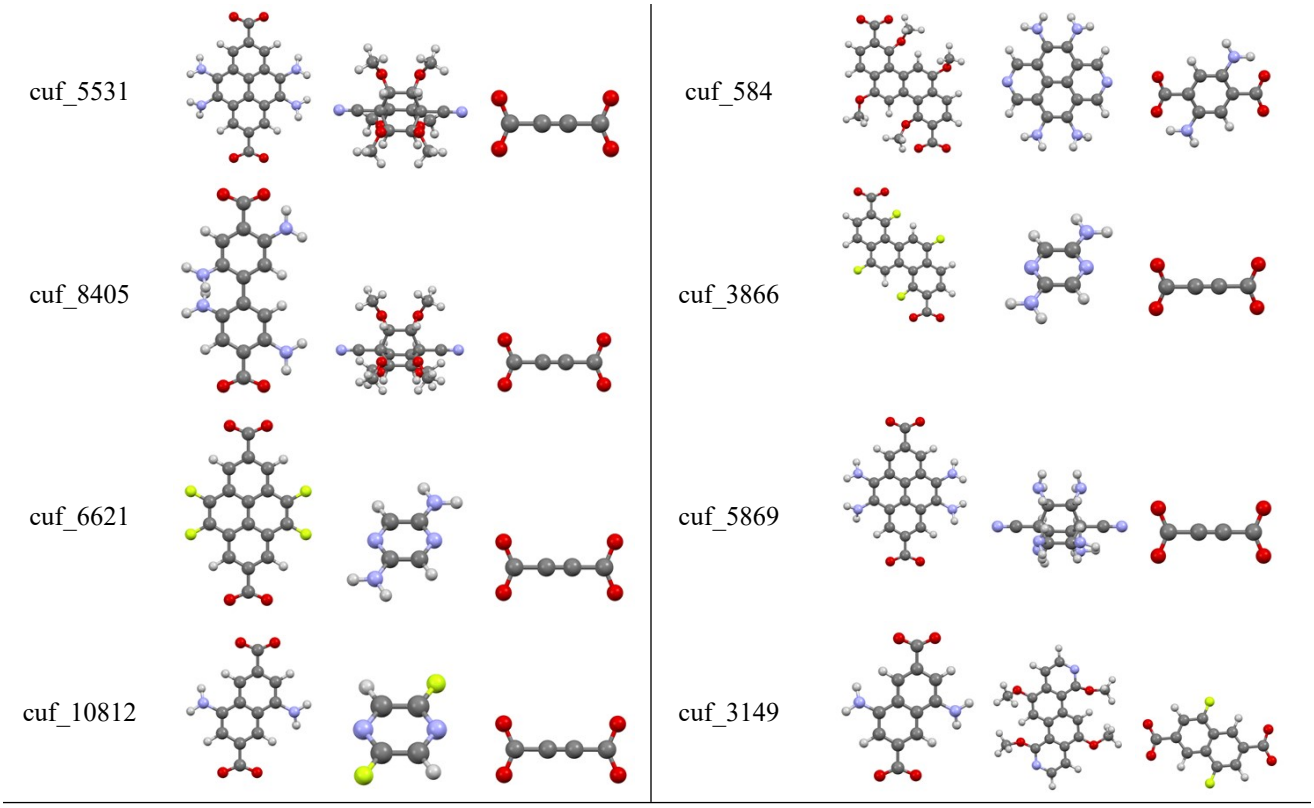
Table S6. 20 best performing MOF adsorbents for the N_2/H_2 separation.

Structure	Functional Group	$S_{ads,N_2/H_2}$	ΔN_{N_2} (mol/kg)	R_{N_2} (%)	GCD (Å)	PLD (Å)	LCD (Å)	SA (m^2/g)	Void Fr.	Pore Vol. (cm^3/g)	OSPS
cuf_110	OCH_3−OCH_3	11.0	0.5	89.0	6.16	4.27	6.16	2083.5	0.534	0.611	291.8
cuf_916	OCH_3−OCH_3	11.7	0.4	89.5	5.79	4.90	5.78	1413.7	0.449	0.484	290.9
cuf_824	NH_2−OCH_3	10.7	0.4	89.3	6.14	5.72	6.14	1868.0	0.536	0.567	281.3
cuf_7826	NH_2−NH_2	10.5	0.4	89.0	5.89	4.75	5.87	1708.8	0.529	0.564	277.0
cuf_3153	NH_2−OCH_3	10.7	0.4	90.0	6.38	4.31	6.38	1705.1	0.501	0.541	276.2
cuf_2160	NH_2−OCH_3	9.9	0.4	89.1	6.38	4.81	6.38	2321.2	0.559	0.679	275.1
cuf_2320	NH_2−OCH_3	10.6	0.4	88.6	6.59	5.62	6.59	1791.2	0.492	0.564	274.5
cuf_812	OCH_3−OCH_3	10.7	0.4	89.5	5.99	5.69	5.99	1363.3	0.474	0.485	273.9
cuf_2984	NH_2−OCH_3	10.5	0.4	89.2	6.19	4.83	6.14	1938.5	0.520	0.596	273.4
cuf_818	F−OCH_3	10.3	0.4	89.5	6.23	5.72	6.23	2018.3	0.550	0.578	273.4
cuf_1210	NH_2−OCH_3	10.3	0.4	89.4	5.89	5.06	5.89	1737.7	0.500	0.573	273.3
cuf_402	NH_2−OCH_3	9.5	0.4	89.2	6.16	4.37	6.16	2445.9	0.585	0.711	272.3
cuf_2878	NH_2−NH_2	9.8	0.4	89.7	6.15	5.66	6.15	2274.3	0.565	0.645	268.6
cuf_3143	OCH_3−OCH_3	10.6	0.4	89.1	5.44	3.94	5.43	1136.1	0.437	0.455	263.7
cuf_3866	F−NH_2	9.8	0.4	89.6	6.25	5.74	6.20	2030.1	0.573	0.574	262.5
cuf_2866	NH_2−OCH_3	10.0	0.4	88.9	5.99	5.66	5.99	1696.5	0.517	0.568	262.3
cuf_3164	F−NH_2−OCH_3	9.9	0.4	89.4	5.90	4.64	5.90	1761.1	0.515	0.536	257.5
cuf_3023	OCH_3−OCH_3	9.4	0.4	89.2	6.07	4.84	6.07	1955.3	0.507	0.579	257.5
cuf_7827	F−NH_2	9.5	0.4	88.9	5.89	4.75	5.87	1722.2	0.545	0.577	257.4
cuf_586	NH_2−OCH_3	8.9	0.4	88.8	6.50	5.72	6.50	2140.3	0.559	0.641	256.5

GCD = global cavity diameter, PLD = pore limiting diameter, LCD = largest cavity diameter, SA = surface area, Void Fr. = void fraction, Pore Vol. = pore volume, OSPS = overall separation performance score

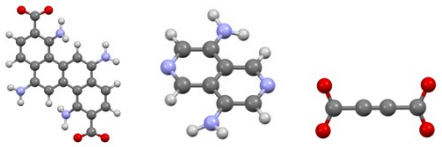
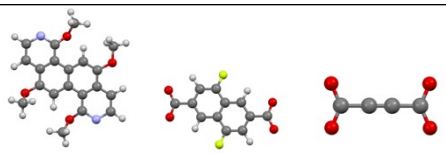
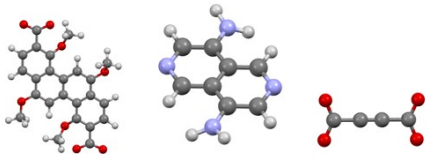
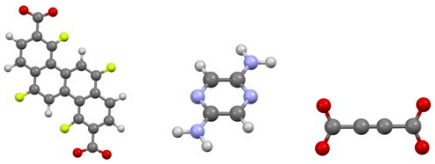
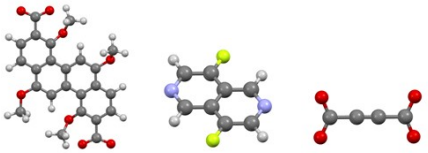
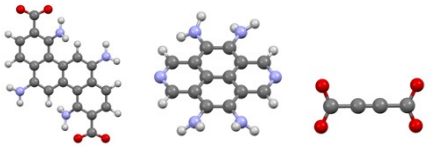
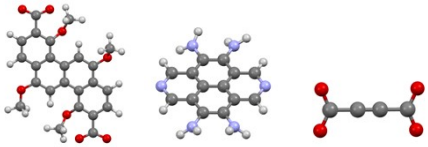
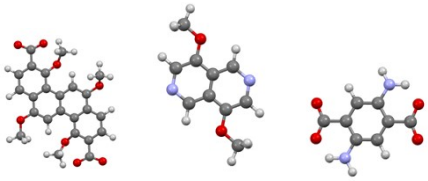
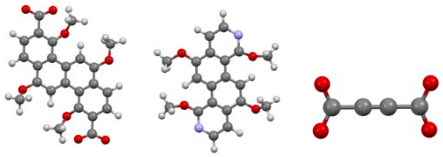
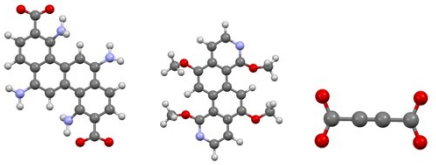
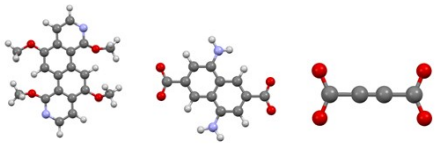
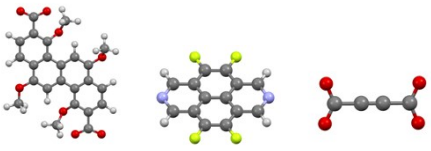
Table S7. Representations of the linkers in the top 20 MOFs for the CF_4/CH_4 separation.

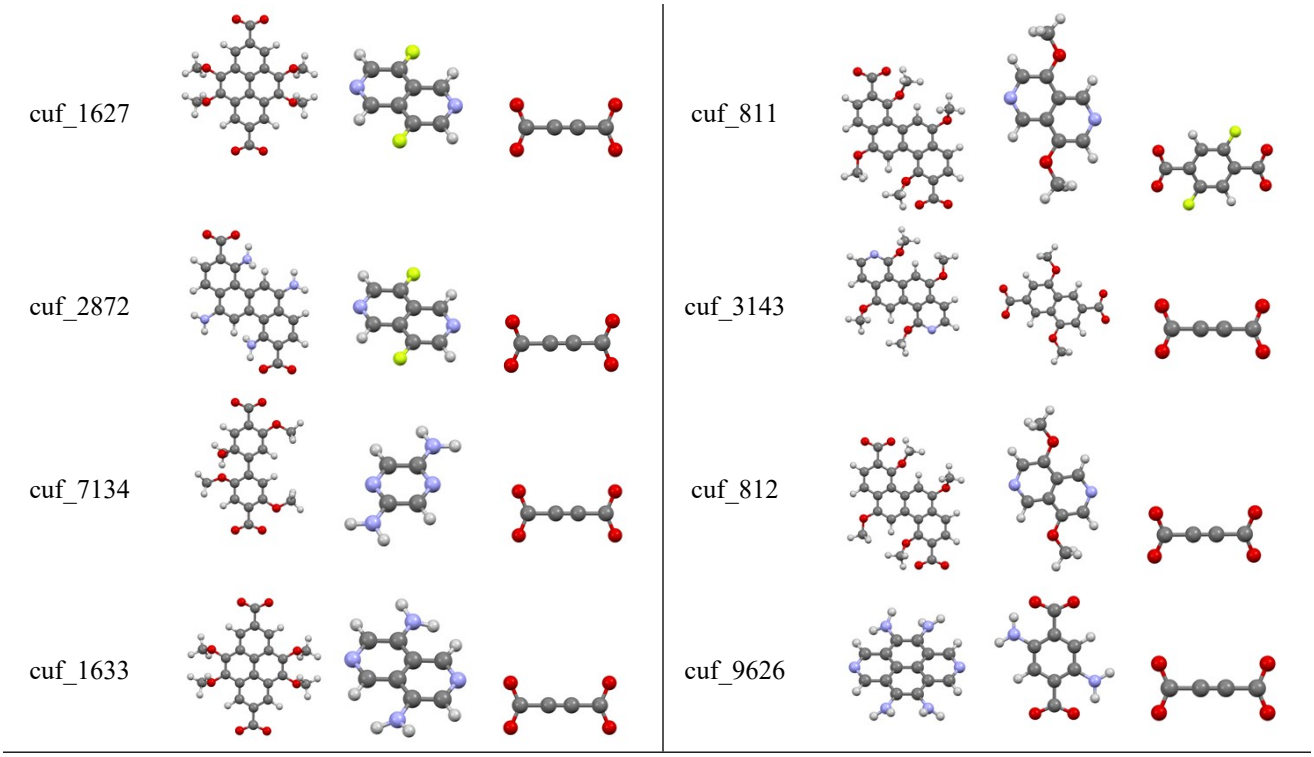
Structure	Representation	Structure	Representation
pMOF_10		cuf_800	
pMOF_26		cuf_2789	
pMOF_8		cuf_2854	
cuf_3865		cuf_5547	
cuf_6620		cuf_8442	
cuf_9854		pMOF_492	



Atom coloring is as follows: Gray: C, Red: O, White: H, Blue: N, Yellow: F.

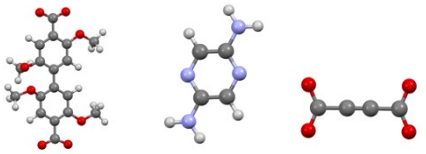
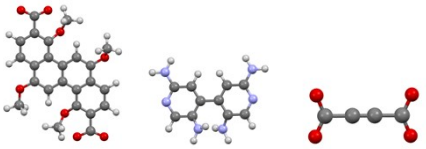
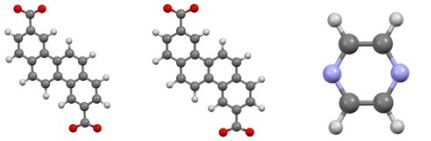
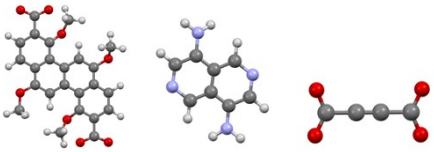
Table S8. Representations of the linkers in the top 20 MOFs for the CH_4/H_2 separation.

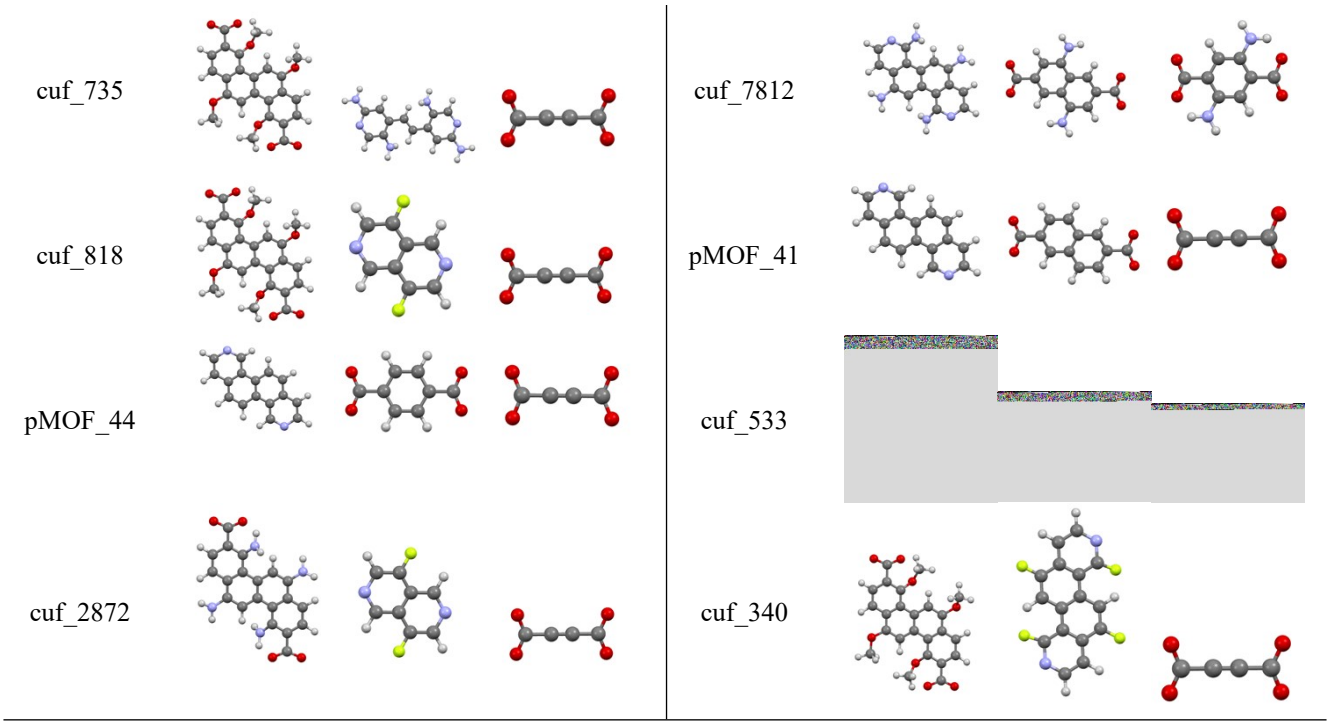
Structure	Representation	Structure	Representation
cuf_2878		cuf_3160	
cuf_824		cuf_3866	
cuf_818		cuf_2640	
cuf_586		cuf_810	
cuf_110		cuf_2160	
cuf_3153		cuf_533	



Atom coloring is as follows: Gray: C, Red: O, White: H, Blue: N, Yellow: F.

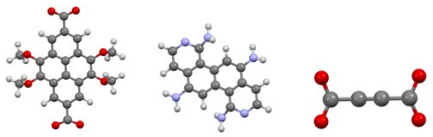
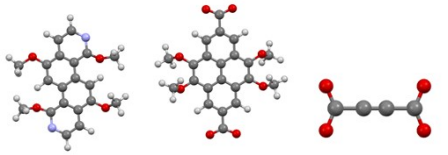
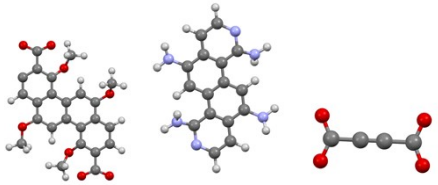
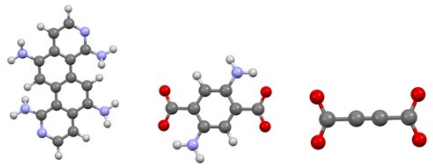
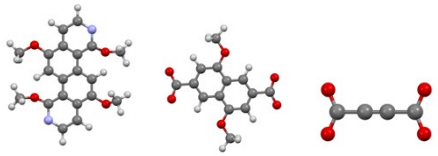
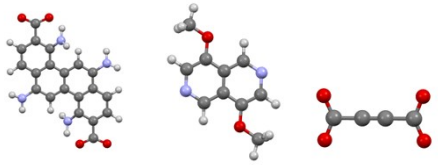
Table S9. Representations of the linkers in the top 20 MOFs for the CH_4/N_2 separation.

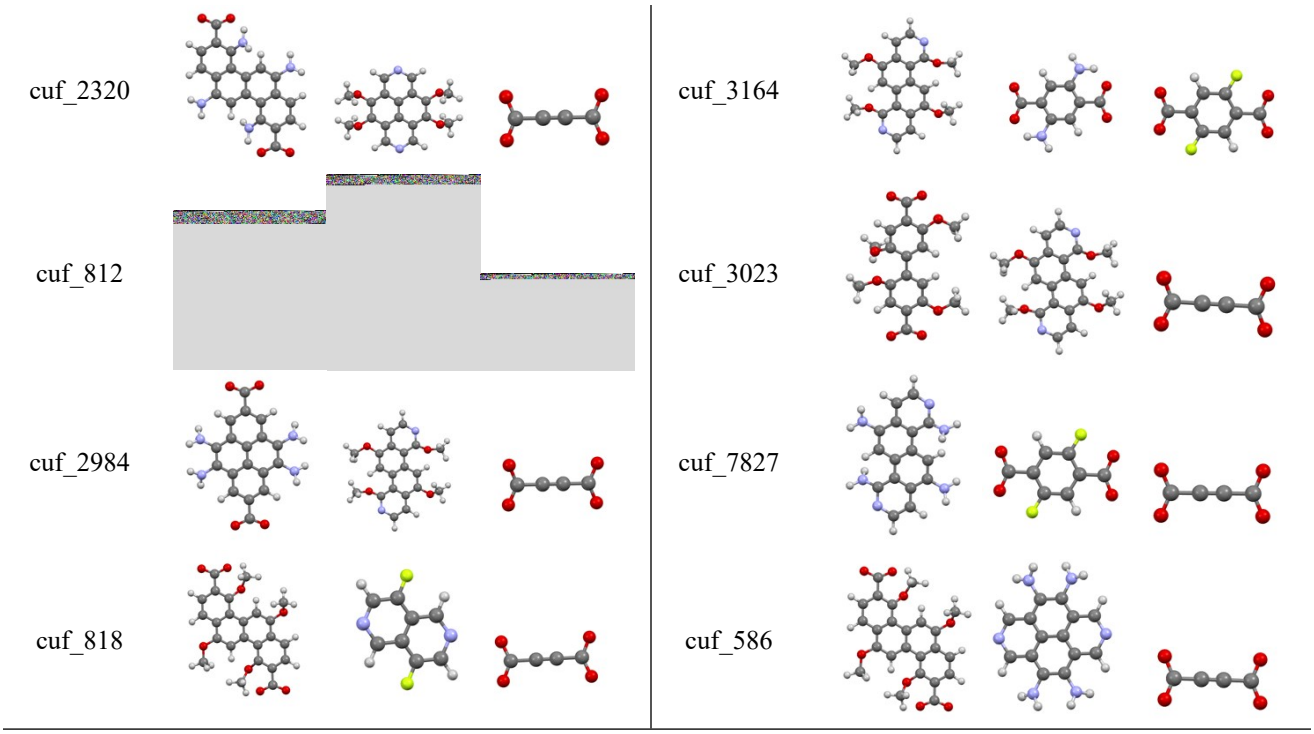
Structure	Representation	Structure	Representation
cuf_2878		cuf_7134	
cuf_1627		cuf_809	
cuf_586		pMOF_513	
cuf_810		cuf_824	
cuf_1633		cuf_110	
cuf_811		cuf_2640	



Atom coloring is as follows: Gray: C, Red: O, White: H, Blue: N, Yellow: F.

Table S10. Representations of the linkers in the top 20 MOFs for the N_2/H_2 separation.

Structure	Representation	Structure	Representation
cuf_110		cuf_1210	
cuf_916		cuf_402	
cuf_824		cuf_2878	
cuf_7826		cuf_3143	
cuf_3153		cuf_3866	
cuf_2160		cuf_2866	



Atom coloring is as follows: Gray: C, Red: O, White: H, Blue: N, Yellow: F.