

Electronic Supplementary Information (ESI)

Stability of *n*-alkanes and *n*-perfluoroalkanes against horizontal displacement on a graphite surface

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1. Comparison of E_{int} and ΔE_{int} values obtained by B3LYP-D3 and MP2 calculations

In order to verify the accuracy of the ΔE_{int} obtained by B3LYP-D3 calculation, the ΔE_{int} for $\text{C}_{54}\text{H}_{18}$ (circumcoronene) complexes with propane or perfluoropropane obtained by the B3LYP-D3 calculations were compared with those obtained by the MP2 calculations. The average distances of the carbon atoms of propane and perfluoropropane from the π plane of $\text{C}_{54}\text{H}_{18}$ in the optimised geometry were 3.50 and 4.08 Å, respectively. The interaction energies were calculated with moving propane and perfluoropropane horizontally along x - and y -axes while keeping the distance from the π plane of $\text{C}_{54}\text{H}_{18}$. The calculated E_{int} and ΔE_{int} values are listed in Tables S1–S4 and S5–S8, respectively. Figs. 1 and S1 show the plots of ΔE_{int} values (Tables S5–S8) associated with the horizontal displacement along x - and y -axes, respectively. The E_{int} obtained by the MP2 calculations show basis set dependence, and the E_{int} obtained by the B3LYP-D3 calculation are slightly more negative than those obtained by the MP2 calculations. However, the ΔE_{int} values obtained by the B3LYP-D3 calculations and those obtained by the MP2 calculations are close, suggesting that the ΔE_{int} obtained by the B3LYP-D3 calculations are sufficiently accurate to discuss the alkyl chain length dependence of ΔE_{int} and the effect of fluorination on ΔE_{int} .

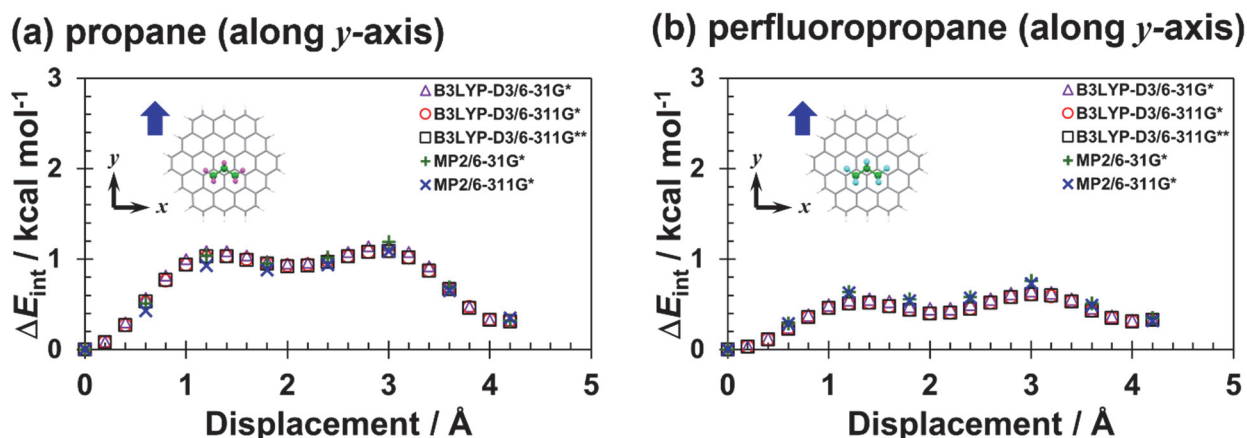


Fig. S1 Plots of ΔE_{int} for propane and perfluoropropane associated with horizontal displacements along y -axis obtained by B3LYP-D3 and MP2 calculations: (a) propane; (b) perfluoropropane. Purple triangles, red circles and black squares correspond to ΔE_{int} obtained by B3LYP-D3/6-31G*, B3LYP-D3/6-311G*, and B3LYP-D3/6-311G** calculations, respectively. Green plus and blue cross marks correspond to ΔE_{int} obtained by MP2/6-31G*, MP2/6-311G* calculations, respectively.

Table S1 E_{int} of propane calculated at each displacement on $\text{C}_{54}\text{H}_{18}$. $E_{\text{int}}(0)$ is the E_{int} when displacement is 0 Å (coloured in red). The symbol x indicates the horizontal displacement along x -axis.

Displacement (Å)	C_3H_8 ^a				
	x				
	B3LYP-D3 /6-31G*	B3LYP-D3 /6-311G*	B3LYP-D3 /6-311G**	MP2 /6-31G*	MP2 /6-311G*
0	-6.84	-7.05	-7.12	-4.29	-6.00
0.2	-6.77	-6.98	-7.05		
0.4	-6.58	-6.80	-6.87	-4.05	-5.77
0.6	-6.33	-6.55	-6.62		
0.8	-6.08	-6.31	-6.38	-3.55	-5.31
1.0	-5.89	-6.12	-6.20		
1.2	-5.80	-6.04	-6.11	-3.27	-5.05
1.4	-5.83	-6.07	-6.14		
1.6	-5.96	-6.20	-6.27	-3.44	-5.20
1.8	-6.16	-6.40	-6.47		
2.0	-6.38	-6.60	-6.67	-3.84	-5.56
2.2	-6.53	-6.75	-6.82		
2.4	-6.56	-6.78	-6.85	-4.02	-5.71

^a Energy in kcal mol⁻¹.

Table S2 E_{int} of perfluoropropane at each displacement on $\text{C}_{54}\text{H}_{18}$. $E_{\text{int}}(0)$ is the E_{int} when displacement is 0 Å (coloured in red). The symbol x indicates the horizontal displacement along x -axis.

Displacement (Å)	C_3F_8^a				
	x				
	B3LYP-D3 /6-31G*	B3LYP-D3 /6-311G*	B3LYP-D3 /6-311G**	MP2 /6-31G*	MP2 /6-311G*
0	-5.72	-5.64	-5.64	-4.08	-3.67
0.2	-5.68	-5.60	-5.60		
0.4	-5.59	-5.52	-5.52	-3.93	-3.52
0.6	-5.46	-5.41	-5.40		
0.8	-5.33	-5.28	-5.28	-3.63	-3.23
1.0	-5.22	-5.18	-5.18		
1.2	-5.16	-5.12	-5.12	-3.44	-3.04
1.4	-5.16	-5.12	-5.12		
1.6	-5.21	-5.16	-5.16	-3.50	-3.11
1.8	-5.29	-5.23	-5.23		
2.0	-5.37	-5.29	-5.29	-3.70	-3.30
2.2	-5.40	-5.32	-5.32		
2.4	-5.38	-5.30	-5.30	-3.74	-3.34

^a Energy in kcal mol⁻¹.

Table S3 E_{int} of propane at each displacement on $\text{C}_{54}\text{H}_{18}$. $E_{\text{int}}(0)$ is the E_{int} when displacement is 0 Å (coloured in red). The symbol y indicates the horizontal displacement along y -axis.

Displacement (Å)	C_3H_8 ^a				
	y				
	B3LYP-D3 /6-31G*	B3LYP-D3 /6-311G*	B3LYP-D3 /6-311G**	MP2 /6-31G*	MP2 /6-311G*
0	-6.84	-7.05	-7.12	-4.29	-6.00
0.2	-6.75	-6.97	-7.04		
0.4	-6.54	-6.78	-6.85		
0.6	-6.27	-6.53	-6.59	-3.78	-5.57
0.8	-6.02	-6.29	-6.35		
1.0	-5.84	-6.11	-6.18		
1.2	-5.75	-6.03	-6.09	-3.25	-5.07
1.4	-5.75	-6.02	-6.09		
1.6	-5.80	-6.05	-6.13		
1.8	-5.86	-6.10	-6.17	-3.34	-5.12
2.0	-5.89	-6.12	-6.20		
2.2	-5.88	-6.11	-6.19		
2.4	-5.83	-6.07	-6.15	-3.27	-5.06
2.6	-5.76	-6.02	-6.09		
2.8	-5.70	-5.97	-6.04		
3.0	-5.69	-5.96	-6.03	-3.10	-4.91
3.2	-5.76	-6.03	-6.10		
3.4	-5.92	-6.18	-6.25		
3.6	-6.14	-6.38	-6.45	-3.60	-5.35
3.8	-6.36	-6.58	-6.66		
4.0	-6.51	-6.72	-6.79		
4.2	-6.52	-6.73	-6.81	-3.97	-5.65

^a Energy in kcal mol⁻¹.

Table S4 E_{int} of perfluoropropane at each displacement on $\text{C}_{54}\text{H}_{18}$. $E_{\text{int}}(0)$ is the E_{int} when displacement is 0 Å (coloured in red). The symbol y indicates the horizontal displacement along y -axis.

Displacement (Å)	C_3F_8 ^a				
	y				
	B3LYP-D3 /6-31G*	B3LYP-D3 /6-311G*	B3LYP-D3 /6-311G**	MP2 /6-31G*	MP2 /6-311G*
0	-5.72	-5.64	-5.64	-4.08	-3.67
0.2	-5.69	-5.61	-5.61		
0.4	-5.60	-5.53	-5.53		
0.6	-5.47	-5.41	-5.41	-3.79	-3.38
0.8	-5.34	-5.28	-5.28		
1.0	-5.23	-5.18	-5.18		
1.2	-5.17	-5.13	-5.13	-3.44	-3.04
1.4	-5.16	-5.12	-5.12		
1.6	-5.19	-5.16	-5.16		
1.8	-5.24	-5.20	-5.20	-3.52	-3.13
2.0	-5.27	-5.24	-5.24		
2.2	-5.27	-5.23	-5.23		
2.4	-5.22	-5.19	-5.19	-3.50	-3.10
2.6	-5.16	-5.12	-5.12		
2.8	-5.10	-5.06	-5.06		
3.0	-5.07	-5.03	-5.03	-3.32	-2.94
3.2	-5.09	-5.05	-5.04		
3.4	-5.16	-5.11	-5.11		
3.6	-5.26	-5.21	-5.21	-3.57	-3.18
3.8	-5.35	-5.29	-5.29		
4.0	-5.40	-5.33	-5.33		
4.2	-5.38	-5.31	-5.31	-3.73	-3.35

^a Energy in kcal mol⁻¹.

Table S5 ΔE_{int} values of propane at each displacement on $\text{C}_{54}\text{H}_{18}$. The plots of ΔE_{int} as a function of displacement are shown in Fig. 1(a). The symbol x indicates the horizontal displacement along x -axis.

Displacement (Å)	C_3H_8^a				
	x				
	B3LYP-D3 /6-31G*	B3LYP-D3 /6-311G*	B3LYP-D3 /6-311G**	MP2 /6-31G*	MP2 /6-311G*
0	0	0	0	0	0
0.2	0.07	0.07	0.07		
0.4	0.26	0.25	0.25	0.24	0.23
0.6	0.51	0.50	0.50		
0.8	0.76	0.74	0.74	0.74	0.69
1.0	0.95	0.93	0.92		
1.2	1.04	1.01	1.01	1.02	0.95
1.4	1.01	0.98	0.98		
1.6	0.88	0.85	0.85	0.85	0.80
1.8	0.68	0.65	0.65		
2.0	0.46	0.45	0.45	0.45	0.44
2.2	0.31	0.30	0.30		
2.4	0.28	0.27	0.27	0.27	0.29

^a Energy in kcal mol⁻¹.

Table S6 ΔE_{int} values of perfluoropropane at each displacement on $\text{C}_{54}\text{H}_{18}$. The plots of ΔE_{int} as a function of displacement are shown in Fig. 1(b). The symbol x indicates the horizontal displacement along x -axis.

Displacement (Å)	C_3F_8^a				
	x				
	B3LYP-D3 /6-31G*	B3LYP-D3 /6-311G*	B3LYP-D3 /6-311G**	MP2 /6-31G*	MP2 /6-311G*
0	0	0	0	0	0
0.2	0.04	0.04	0.04		
0.4	0.13	0.12	0.12	0.15	0.15
0.6	0.26	0.23	0.24		
0.8	0.39	0.36	0.36	0.45	0.44
1.0	0.50	0.46	0.46		
1.2	0.56	0.52	0.52	0.64	0.63
1.4	0.56	0.52	0.52		
1.6	0.51	0.48	0.48	0.58	0.56
1.8	0.43	0.41	0.41		
2.0	0.35	0.35	0.35	0.38	0.37
2.2	0.32	0.32	0.32		
2.4	0.34	0.34	0.34	0.34	0.33

^a Energy in kcal mol⁻¹.

Table S7 ΔE_{int} values of propane at each displacement on $\text{C}_{54}\text{H}_{18}$. The plots of ΔE_{int} as a function of displacement are shown in Fig. S1(a). The symbol y indicates the horizontal displacement along y -axis.

Displacement (Å)	C_3H_8^a				
	y				
	B3LYP-D3 /6-31G*	B3LYP-D3 /6-311G*	B3LYP-D3 /6-311G**	MP2 /6-31G*	MP2 /6-311G*
0	0	0	0	0	0
0.2	0.09	0.08	0.08		
0.4	0.30	0.27	0.27		
0.6	0.57	0.52	0.53	0.51	0.43
0.8	0.82	0.76	0.77		
1.0	1.00	0.94	0.94		
1.2	1.09	1.02	1.03	1.04	0.93
1.4	1.09	1.03	1.03		
1.6	1.04	1.00	0.99		
1.8	0.98	0.95	0.95	0.95	0.88
2.0	0.95	0.93	0.92		
2.2	0.96	0.94	0.93		
2.4	1.01	0.98	0.97	1.02	0.94
2.6	1.08	1.03	1.03		
2.8	1.14	1.08	1.08		
3.0	1.15	1.09	1.09	1.19	1.09
3.2	1.08	1.02	1.02		
3.4	0.92	0.87	0.87		
3.6	0.70	0.67	0.67	0.69	0.65
3.8	0.48	0.47	0.46		
4.0	0.33	0.33	0.33		
4.2	0.32	0.32	0.31	0.32	0.35

^a Energy in kcal mol⁻¹.

Table S8 ΔE_{int} values of perfluoropropane at each displacement on $\text{C}_{54}\text{H}_{18}$. The plots of ΔE_{int} as a function of displacement are shown in Fig. S1(b). The symbol y indicates the horizontal displacement along y -axis.

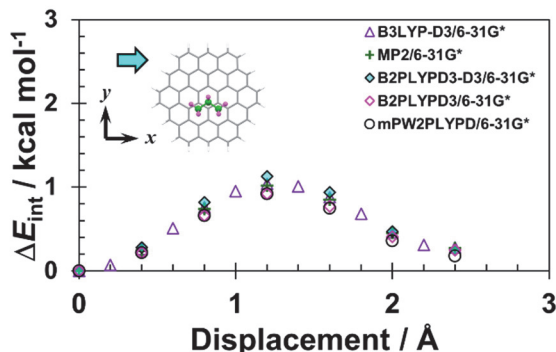
Displacement (Å)	$\text{C}_3\text{F}_8^{\text{a}}$				
	y				
	B3LYP-D3 /6-31G*	B3LYP-D3 /6-311G*	B3LYP-D3 /6-311G**	MP2 /6-31G*	MP2 /6-311G*
0	0	0	0	0	0
0.2	0.03	0.03	0.03		
0.4	0.12	0.11	0.11		
0.6	0.25	0.23	0.23	0.29	0.29
0.8	0.38	0.36	0.36		
1.0	0.49	0.46	0.46		
1.2	0.55	0.51	0.51	0.64	0.63
1.4	0.56	0.52	0.52		
1.6	0.53	0.48	0.48		
1.8	0.48	0.44	0.44	0.56	0.54
2.0	0.45	0.40	0.40		
2.2	0.45	0.41	0.41		
2.4	0.50	0.45	0.45	0.58	0.57
2.6	0.56	0.52	0.52		
2.8	0.62	0.58	0.58		
3.0	0.65	0.61	0.61	0.76	0.73
3.2	0.63	0.59	0.60		
3.4	0.56	0.53	0.53		
3.6	0.46	0.43	0.43	0.51	0.49
3.8	0.37	0.35	0.35		
4.0	0.32	0.31	0.31		
4.2	0.34	0.33	0.33	0.35	0.32

^a Energy in kcal mol⁻¹.

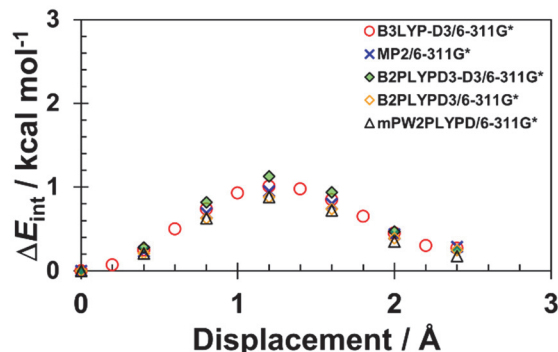
2. Comparison of E_{int} and ΔE_{int} values obtained by B3LYP-D3, dispersion-corrected double hybrid DFT (B2PLYP, mPW2PLYP) and MP2 calculations

In order to further verify the accuracy of the ΔE_{int} obtained by B3LYP-D3 calculation, the ΔE_{int} for $\text{C}_{54}\text{H}_{18}$ (circumcoronene) complexes with propane or perfluoropropane obtained by the B3LYP-D3 calculations were compared with those obtained by the dispersion-corrected double hybrid DFT and MP2 calculations. The calculated E_{int} and ΔE_{int} values are listed in Tables S9–S12 and S13–S16, respectively. The ΔE_{int} values are plotted as a function of displacement. As shown in Figs. S2 and S3, all the calculated ΔE_{int} values by the B3LYP-D3 were close to those obtained by the MP2 and dispersion-corrected double hybrid DFT calculations even with different basis sets. This result suggests that the choice of calculation method has little effect on the calculated ΔE_{int} , and that the present B3LYP-D3 calculation is sufficiently reliable to discuss the effects of alkyl chain length and fluorination on ΔE_{int} .

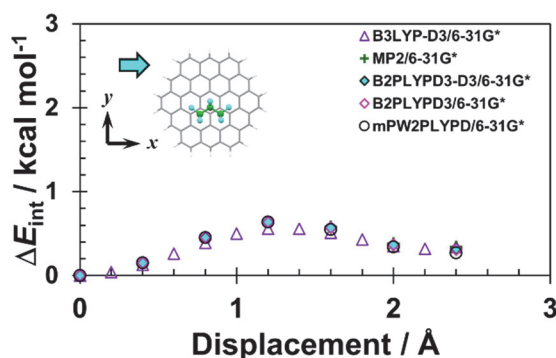
(a) 6-31G*_propane (x)



(b) 6-311G*_propane (x)



(c) 6-31G*_perfluoropropane (x)



(d) 6-311G*_perfluoropropane (x)

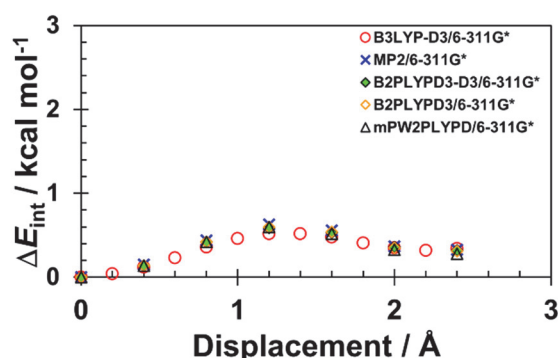


Fig. S2 Plots of ΔE_{int} for propane and perfluoropropane associated with horizontal displacements along x -axis obtained by B3LYP-D3, dispersion-corrected double hybrid DFT and MP2 calculations with different basis sets: (a) ΔE_{int} for propane obtained using 6-31G* basis set; (b) ΔE_{int} for propane using 6-311G* basis set; (c) ΔE_{int} for perfluoropropane using 6-31G* basis set; (d) ΔE_{int} for perfluoropropane using 6-311G* basis set. In (a) and (c), purple triangles, green plus marks, cyan rhombi, pink rhombi, and black circles correspond to ΔE_{int} obtained by B3LYP-D3/6-31G*, MP2/6-31G*, B2PLYPD3-D3/6-31G*, B2PLYPD3/6-31G*, mPW2PLYPD/6-31G* calculations, respectively. In (b) and (d), red circles, blue cross marks, light green rhombi, orange rhombi, black triangles correspond to ΔE_{int} obtained by B3LYP-D3/6-311G*, MP2/6-311G*, B2PLYPD3-D3/6-311G*, B2PLYPD3/6-311G*, mPW2PLYPD/6-311G* calculations, respectively. B2PLYPD3-D3 is B2PLYP calculation with D3 correction. B2PLYPD3 is B2PLYP calculation with D3BJ correction.

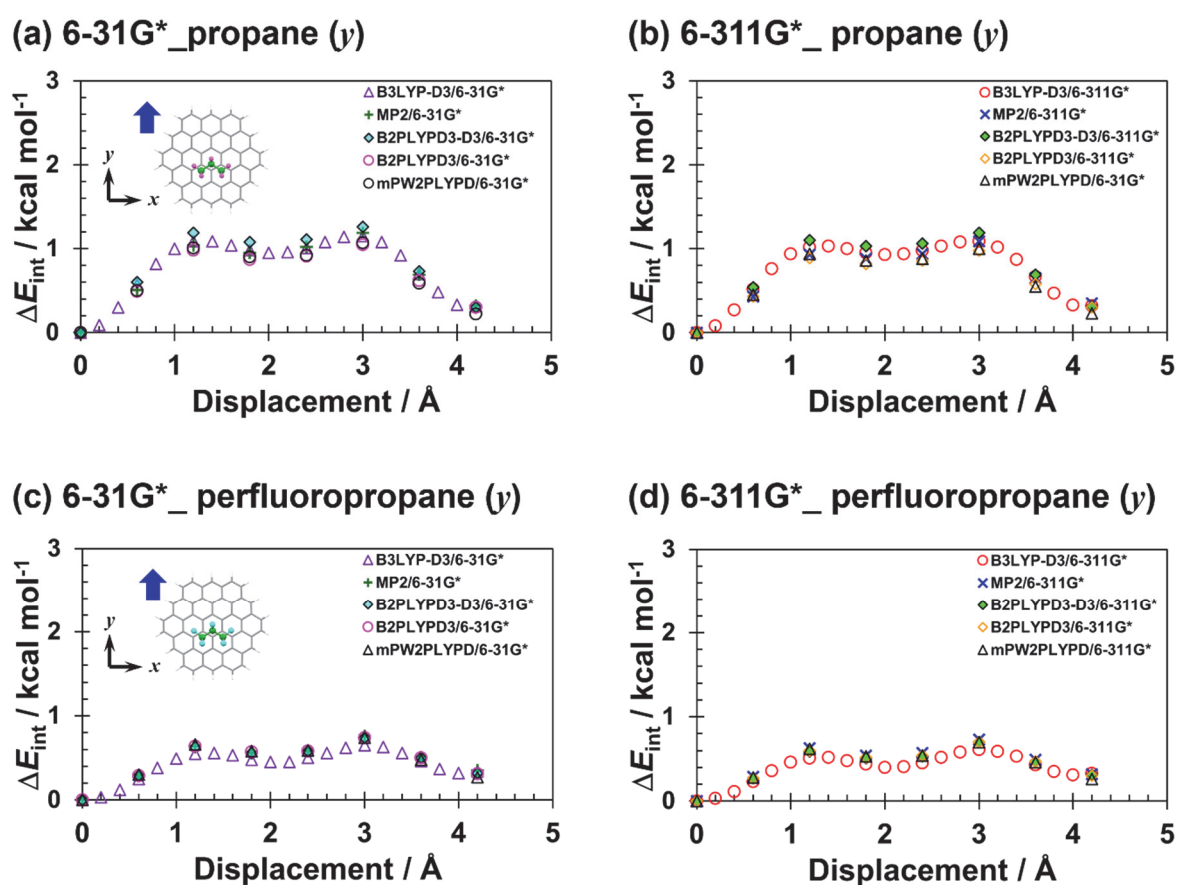


Fig. S3 Plots of ΔE_{int} for propane and perfluoropropane associated with horizontal displacements along y -axis obtained by B3LYP-D3, dispersion-corrected double hybrid DFT and MP2 calculations with different basis sets: (a) ΔE_{int} for propane obtained using 6-31G* basis set; (b) ΔE_{int} for propane using 6-311G* basis set; (c) ΔE_{int} for perfluoropropane using 6-31G* basis set; (d) ΔE_{int} for perfluoropropane using 6-311G* basis set. In (a) and (c), purple triangles, green plus marks, cyan rhombi, pink circles,

and black circles correspond to ΔE_{int} obtained by B3LYP-D3/6-31G*, MP2/6-31G*, B2PLYPD3-D3/6-31G*, B2PLYPD3/6-31G*, mPW2PLYPD/6-31G* calculations, respectively. In (b) and (d), red circles, blue cross marks, light green rhombi, orange rhombi, black triangles correspond to ΔE_{int} obtained by B3LYP-D3/6-311G*, MP2/6-311G*, B2PLYPD3-D3/6-311G*, B2PLYPD3/6-311G*, mPW2PLYPD/6-311G* calculations, respectively. B2PLYPD3-D3 is B2PLYP calculation with D3 correction. B2PLYPD3 is B2PLYP calculation with D3BJ correction.

Table S9 E_{int} of propane at each displacement on C₅₄H₁₈. $E_{\text{int}}(0)$ is the E_{int} when displacement is 0 Å (coloured in red). The symbol x indicates the horizontal displacement along x -axis.

Displacement (Å)	C ₃ H ₈ ^a					
	x					
	B2PLYPD3- D3/6-31G*	B2PLYPD3 /6-31G*	mPW2PLYPD/ 6-31G*	B2PLYPD3- D3/6-311G*	B2PLYPD3 /6-311G*	mPW2PLYPD/ 6-311G*
0	-5.06	-5.03	-4.68	-5.82	-5.79	-5.45
0.2						
0.4	-4.78	-4.81	-4.46	-5.56	-5.58	-5.24
0.6						
0.8	-4.24	-4.37	-4.02	-5.03	-5.16	-4.82
1.0						
1.2	-3.93	-4.11	-3.76	-4.73	-4.91	-4.57
1.4						
1.6	-4.12	-4.26	-3.93	-4.92	-5.05	-4.73
1.8						
2.0	-4.59	-4.62	-4.32	-5.37	-5.40	-5.1
2.2						
2.4	-4.81	-4.78	-4.50	-5.57	-5.54	-5.27

^a Energy in kcal mol⁻¹.

Table S10 E_{int} of fluoropropane at each displacement on C_5H_{18} . $E_{\text{int}}(0)$ is the E_{int} when displacement is 0 Å (coloured in red). The symbol x indicates the horizontal displacement along x -axis.

Displacement (Å)	C_3F_8 ^a					
	x					
	B2PLYPD3- D3/6-31G*	B2PLYPD3 /6-31G*	mPW2PLYPD/ 6-31G*	B2PLYPD3- D3/6-311G*	B2PLYPD3 /6-311G*	mPW2PLYPD/ 6-311G*
0	-4.57	-4.47	-5.29	-4.46	-4.36	-5.25
0.2						
0.4	-4.42	-4.32	-5.14	-4.32	-4.22	-5.11
0.6						
0.8	-4.12	-4.01	-4.84	-4.04	-3.94	-4.83
1.0						
1.2	-3.93	-3.83	-4.65	-3.87	-3.76	-4.65
1.4						
1.6	-4.00	-3.90	-4.74	-3.93	-3.82	-4.73
1.8						
2.0	-4.2	-4.10	-4.95	-4.10	-4.01	-4.92
2.2						
2.4	-4.25	-4.16	-5.02	-4.14	-4.05	-4.97

^a Energy in kcal mol⁻¹.

Table S11 E_{int} of propane at each displacement on C_5H_{18} . $E_{\text{int}}(0)$ is the E_{int} when displacement is 0 Å (coloured in red). The symbol y indicates the horizontal displacement along y -axis.

Displacement (Å)	C_3H_8 ^a					
	y					
	B2PLYPD3- D3/6-31G*	B2PLYPD3 /6-31G*	mPW2PLYPD/ 6-31G*	B2PLYPD3- D3/6-311G*	B2PLYPD3 /6-311G*	mPW2PLYPD/ 6-311G*
0	-5.06	-5.03	-4.68	-5.82	-5.79	-5.45
0.2						
0.4						
0.6	-4.46	-4.54	-4.18	-5.28	-5.36	-5.00
0.8						
1.0						
1.2	-3.87	-4.05	-3.67	-4.72	-4.9	-4.51
1.4						
1.6						
1.8	-3.98	-4.16	-3.78	-4.79	-4.97	-4.59
2.0						
2.2						
2.4	-3.95	-4.12	-3.76	-4.76	-4.93	-4.57
2.6						
2.8						
3.0	-3.80	-3.98	-3.61	-4.63	-4.81	-4.45
3.2						
3.4						
3.6	-4.33	-4.41	-4.09	-5.13	-5.21	-4.90
3.8						
4.0						
4.2	-4.76	-4.73	-4.46	-5.51	-5.49	-5.22

^a Energy in kcal mol⁻¹.

Table S12 E_{int} of propane at each displacement on $\text{C}_{54}\text{F}_{18}$. $E_{\text{int}}(0)$ is the E_{int} when displacement is 0 Å (coloured in red). The symbol y indicates the horizontal displacement along y -axis.

Displacement (Å)	C_3F_8 ^a					
	y					
	B2PLYPD3- D3/6-31G*	B2PLYPD3 /6-31G*	mPW2PLYPD/ 6-31G*	B2PLYPD3- D3/6-311G*	B2PLYPD3 /6-311G*	mPW2PLYPD/ 6-311G*
0	-4.57	-4.47	-5.29	-4.46	-4.36	-5.25
0.2						
0.4						
0.6	-4.28	-4.18	-4.99	-4.19	-4.09	-4.97
0.8						
1.0						
1.2	-3.94	-3.83	-4.63	-3.87	-3.76	-4.63
1.4						
1.6						
1.8	-4.01	-3.9	-4.71	-3.95	-3.84	-4.72
2.0						
2.2						
2.4	-3.99	-3.89	-4.70	-3.93	-3.82	-4.71
2.6						
2.8						
3.0	-3.83	-3.73	-4.55	-3.76	-3.66	-4.55
3.2						
3.4						
3.6	-4.07	-3.97	-4.81	-3.99	-3.89	-4.79
3.8						
4.0						
4.2	-4.25	-4.16	-5.02	-4.15	-4.06	-4.99

^a Energy in kcal mol⁻¹.

Table S13 ΔE_{int} values of propane at each displacement on $\text{C}_{54}\text{H}_{18}$. The plots of ΔE_{int} as a function of displacement are shown in Fig. 2(a, b). The symbol x indicates the horizontal displacement along x -axis.

Displacement (Å)	C_3H_8 ^a					
	x					
	B2PLYPD3- D3/6-31G*	B2PLYPD3 /6-31G*	mPW2PLYPD/ 6-31G*	B2PLYPD3- D3/6-311G*	B2PLYPD3 /6-311G*	mPW2PLYPD/ 6-311G*
0	0	0	0	0	0	0
0.2						
0.4	0.28	0.22	0.22	0.26	0.21	0.21
0.6						
0.8	0.82	0.66	0.66	0.79	0.63	0.63
1.0						
1.2	1.13	0.92	0.92	1.09	0.88	0.88
1.4						
1.6	0.94	0.77	0.75	0.90	0.74	0.72
1.8						
2.0	0.47	0.41	0.36	0.45	0.39	0.35
2.2						
2.4	0.25	0.25	0.18	0.25	0.25	0.18

^a Energy in kcal mol^{-1} .

Table S14 ΔE_{int} values of perfluoropropane at each displacement on $\text{C}_{54}\text{H}_{18}$. The plots of ΔE_{int} as a function of displacement are shown in Fig. 2(c, d). The symbol x indicates the horizontal displacement along x -axis.

Displacement (Å)	C_3F_8 ^a					
	x					
	B2PLYPD3- D3/6-31G*	B2PLYPD3 /6-31G*	mPW2PLYPD/ 6-31G*	B2PLYPD3- D3/6-311G*	B2PLYPD3 /6-311G*	mPW2PLYPD/ 6-311G*
0	0	0	0	0	0	0
0.2						
0.4	0.15	0.15	0.15	0.14	0.14	0.14
0.6						
0.8	0.45	0.46	0.45	0.42	0.42	0.42
1.0						
1.2	0.64	0.64	0.64	0.59	0.6	0.6
1.4						
1.6	0.57	0.57	0.55	0.53	0.54	0.52
1.8						
2.0	0.37	0.37	0.34	0.36	0.35	0.33
2.2						
2.4	0.32	0.31	0.27	0.32	0.31	0.28

^a Energy in kcal mol^{-1} .

Table S15 ΔE_{int} values of propane at each displacement on $\text{C}_{54}\text{H}_{18}$. The plots of ΔE_{int} as a function of displacement are shown in Fig. S3(a, b). The symbol y indicates the horizontal displacement along y -axis.

Displacement (Å)	C_3H_8 ^a					
	y					
	B2PLYPD3- D3/6-31G*	B2PLYPD3 /6-31G*	mPW2PLYPD/ 6-31G*	B2PLYPD3- D3/6-311G*	B2PLYPD3 /6-311G*	mPW2PLYPD/ 6-311G*
0	0	0	0	0	0	0
0.2						
0.4						
0.6	0.6	0.49	0.50	0.54	0.43	0.45
0.8						
1.0						
1.2	1.19	0.98	1.01	1.10	0.89	0.94
1.4						
1.6						
1.8	1.08	0.87	0.9	1.03	0.82	0.86
2.0						
2.2						
2.4	1.11	0.91	0.92	1.06	0.86	0.88
2.6						
2.8						
3.0	1.26	1.05	1.07	1.19	0.98	1.00
3.2						
3.4						
3.6	0.73	0.62	0.59	0.69	0.58	0.55
3.8						
4.0						
4.2	0.30	0.30	0.22	0.31	0.30	0.23

^a Energy in kcal mol⁻¹.

Table S16 ΔE_{int} values of perfluoropropane at each displacement on $\text{C}_{54}\text{H}_{18}$. The plots of ΔE_{int} as a function of displacement are shown in Fig. S3(c, d). The symbol y indicates the horizontal displacement along y -axis.

Displacement (Å)	C_3F_8 ^a					
	y					
	B2PLYPD3- D3/6-31G*	B2PLYPD3 /6-31G*	mPW2PLYPD/ 6-31G*	B2PLYPD3- D3/6-311G*	B2PLYPD3 /6-311G*	mPW2PLYPD/ 6-311G*
0	0	0	0	0	0	0
0.2						
0.4						
0.6	0.29	0.29	0.30	0.27	0.27	0.28
0.8						
1.0						
1.2	0.63	0.64	0.66	0.59	0.60	0.62
1.4						
1.6						
1.8	0.56	0.57	0.58	0.51	0.52	0.53
2.0						
2.2						
2.4	0.58	0.58	0.59	0.53	0.54	0.54
2.6						
2.8						
3.0	0.74	0.74	0.74	0.70	0.70	0.70
3.2						
3.4						
3.6	0.50	0.50	0.48	0.47	0.47	0.46
3.8						
4.0						
4.2	0.32	0.31	0.27	0.31	0.30	0.26

^a Energy in kcal mol⁻¹.

3. Comparison of E_{int} and ΔE_{int} values obtained by B3LYP-D3, PBE0-D3 and BLYP-D3

To examine the effect of DFT functional on E_{int} and ΔE_{int} values, the energy values obtained by B3LYP-D3, PBE0-D3 and BLYP-D3 were compared for $\text{C}_{54}\text{H}_{18}$ -propane and $\text{C}_{54}\text{H}_{18}$ -fluoropropane complexes. The calculated E_{int} and ΔE_{int} values obtained using the PBE0 and BLYP functionals are listed in Tables S17 and 18, and the ΔE_{int} plots as a function of displacement are shown in Fig. S4. The calculated ΔE_{int} values obtained by the PBE0-D3 and BLYP-D3 are close to those obtained by the B3LYP-D3, suggesting that choice of DFT functional also has little effect on the calculated ΔE_{int} .

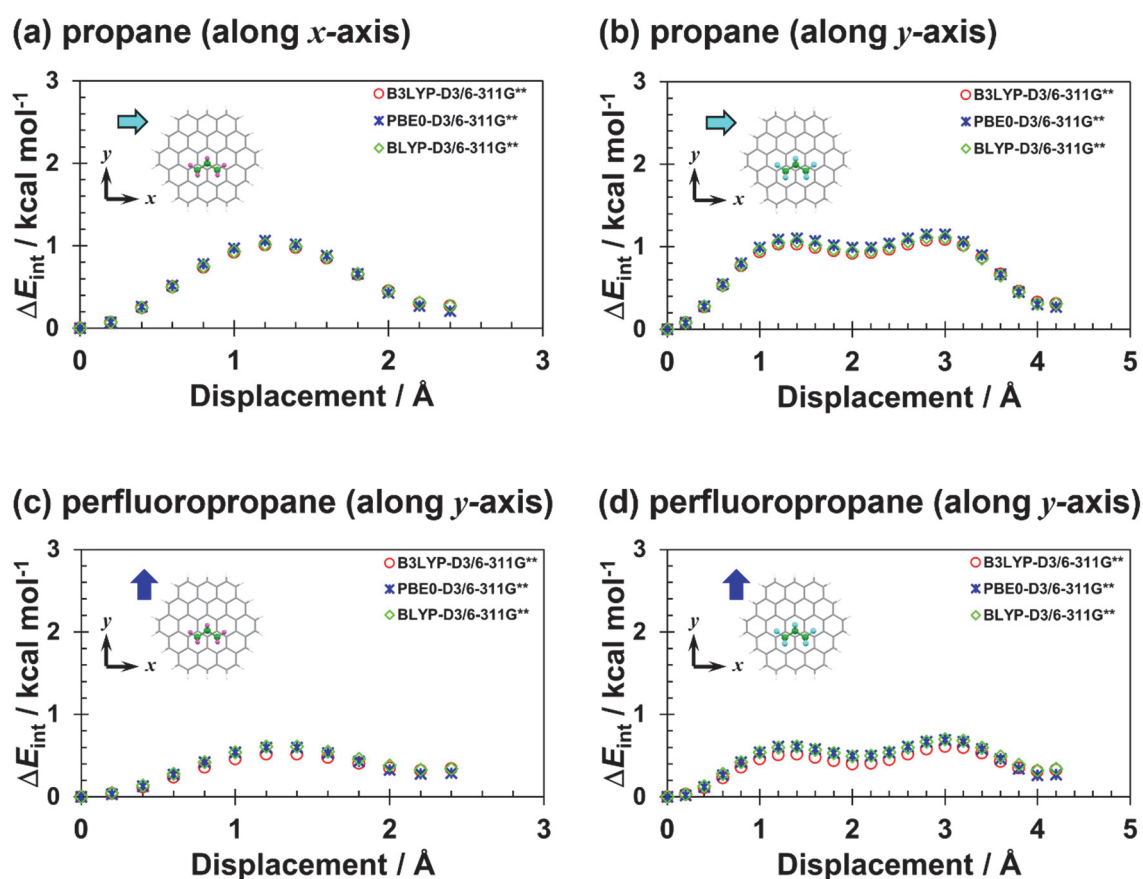


Fig. S4 Plots of ΔE_{int} for propane (a, b) and perfluoropropane (c, d) associated with horizontal displacements along x and y -axes obtained by B3LYP-D3, PBE0-D3 and BLYP-D3 calculations. Red circles, blue asterisk marks and light green rhombi correspond to ΔE_{int} obtained by B3LYP-D3/6-311G**, PBE0-D3/6-311G** and BLYP-D3/6-311G** calculations, respectively.

Table S17 E_{int} and ΔE_{int} values of propane and perfluoropropane at each displacement on $\text{C}_{54}\text{H}_{18}$ obtained by PBE0-D3/6-311G** calculations. $E_{\text{int}}(0)$ is the E_{int} when displacement is 0 Å (coloured in red). The plots of ΔE_{int} as a function of displacement are shown in Fig. S4. The symbols x and y indicate the horizontal displacement along x - and y -axes, respectively.

Displacement (Å)	$\text{C}_3\text{H}_8^{\text{a}}$				$\text{C}_3\text{F}_8^{\text{a}}$			
	E_{int}		ΔE_{int}		E_{int}		ΔE_{int}	
	x	y	x	y	x	y	x	y
0	-6.81	-6.81	0	0	-5.12	-5.12	0	0
0.2	-6.74	-6.73	0.07	0.08	-5.09	-5.10	0.03	0.02
0.4	-6.55	-6.53	0.26	0.28	-4.99	-5.00	0.13	0.12
0.6	-6.29	-6.26	0.52	0.55	-4.85	-4.86	0.27	0.26
0.8	-6.03	-6.01	0.78	0.80	-4.70	-4.70	0.42	0.42
1.0	-5.84	-5.82	0.97	0.99	-4.58	-4.58	0.54	0.54
1.2	-5.75	-5.72	1.06	1.09	-4.52	-4.51	0.6	0.61
1.4	-5.79	-5.71	1.02	1.10	-4.52	-4.51	0.6	0.61
1.6	-5.93	-5.74	0.88	1.07	-4.59	-4.54	0.53	0.58
1.8	-6.15	-5.79	0.66	1.02	-4.69	-4.59	0.43	0.53
2.0	-6.38	-5.82	0.43	0.99	-4.79	-4.62	0.33	0.50
2.2	-6.54	-5.82	0.27	0.99	-4.84	-4.62	0.28	0.50
2.4	-6.60	-5.77	0.21	1.04	-4.83	-4.58	0.29	0.54
2.6		-5.71		1.10		-4.51		0.61
2.8		-5.66		1.15		-4.45		0.67
3.0		-5.66		1.15		-4.43		0.69
3.2		-5.75		1.06		-4.45		0.67
3.4		-5.91		0.90		-4.54		0.58
3.6		-6.14		0.67		-4.66		0.46
3.8		-6.36		0.45		-4.78		0.34
4.0		-6.51		0.30		-4.86		0.26
4.2		-6.54		0.27		-4.85		0.27

^a Energy in kcal mol⁻¹.

Table S18 E_{int} and ΔE_{int} values of propane and perfluoropropane at each displacement on $\text{C}_{54}\text{H}_{18}$ obtained by BLYP-D3/6-311G** calculations. $E_{\text{int}}(0)$ is the E_{int} when displacement is 0 Å (coloured in red). The plots of ΔE_{int} as a function of displacement are shown in Fig. S4. The symbols x and y indicate the horizontal displacement along x - and y -axes, respectively.

Displacement (Å)	C_3H_8^a				C_3F_8^a			
	E_{int}		ΔE_{int}		E_{int}		ΔE_{int}	
	x	y	x	y	x	y	x	y
0	-7.51	-7.51	0	0	-5.64	-5.64	0	0
0.2	-7.44	-7.43	0.07	0.08	-5.59	-5.61	0.05	0.03
0.4	-7.26	-7.23	0.25	0.28	-5.50	-5.51	0.14	0.13
0.6	-7.01	-6.98	0.50	0.53	-5.36	-5.36	0.28	0.28
0.8	-6.76	-6.73	0.75	0.78	-5.22	-5.22	0.42	0.42
1.0	-6.58	-6.55	0.93	0.96	-5.10	-5.10	0.54	0.54
1.2	-6.49	-6.46	1.02	1.05	-5.03	-5.04	0.61	0.60
1.4	-6.52	-6.45	0.99	1.06	-5.03	-5.03	0.61	0.61
1.6	-6.65	-6.49	0.86	1.02	-5.09	-5.07	0.55	0.57
1.8	-6.85	-6.54	0.66	0.97	-5.18	-5.11	0.46	0.53
2.0	-7.06	-6.57	0.45	0.94	-5.26	-5.15	0.38	0.49
2.2	-7.20	-6.56	0.31	0.95	-5.31	-5.14	0.33	0.50
2.4	-7.24	-6.52	0.27	0.99	-5.30	-5.10	0.34	0.54
2.6		-6.45		1.06		-5.04		0.60
2.8		-6.4		1.11		-4.97		0.67
3.0		-6.4		1.11		-4.94		0.70
3.2		-6.49		1.02		-4.96		0.68
3.4		-6.65		0.86		-5.04		0.60
3.6		-6.86		0.65		-5.15		0.49
3.8		-7.06		0.45		-5.25		0.39
4.0		-7.20		0.31		-5.32		0.32
4.2		-7.20		0.31		-5.30		0.34

^a Energy in kcal mol⁻¹.

4. Two-dimensional scan of ΔE_{int} for $\text{C}_{54}\text{H}_{18}$ complexes with propane and perfluoropropane

Energy calculations were performed on a region scanned two-dimensionally along the x - and y -axes of the $\text{C}_{54}\text{H}_{18}$, with the central carbon positions of propane and perfluoropropane in the optimised structures taken as the origin ($x=0, y=0$) (Tables S19 and S20). The scanned regions are shown in red (Fig. S5(a-f)). Fig. S5(g) and (h) shows the ΔE_{int} values associated with y -axis displacement, while x -axis displacement was fixed in the range of 0–2.4 Å with 0.4 Å increments (Tables S21 and S22). In the plot for x -axis displacement of 1.2 Å (blue circle), the ΔE_{int} values for propane and perfluoropropane at y -axis displacement of 2.0 Å were almost the same as those at the origin ($x=0, y=0$). However, the structures at the positions $x=1.2, y=2.0$ (Fig. I(b) and (e)) are almost identical to those at the origin ($x=0, y=0$). All ΔE_{int} values except for those at the origin ($x=0, y=0$) and position $x=1.2, y=2.0$ are larger. Hence, we can conclude that the optimised structures corresponding to the origin ($x=0, y=0$) are the most stable structures.

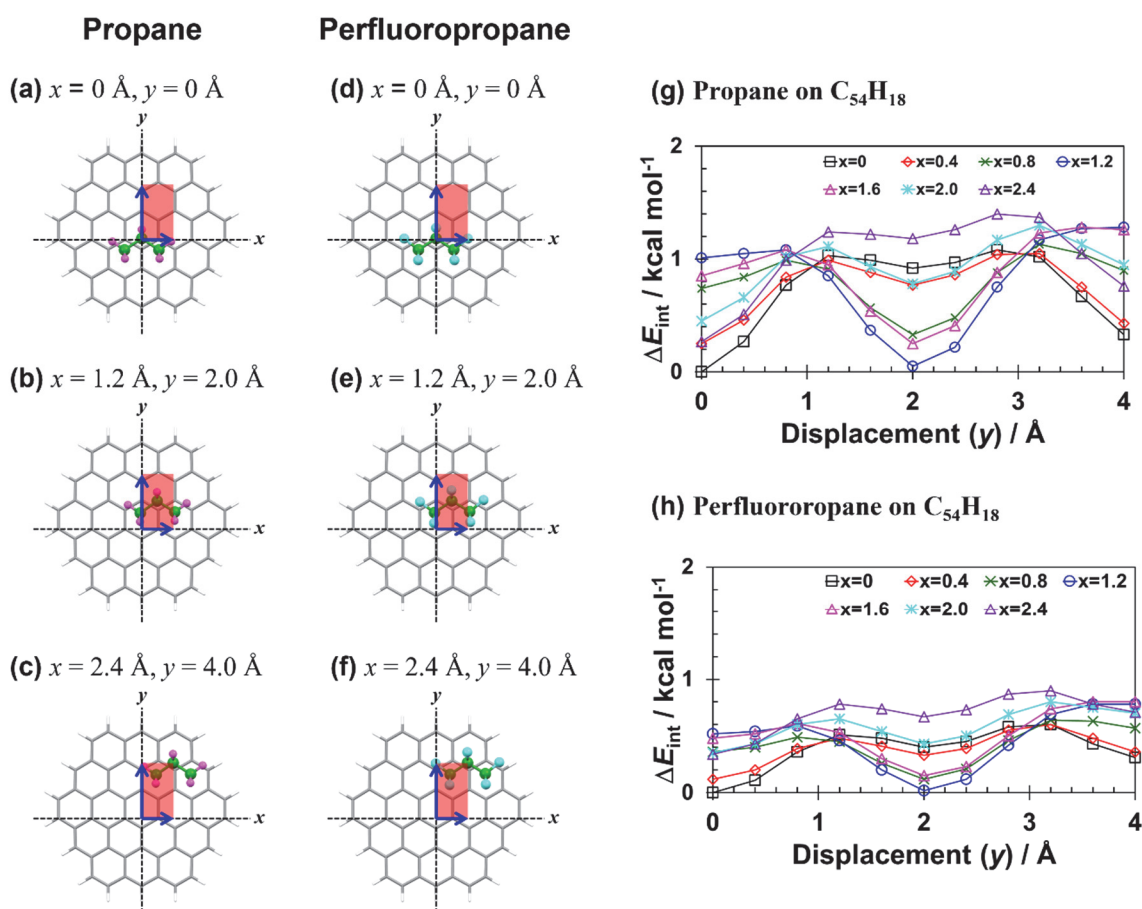


Fig. S5 Geometries of C₅₄H₁₈ complexes with propane and perfluoropropane: (a,d) Geometry of complex at the optimal position; (b, e) the molecules were moved to the position $x=1.2, y=2.0$ Å; (c, f) the molecules were moved to the position $x=2.4, y=4.0$ Å; Plots of ΔE_{int} obtained by B3LYP-D3/6-311G** level calculations for (g) propane and (h) perfluoropropane associated with the displacement along y -axis, while x -axis displacement was fixed in the range of 0 – 2.4 Å with 0.4 Å increments.

Table S19 E_{int} values of propane on a region scanned two-dimensionally along the x - and y - axes of the C₅₄H₁₈, with the central carbon position of propane in the optimised structures taken as the origin ($x=0, y=0$) obtained by B3LYP-D3/6-311G** calculations. The E_{int} values at the origin ($E_{\text{int}}(0)$) and that at the position $x=1.2, y=2.0$ are coloured in red and blue, respectively.

Displacement along y -axis (Å)	E_{int} for C ₃ H ₈ ^a						
	Displacement along x -axis (Å)						
	0	0.4	0.8	1.2	1.6	2.0	2.4
0	-7.12	-6.87	-6.38	-6.11	-6.27	-6.67	-6.85
0.4	-6.85	-6.66	-6.28	-6.07	-6.16	-6.46	-6.61
0.8	-6.35	-6.28	-6.13	-6.04	-6.04	-6.10	-6.13
1.2	-6.09	-6.13	-6.21	-6.27	-6.17	-6.01	-5.88
1.6	-6.13	-6.24	-6.55	-6.75	-6.58	-6.19	-5.90
2.0	-6.20	-6.35	-6.79	-7.07	-6.87	-6.34	-5.94
2.4	-6.15	-6.26	-6.64	-6.90	-6.71	-6.23	-5.86
2.8	-6.04	-6.08	-6.24	-6.37	-6.24	-5.95	-5.72
3.2	-6.10	-6.07	-5.99	-5.95	-5.89	-5.82	-5.75
3.6	-6.45	-6.37	-6.07	-5.85	-5.84	-5.99	-6.07
4.0	-6.79	-6.69	-6.22	-5.84	-5.86	-6.17	-6.36

^a Energy in kcal mol⁻¹.

Table S20 E_{int} values of perfluoropropane on a region scanned two-dimensionally along the x - and y -axes of the $\text{C}_{54}\text{H}_{18}$, with the central carbon position of perfluoropropane in the optimised structures taken as the origin ($x=0$, $y=0$) obtained by B3LYP-D3/6-311G** calculations. The E_{int} values at the origin ($E_{\text{int}}(0)$) and that at the position $x=1.2$, $y=2.0$ are coloured in red and blue, respectively.

	E_{int} for C_3F_8 ^a						
Displacement along y -axis (Å)	Displacement along x -axis (Å)						
	0	0.4	0.8	1.2	1.6	2.0	2.4
0	-5.64	-5.52	-5.28	-5.12	-5.16	-5.29	-5.30
0.4	-5.53	-5.44	-5.24	-5.10	-5.12	-5.21	-5.21
0.8	-5.28	-5.25	-5.15	-5.05	-5.03	-5.04	-4.99
1.2	-5.13	-5.16	-5.19	-5.18	-5.11	-4.99	-4.86
1.6	-5.16	-5.23	-5.38	-5.44	-5.34	-5.10	-4.90
2.0	-5.24	-5.31	-5.52	-5.62	-5.49	-5.21	-4.97
2.4	-5.19	-5.25	-5.43	-5.52	-5.41	-5.14	-4.91
2.8	-5.06	-5.09	-5.18	-5.22	-5.14	-4.95	-4.77
3.2	-5.04	-5.04	-5.00	-4.95	-4.90	-4.84	-4.74
3.6	-5.21	-5.16	-5.01	-4.86	-4.84	-4.89	-4.86
4.0	-5.33	-5.28	-5.07	-4.86	-4.84	-4.94	-4.93

^a Energy in kcal mol⁻¹.

Table S21 ΔE_{int} values of propane on a region scanned two-dimensionally along the x - and y - axes of the C_3H_8 , with the central carbon position of propane in the optimised structures taken as the origin ($x=0, y=0$) obtained by B3LYP-D3/6-311G** calculations. The ΔE_{int} values at the origin and that at the position $x=1.2, y=2.0$ are coloured in red and blue, respectively.

	ΔE_{int} for C_3H_8 ^a						
Displacement along y -axis (Å)	Displacement along x -axis (Å)						
	0	0.4	0.8	1.2	1.6	2.0	2.4
0	0	0.25	0.74	1.01	0.85	0.45	0.27
0.4	0.27	0.46	0.84	1.05	0.96	0.66	0.51
0.8	0.77	0.84	0.99	1.08	1.08	1.02	0.99
1.2	1.03	0.99	0.91	0.85	0.95	1.11	1.24
1.6	0.99	0.88	0.57	0.37	0.54	0.93	1.22
2.0	0.92	0.77	0.33	0.05	0.25	0.78	1.18
2.4	0.97	0.86	0.48	0.22	0.41	0.89	1.26
2.8	1.08	1.04	0.88	0.75	0.88	1.17	1.40
3.2	1.02	1.05	1.13	1.17	1.23	1.30	1.37
3.6	0.67	0.75	1.05	1.27	1.28	1.13	1.05
4.0	0.33	0.43	0.90	1.28	1.26	0.95	0.76

^a Energy in kcal mol⁻¹.

Table S22 ΔE_{int} values of perfluoropropane on a region scanned two-dimensionally along the x - and y - axes of the C_5H_{18} , with the central carbon position of perfluoropropane in the optimised structures taken as the origin ($x=0, y=0$) obtained by B3LYP-D3/6-311G** calculations. The ΔE_{int} values at the origin and that at the position $x=1.2, y=2.0$ are coloured in red and blue, respectively.

	ΔE_{int} for C_3F_8 ^a						
Displacement along y -axis (Å)	Displacement along x -axis (Å)						
	0	0.4	0.8	1.2	1.6	2.0	2.4
0	0	0.12	0.36	0.52	0.48	0.35	0.34
0.4	0.11	0.20	0.40	0.54	0.52	0.43	0.43
0.8	0.36	0.39	0.49	0.59	0.61	0.60	0.65
1.2	0.51	0.48	0.45	0.46	0.53	0.65	0.78
1.6	0.48	0.41	0.26	0.20	0.30	0.54	0.74
2.0	0.40	0.33	0.12	0.02	0.15	0.43	0.67
2.4	0.45	0.39	0.21	0.12	0.23	0.50	0.73
2.8	0.58	0.55	0.46	0.42	0.50	0.69	0.87
3.2	0.60	0.60	0.64	0.69	0.74	0.80	0.90
3.6	0.43	0.48	0.63	0.78	0.80	0.75	0.78
4.0	0.31	0.36	0.57	0.78	0.80	0.70	0.71

^a Energy in kcal mol⁻¹.

5. Optimised geometries of $C_{96}H_{24}$ complexes with *n*-alkanes and *n*-perfluoroalkanes

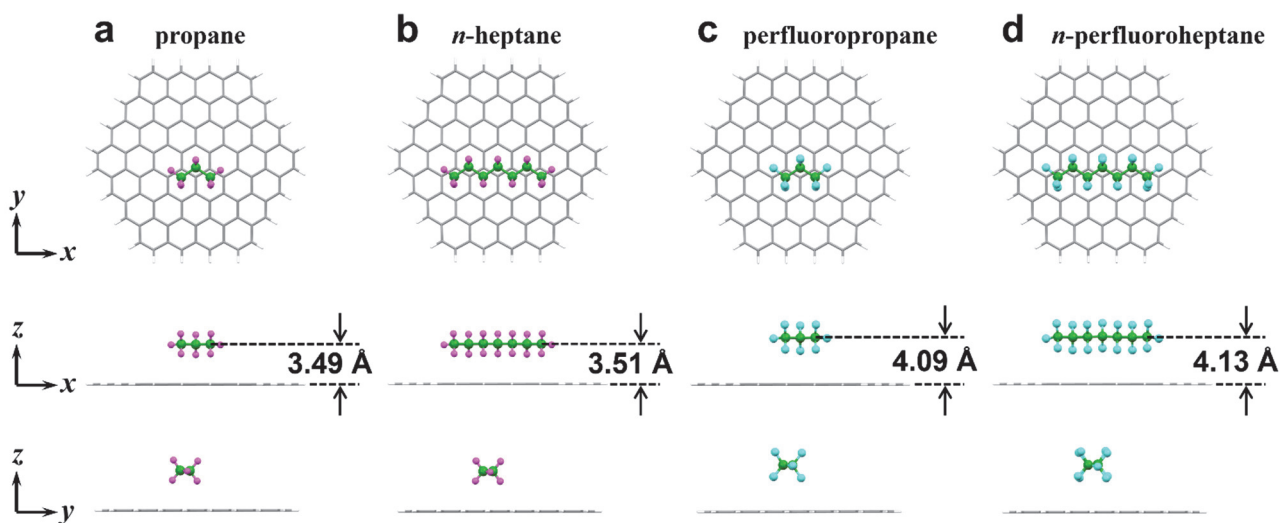


Fig. S6 Optimised geometries of $C_{96}H_{24}$ complexes with *n*-alkanes and *n*-perfluoroalkanes, as viewed from three directions. Carbon, hydrogen, and fluorine atoms of adsorbed molecules are colored in green, pink, and cyan, respectively: (a) propane; (b) *n*-heptane; (c) perfluoropropane; (d) *n*-perfluoroheptane.

6. E_{int} and ΔE_{int} values at each displacement on C_9H_{24}

Table S23 E_{int} at each displacement on C_9H_{24} along x - and y -axes. $E_{\text{int}}(0)$ is the E_{int} when displacement is 0 Å (coloured in red). The symbols x and y indicate the horizontal displacement along x - and y -axes, respectively.

Displacement (Å)	$\text{C}_3\text{H}_8^{\text{a}}$		$\text{C}_5\text{H}_{12}^{\text{a}}$		$\text{C}_7\text{H}_{16}^{\text{a}}$		$\text{C}_3\text{F}_8^{\text{a}}$		$\text{C}_5\text{F}_{12}^{\text{a}}$		$\text{C}_7\text{F}_{16}^{\text{a}}$	
	x	y	x	y	x	y	x	y	x	y	x	y
0	-7.36	-7.36	-11.63	-11.63	-15.78	-15.78	-5.96	-5.96	-9.30	-9.30	-12.51	-12.51
0.2	-7.29	-7.27	-11.52	-11.54	-15.64	-15.62	-5.93	-5.93	-9.26	-9.25	-12.46	-12.46
0.4	-7.10	-7.05	-11.23	-11.24	-15.26	-15.20	-5.85	-5.82	-9.14	-9.12	-12.31	-12.29
0.6	-6.85	-6.79	-10.83	-10.82	-14.74	-14.64	-5.74	-5.69	-8.98	-8.93	-12.10	-12.05
0.8	-6.60	-6.54	-10.44	-10.39	-14.22	-14.08	-5.63	-5.55	-8.82	-8.73	-11.88	-11.80
1.0	-6.42	-6.36	-10.14	-10.05	-13.82	-13.67	-5.53	-5.45	-8.69	-8.57	-11.70	-11.59
1.2	-6.34	-6.27	-10.00	-9.86	-13.63	-13.45	-5.49	-5.39	-8.62	-8.48	-11.61	-11.48
1.4	-6.38	-6.26	-10.06	-9.81	-13.71	-13.43	-5.51	-5.39	-8.64	-8.47	-11.61	-11.47
1.6	-6.53	-6.30	-10.30	-9.86	-14.01	-13.52	-5.58	-5.43	-8.74	-8.53	-11.71	-11.54
1.8	-6.76	-6.34	-10.65	-9.95	-14.46	-13.63	-5.68	-5.48	-8.87	-8.60	-11.85	-11.64
2.0	-7.01	-6.35	-11.03	-10.02	-14.94	-13.71	-5.78	-5.51	-9.01	-8.65	-11.99	-11.71
2.2	-7.20	-6.34	-11.34	-10.03	-15.31	-13.70	-5.86	-5.52	-9.11	-8.64	-12.09	-11.71
2.4	-7.29	-6.30	-11.47	-9.99	-15.46	-13.61	-5.88	-5.48	-9.14	-8.59	-12.09	-11.64
2.6		-6.25		-9.90		-13.47		-5.43		-8.50		-11.53
2.8		-6.22		-9.81		-13.34		-5.38		-8.42		-11.43
3.0		-6.23		-9.78		-13.33		-5.37		-8.38		-11.38
3.2		-6.33		-9.88		-13.49		-5.41		-8.43		-11.44
3.4		-6.52		-10.13		-13.85		-5.51		-8.54		-11.59
3.6		-6.77		-10.51		-14.37		-5.64		-8.71		-11.82
3.8		-7.02		-10.93		-14.91		-5.76		-8.88		-12.04
4.0		-7.22		-11.28		-15.35		-5.86		-9.02		-12.21
4.2		-7.29		-11.45		-15.53		-5.89		-9.06		-12.27

^a Energy in kcal mol⁻¹.

Table S24 ΔE_{int} values at each displacement on $\text{C}_{96}\text{H}_{24}$ along x - and y -axes. The plots of ΔE_{int} as a function of displacement are shown in Figs. 3 and 4. ΔE_{int} when $x = 1.2 \text{ \AA}$ and $y = 1.4 \text{ \AA}$ (coloured in blue) are $\Delta E_{\text{int}(\text{max})}$. The symbols x and y indicate the horizontal displacement along x - and y -axes, respectively.

Displacement (\AA)	$\text{C}_3\text{H}_8^{\text{a}}$		$\text{C}_5\text{H}_{12}^{\text{a}}$		$\text{C}_7\text{H}_{16}^{\text{a}}$		$\text{C}_3\text{F}_8^{\text{a}}$		$\text{C}_5\text{F}_{12}^{\text{a}}$		$\text{C}_7\text{F}_{16}^{\text{a}}$	
	x	y	x	y	x	y	x	y	x	y	x	y
0	0	0	0	0	0	0	0	0	0	0	0	0
0.2	0.07	0.09	0.11	0.09	0.14	0.16	0.03	0.03	0.04	0.05	0.05	0.05
0.4	0.26	0.31	0.40	0.39	0.52	0.58	0.11	0.14	0.16	0.18	0.20	0.22
0.6	0.51	0.57	0.80	0.81	1.04	1.14	0.22	0.27	0.32	0.37	0.41	0.46
0.8	0.76	0.82	1.19	1.24	1.56	1.70	0.33	0.41	0.48	0.57	0.63	0.71
1.0	0.94	1.00	1.49	1.58	1.96	2.11	0.43	0.51	0.61	0.73	0.81	0.92
1.2	1.02	1.09	1.63	1.77	2.15	2.33	0.47	0.57	0.68	0.82	0.90	1.03
1.4	0.98	1.10	1.57	1.82	2.07	2.35	0.45	0.57	0.66	0.83	0.90	1.04
1.6	0.83	1.06	1.33	1.77	1.77	2.26	0.38	0.53	0.56	0.77	0.80	0.97
1.8	0.60	1.02	0.98	1.68	1.32	2.15	0.28	0.48	0.43	0.70	0.66	0.87
2.0	0.35	1.01	0.60	1.61	0.84	2.07	0.18	0.45	0.29	0.65	0.52	0.80
2.2	0.16	1.02	0.29	1.60	0.47	2.08	0.10	0.44	0.19	0.66	0.42	0.80
2.4	0.07	1.06	0.16	1.64	0.32	2.17	0.08	0.48	0.16	0.71	0.42	0.87
2.6		1.11		1.73		2.31		0.53		0.80		0.98
2.8		1.14		1.82		2.44		0.58		0.88		1.08
3.0		1.13		1.85		2.45		0.59		0.92		1.13
3.2		1.03		1.75		2.29		0.55		0.87		1.07
3.4		0.84		1.50		1.93		0.45		0.76		0.92
3.6		0.59		1.12		1.41		0.32		0.59		0.69
3.8		0.34		0.70		0.87		0.20		0.42		0.47
4.0		0.14		0.35		0.43		0.10		0.28		0.30
4.2		0.07		0.18		0.25		0.07		0.24		0.24

^a Energy in kcal mol^{-1} .

7. Cause of ΔE_{int} change by horizontal displacement

To elucidate the cause of the change in ΔE_{int} with horizontal displacement, the contributions of the change in each energy term such as electrostatic (E_{es}), induction (E_{ind}), short-range (E_{short}) and dispersion (E_{disp}) interactions for *n*-pentane and *n*-perfluoropentane on $\text{C}_{96}\text{H}_{24}$, were analysed while moving horizontally along *y*-axis. The calculations were performed according to our previous study.^{S1} The E_{es} and E_{ind} values were calculated using the ORIENT version 3.2.^{S2} The electrostatic energy of the complex was calculated as interactions between distributed multipoles of molecules. Distributed multipoles^{S3,S4} up to hexadecapole on all atoms were obtained from the B3LYP/6-311G** wave functions of an isolated molecule using the GDMA program.^{S5} The induction energy was calculated as interactions of polarizable sites with the electric field produced by the distributed multipoles of monomers.^{S6} The atomic polarizability of carbon ($\alpha = 10$ au) was used for the calculations.^{S7} Distributed multipoles were used only to estimate the electrostatic and induction energies.

The E_{disp} was calculated according to the following equation:

$$E_{\text{disp}} = E_{\text{int}} - E_{\text{b3lyp}},$$

where E_{b3lyp} is B3LYP/6-311G** level interaction energy without the dispersion correction. The contribution of the dispersion correction was assumed to be the contribution of the dispersion force in this work. The E_{short} was calculated as follows:

$$E_{\text{short}} = E_{\text{b3lyp}} - E_{\text{es}} - E_{\text{ind}}$$

The intermolecular interaction energy calculated using the B3LYP functional is approximately the sum of the contributions of the electrostatic, induction and short-range (orbital-orbital) interactions. The results are summarized in Tables S25 and S26 as well as Fig. S7. The contributions of the electrostatic and induction interactions are almost negligible. The dispersion interactions are almost constant and are the major source of attraction. In contrast, the short-range interactions (mainly exchange-repulsion) change greatly associated with the horizontal displacement. The changes of total interaction energies

associated with the horizontal displacements are close to the changes of the short-range interactions, which clearly shows that the short-range (exchange-repulsion) interactions are mainly responsible for the changes of E_{int} , as shown in Fig. S7

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Table S25 Calculated intermolecular interaction energies (E_{int}) for *n*-pentane and *n*-perfluoropentane on C_9H_{24} associated with horizontal displacement along *x*-axis, and the contributions of electrostatic (E_{es}), induction (E_{ind}), dispersion (E_{disp}), and short-range interactions (E_{short}).

Displacement (Å)	<i>n</i> -pentane ^a					<i>n</i> -fluoropentane ^a				
	E_{int}	E_{es}	E_{ind}	E_{disp}	E_{short}	E_{int}	E_{es}	E_{ind}	E_{disp}	E_{short}
0	-11.63	0.48	-0.03	-16.97	4.89	-9.30	-0.12	-0.03	-13.42	4.27
0.2	-11.52	0.27	-0.03	-16.94	5.18	-9.26	-0.06	-0.03	-13.43	4.26
0.4	-11.23	0.15	-0.02	-16.87	5.51	-9.14	-0.03	-0.03	-13.44	4.36
0.6	-10.83	0.08	-0.02	-16.78	5.89	-8.98	-0.02	-0.02	-13.46	4.52
0.8	-10.44	0.04	-0.02	-16.69	6.23	-8.82	-0.01	-0.02	-13.48	4.69
1.0	-10.14	0.02	-0.02	-16.63	6.49	-8.69	0.00	-0.02	-13.49	4.82
1.2	-10.00	0.01	-0.02	-16.59	6.60	-8.62	0.00	-0.02	-13.47	4.87
1.4	-10.06	0.00	-0.01	-16.59	6.54	-8.64	0.00	-0.02	-13.46	4.84
1.6	-10.30	-0.01	-0.01	-16.63	6.35	-8.74	0.00	-0.02	-13.44	4.71
1.8	-10.65	-0.01	-0.01	-16.69	6.06	-8.87	0.00	-0.02	-13.40	4.54
2.0	-11.03	-0.01	-0.01	-16.76	5.75	-9.01	0.00	-0.02	-13.36	4.36
2.2	-11.34	-0.01	-0.01	-16.81	5.49	-9.11	0.00	-0.02	-13.32	4.22
2.4	-11.47	-0.01	-0.01	-16.82	5.37	-9.14	0.00	-0.01	-13.28	4.15

^a Energy in kcal mol⁻¹.

Table S26 Calculated intermolecular interaction energies (E_{int}) for *n*-pentane and *n*-perfluoropentane on C_9H_{24} associated with horizontal displacement along y -axis, and the contributions of electrostatic (E_{es}), induction (E_{ind}), dispersion (E_{disp}), and short-range interactions (E_{short}).

Displacement (Å)	<i>n</i> -pentane ^a					<i>n</i> -fluoropentane ^a				
	E_{int}	E_{es}	E_{ind}	E_{disp}	E_{short}	E_{int}	E_{es}	E_{ind}	E_{disp}	E_{short}
0	-11.63	0.48	-0.03	-16.97	4.89	-9.30	-0.12	-0.03	-13.42	4.27
0.2	-11.54	0.43	-0.03	-16.95	5.01	-9.25	-0.11	-0.03	-13.43	4.32
0.4	-11.24	0.29	-0.03	-16.88	5.38	-9.12	-0.07	-0.03	-13.46	4.44
0.6	-10.82	0.10	-0.03	-16.80	5.91	-8.93	-0.01	-0.03	-13.48	4.59
0.8	-10.39	-0.10	-0.03	-16.72	6.46	-8.73	0.05	-0.03	-13.50	4.75
1.0	-10.05	-0.25	-0.03	-16.67	6.90	-8.57	0.10	-0.03	-13.51	4.88
1.2	-9.86	-0.31	-0.03	-16.65	7.14	-8.48	0.11	-0.03	-13.51	4.95
1.4	-9.81	-0.29	-0.03	-16.65	7.16	-8.47	0.08	-0.03	-13.51	4.99
1.6	-9.86	-0.19	-0.03	-16.64	7.01	-8.53	0.03	-0.03	-13.52	4.99
1.8	-9.95	-0.07	-0.03	-16.63	6.78	-8.60	-0.03	-0.03	-13.51	4.97
2.0	-10.02	0.02	-0.03	-16.62	6.61	-8.65	-0.08	-0.03	-13.51	4.97
2.2	-10.03	0.05	-0.03	-16.61	6.56	-8.64	-0.09	-0.03	-13.49	4.97
2.4	-9.99	0.00	-0.03	-16.61	6.65	-8.59	-0.07	-0.03	-13.49	5.00
2.6	-9.90	-0.09	-0.03	-16.61	6.84	-8.50	-0.01	-0.03	-13.48	5.03
2.8	-9.81	-0.20	-0.03	-16.60	7.02	-8.42	0.05	-0.03	-13.47	5.03
3.0	-9.78	-0.25	-0.03	-16.59	7.09	-8.38	0.11	-0.04	-13.44	4.99
3.2	-9.88	-0.22	-0.03	-16.58	6.95	-8.43	0.13	-0.04	-13.43	4.90
3.4	-10.13	-0.10	-0.03	-16.61	6.62	-8.54	0.12	-0.04	-13.40	4.77
3.6	-10.51	0.07	-0.03	-16.66	6.11	-8.71	0.07	-0.03	-13.36	4.61
3.8	-10.93	0.26	-0.03	-16.72	5.56	-8.88	0.01	-0.03	-13.31	4.45
4.0	-11.28	0.42	-0.03	-16.77	5.10	-9.02	-0.05	-0.03	-13.28	4.34
4.2	-11.45	0.50	-0.03	-16.77	4.86	-9.06	-0.09	-0.04	-13.23	4.29

^a Energy in kcal mol^{-1} .

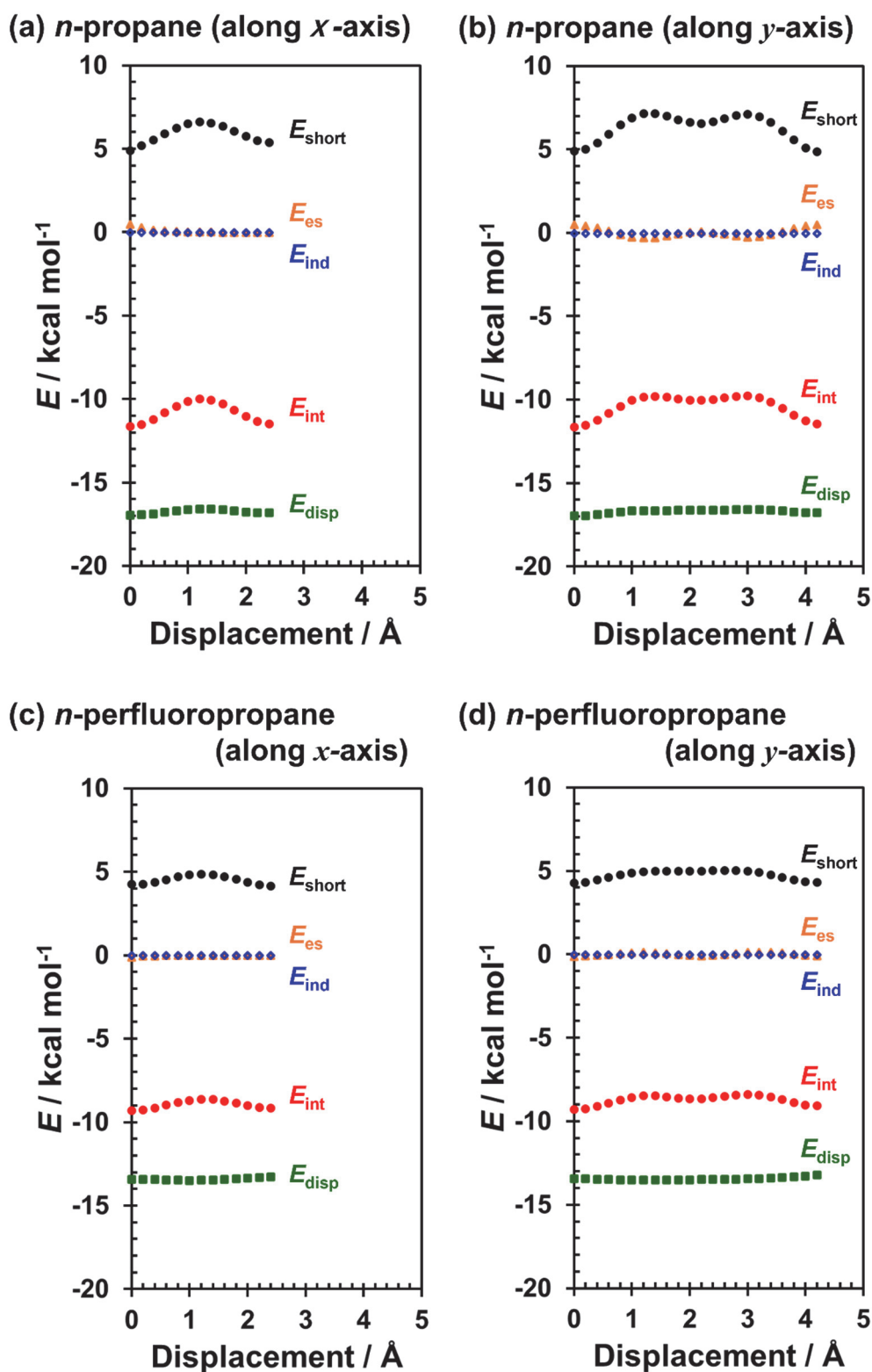


Fig. S7 Plots of interaction energies (E_{int}), the electrostatic (E_{es}), induction (E_{ind}), short-range (E_{short}) and dispersion (E_{disp}) interactions for (a, b) n -pentane and (c, d) n -perfluoropentane on $\text{C}_{96}\text{H}_{24}$ associated with horizontal displacement along x - and y -axes: black circles, orange triangles, blue rhombi, red circles, and green squares correspond to E_{short} , E_{es} , E_{ind} , E_{int} , and E_{disp} , respectively.