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

Supporting Information for

Theoretical insights into volatile iodine adsorption onto COF-DL229

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Totally 6 pages including 5 Tables, 3 Figures, and 2 Equations.

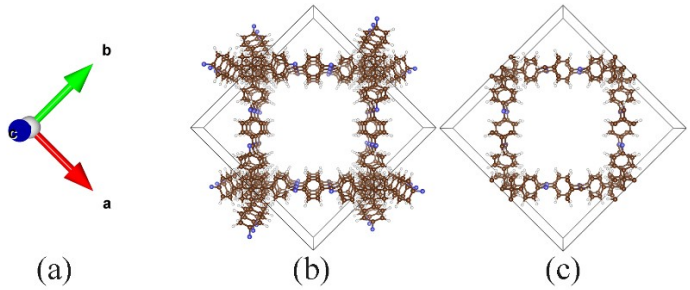

Fig. S1 The 1×1×2 supercell with boundary line displayed with attached atoms near the boundary (b) and without atoms beyond boundary (c). (a) is the coordinate axis. The N, C, and H atoms are shown in blue, brown, and white, respectively.

Table S1 Adsorption energies (E_{ads}, eV) and structural parameters (Å) of I_2 adsorption onto COF-DL229. COF-DL229 was fixed.

Site		E_{ads}	E_{disp}	Δd	I-I	I-N	I-C
IM	vertical	-0.55	-0.40	0	2.74	2.91	
	parallel	-0.55	-0.40	0	2.74	2.89	
PH	vertical	-0.56	-0.41	0	2.74	2.90	
	parallel	-0.55	-0.40	0	2.74	2.89	
CO	vertical	-0.46	-0.41	0	2.70		3.32/3.72
	parallel	-0.37	-0.40	0	2.68		3.98/4.11

Table S2 Total energies (E_{tot}, eV) and adsorption energies (E_{ads}, eV) of various adsorption sites under the condition of that all atoms are relaxed or the skeletons atoms are fixed.

Site		All atoms are relaxed		Skeleton atoms are fixed	
		E_{tot}	E_{ads}[a]	E_{tot}	E_{ads}[a]
IM	vertical	-2534.38	-8.75	-2526.18	-0.55
	parallel	-2534.01	-8.38	-2526.18	-0.55
PH	vertical	-2534.38	-8.75	-2526.19	-0.56
	parallel	-2534.53	-8.90	-2526.18	-0.55
CO	vertical	-2534.89	-9.26	-2526.09	-0.46
	parallel	-2534.67	-9.04	-2526.00	-0.37

[a]: the total energies of clean COF-DL229 and I_2 molecule are -2522.97 and -2.66 eV, respectively.

Table S3 The distances (Å) between I_2 molecules before and after adsorption onto COF-DL229.

Site		I_2 distance (before)	I_2 distance (after)
IM	vertical	14.85	13.76
	parallel	14.00	13.86
PH	vertical	14.85	13.66
	parallel	13.55	14.25
CO	vertical	14.85	12.90
	parallel	12.17	13.56

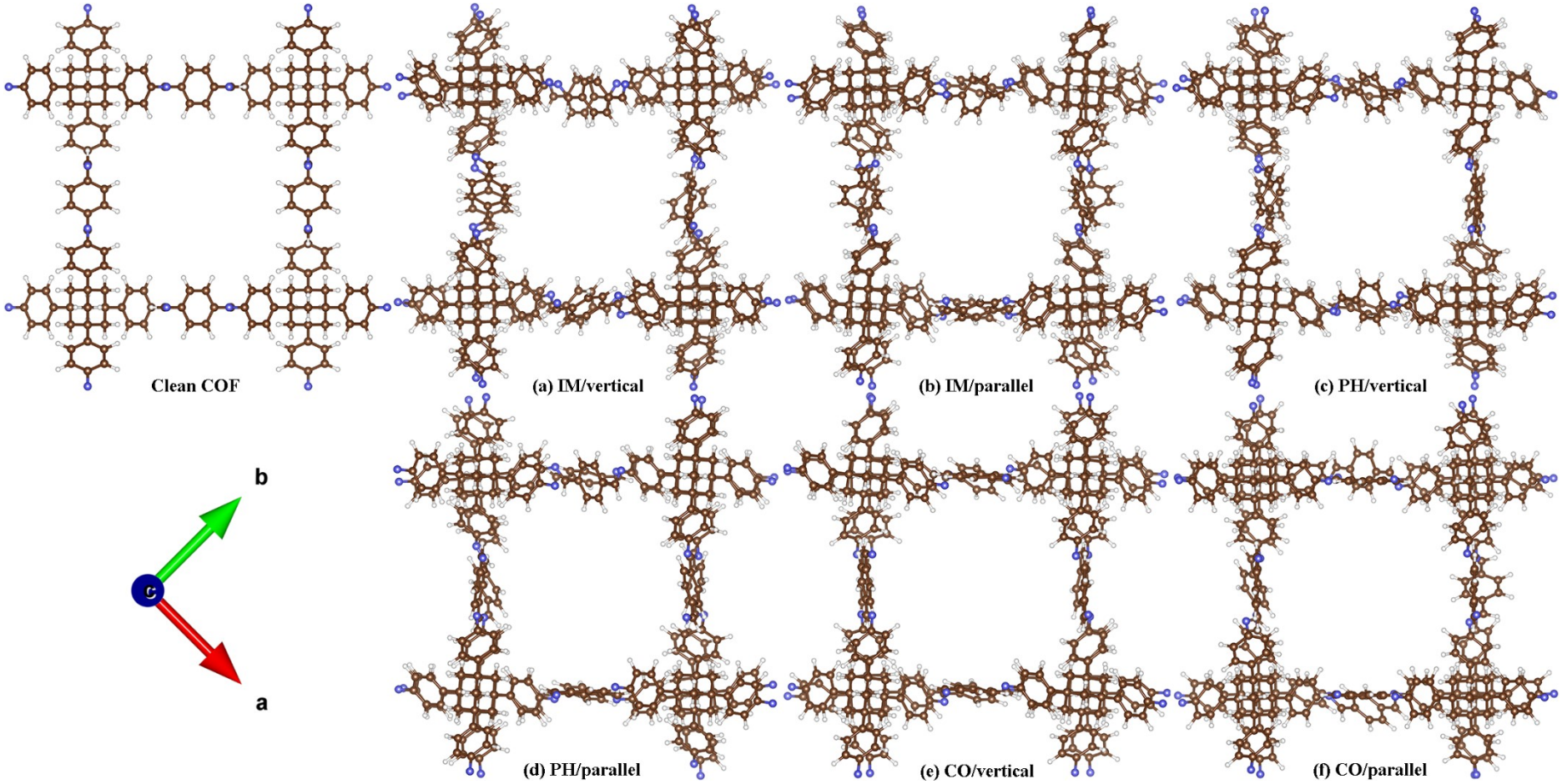

Fig. S2 The skeleton structures comparison before (Clean COF) and after adsorption (a-f). The N, C, and H atoms are shown in blue, brown, and white, respectively.

Table S4 The specific data of deformation energies, interaction energies, and their contributions to adsorption energies of each site in different modes.

Site		E_{ads}	$E_{def}(COF)^a$	$E_{def}(I_2)^a$	$E_{int}(I_2/COF)^a$
IM	vertical	-8.75	-7.91/90.40%	0.04/-0.46%	-0.88/10.06%
	parallel	-8.38	-7.94/94.75%	0.00/0.00%	-0.44/5.25%
PH	vertical	-8.75	-7.94/90.74%	0.04/-0.46%	-0.85/9.71%
	parallel	-8.90	-8.29/93.15%	0.01/-0.11%	-0.62/6.97%
CO	vertical	-9.26	-8.69/93.84%	0.01/-0.11%	-0.58/6.26%
	parallel	-9.04	-8.15/90.15%	0.02/-0.22%	-0.91/10.07%

[a]: The X of X/Y denotes the energy, whereas the Y denotes the percentage contributed to adsorption energy.

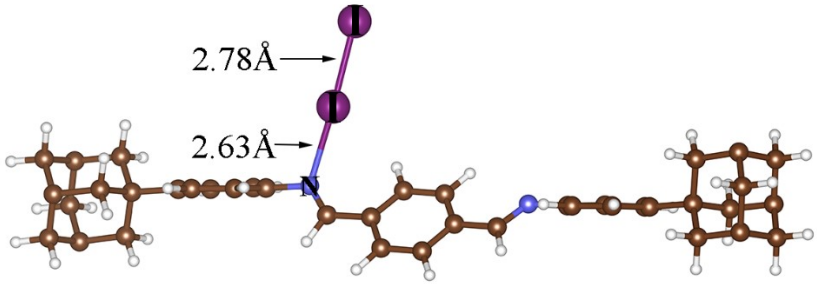

Fig. S3 The corresponding partial structure of the I-N bond at IM site in vertical mode. The N, C, H, and I atoms are shown in blue, brown, white, and purple, respectively.

Table S5 The energies of HOMO, LUMO, and Energy Gap corresponding to the clean COF-DL229 and different adsorption configurations. The unit is eV.

Configuration	E(HOMO)	E(LUMO)	E_{gap}
COF-DL229	-0.58	2.68	3.26
I_2@IM	-0.54	1.17	1.71
I_2@PH	-0.58	0.77	1.35
I_2@CO	-0.67	0.84	1.51

Equations

The integrated crystal orbital Hamilton population (ICOHP) is calculated by the energy integral up to the highest occupied bands. The specific computational equation of ICOHP is given below [1].

$$\mathrm{COHP}_{\mu v}(E, \boldsymbol{k}) = \sum_{j} R\left[P_{\mu v j}^{(proj)}(k) H_{v \mu}^{(proj)}(k)\right] \times \delta\left(\varepsilon_j(k) - E\right)$$

$$\mathrm{ICOHP}\left(\varepsilon_F\right) = \int^{\varepsilon_F} \mathrm{COHP}(E)\, \mathrm{d}E$$

References

[1] V.L. Deringer, A.L. Tchougréeff, R. Dronskowski, Crystal Orbital Hamilton Population (COHP) Analysis As Projected from Plane-Wave Basis Sets, The Journal of Physical Chemistry A 115 (2011) 5461-5466.