

Supporting Information for “Origins of Offset-Stacking in Porous Frameworks”

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S1 One-Dimensional Scans

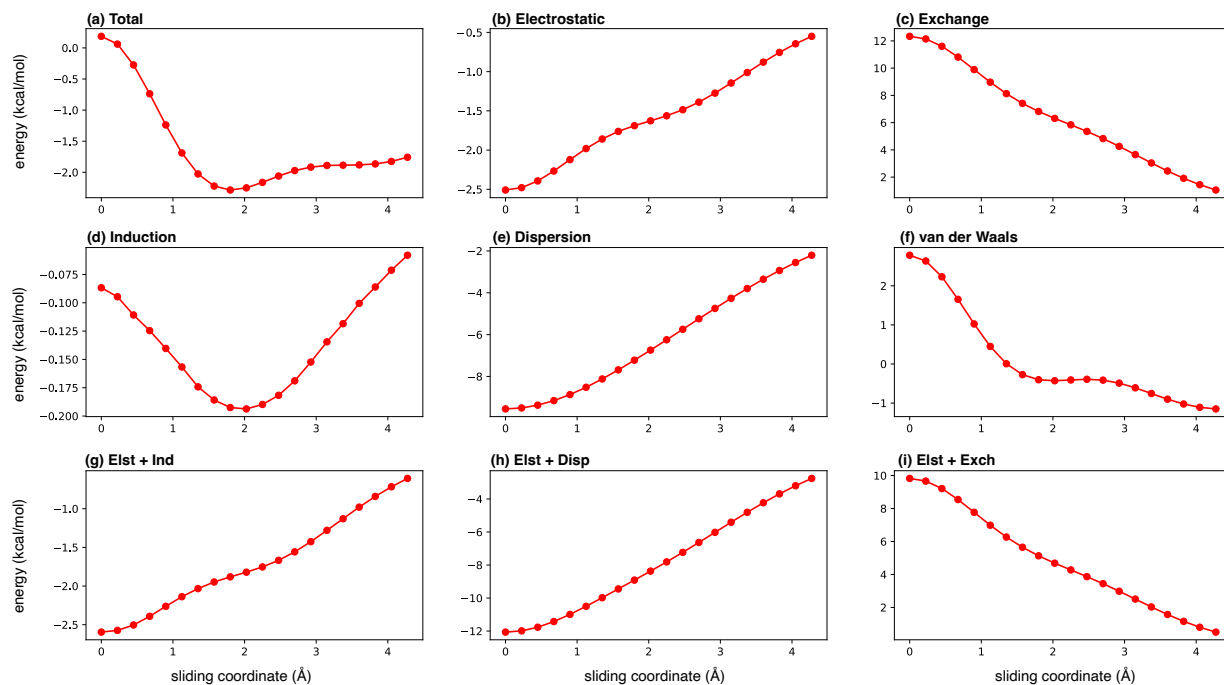


Fig. S1: Interaction potentials for the benzene dimer along a parallel-sliding coordinate at fixed face-to-face distance of 3.4 Å, computed at the XSAPT+MBD/def2-TZVPD level of theory. (Note that the energy scale is different in each panel.) These potentials include (a) the total interaction energy potential, E_{int} , along with its components: (b) electrostatic energy, E_{elst} ; (c) exchange energy, E_{exch} ; (d) induction energy, E_{ind} ; and (e) dispersion energy, E_{disp} . Also plotted are (f) the van der Waals potential, $E_{\text{vdW}} = E_{\text{exch}} + E_{\text{disp}}$; (g) the sum $E_{\text{elst}} + E_{\text{ind}}$, sometimes called “polarized electrostatics”; (h) the sum $E_{\text{elst}} + E_{\text{disp}}$; and (i) the sum $E_{\text{elst}} + E_{\text{exch}}$.

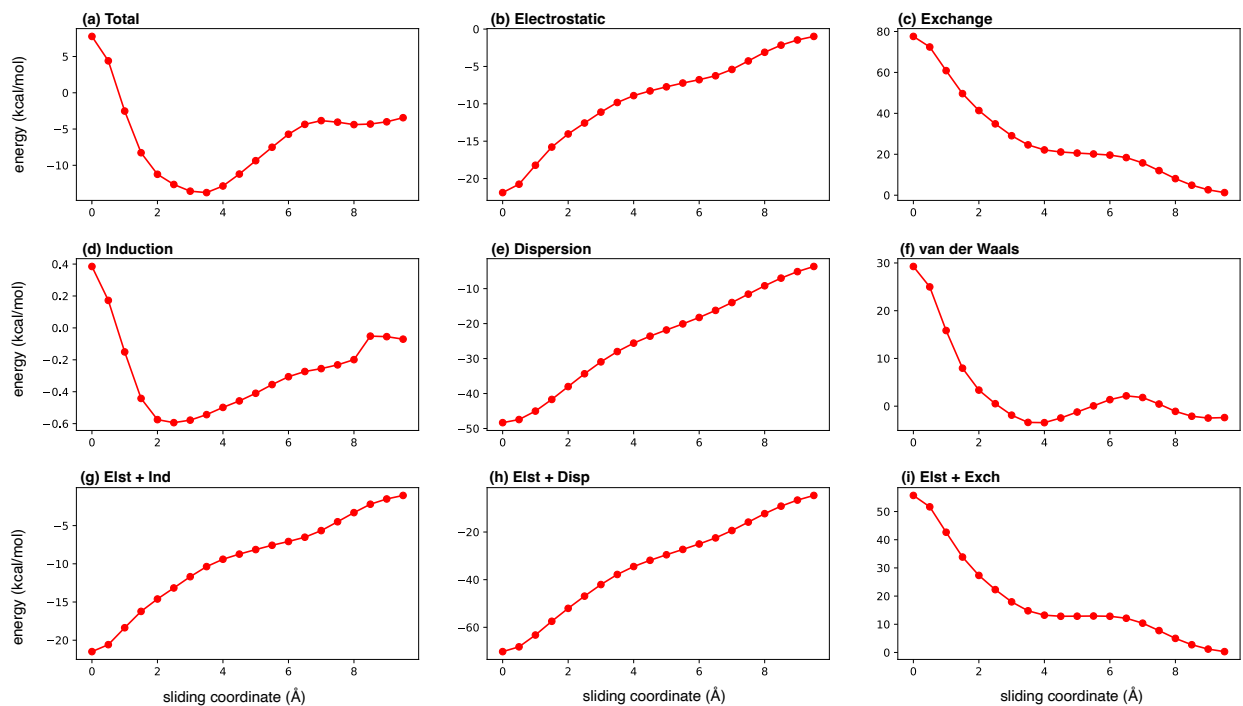


Fig. S2: Interaction potentials for the [18]annulene dimer along a parallel-sliding coordinate at fixed face-to-face distance of 3.2 Å, computed at the XSAPT+MBD/def2-ma-TZVP level of theory. (Note that the energy scale is different in each panel.) These potentials include (a) the total interaction energy potential, E_{int} , along with its components: (b) electrostatic energy, E_{elst} ; (c) exchange energy, E_{exch} ; (d) induction energy, E_{ind} ; and (e) dispersion energy, E_{disp} . Also plotted are (f) the van der Waals potential, $E_{\text{vdW}} = E_{\text{exch}} + E_{\text{disp}}$; (g) the sum $E_{\text{elst}} + E_{\text{ind}}$, sometimes called “polarized electrostatics”; (h) the sum $E_{\text{elst}} + E_{\text{disp}}$; and (i) the sum $E_{\text{elst}} + E_{\text{exch}}$.

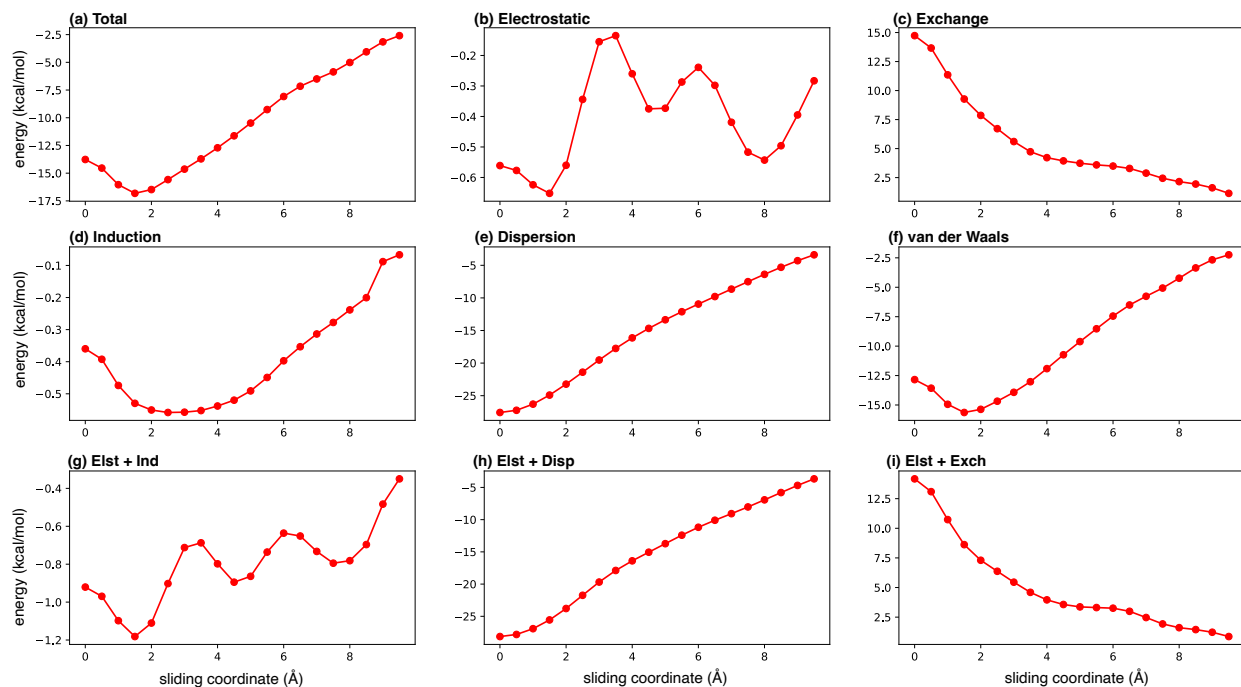


Fig. S3: Interaction potentials for the porphyrin dimer along a parallel-sliding coordinate at fixed face-to-face distance of 3.7 Å, computed at the XSAPT+MBD/def2-ma-TZVP level of theory. (Note that the energy scale is different in each panel.) These potentials include (a) the total interaction energy potential, E_{int} , along with its components: (b) electrostatic energy, E_{elst} ; (c) exchange energy, E_{exch} ; (d) induction energy, E_{ind} ; and (e) dispersion energy, E_{disp} . Also plotted are (f) the van der Waals potential, $E_{\text{vdW}} = E_{\text{exch}} + E_{\text{disp}}$; (g) the sum $E_{\text{elst}} + E_{\text{ind}}$, sometimes called “polarized electrostatics”; (h) the sum $E_{\text{elst}} + E_{\text{disp}}$; and (i) the sum $E_{\text{elst}} + E_{\text{exch}}$.

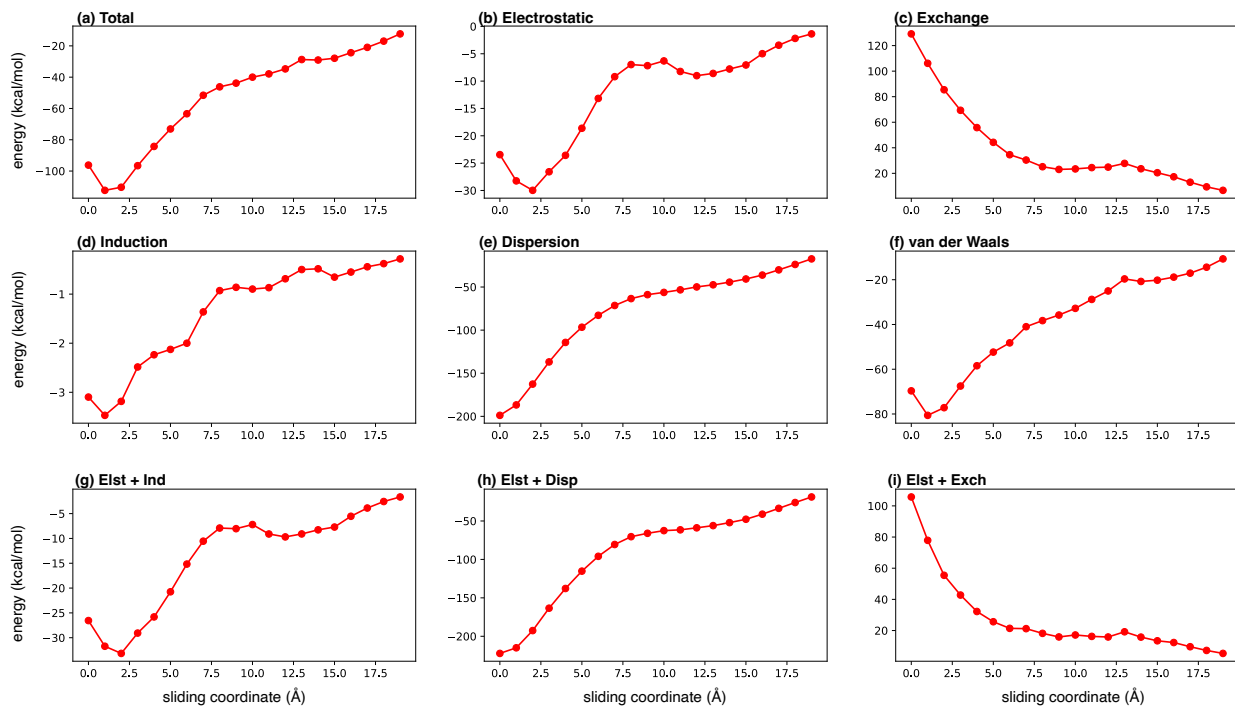


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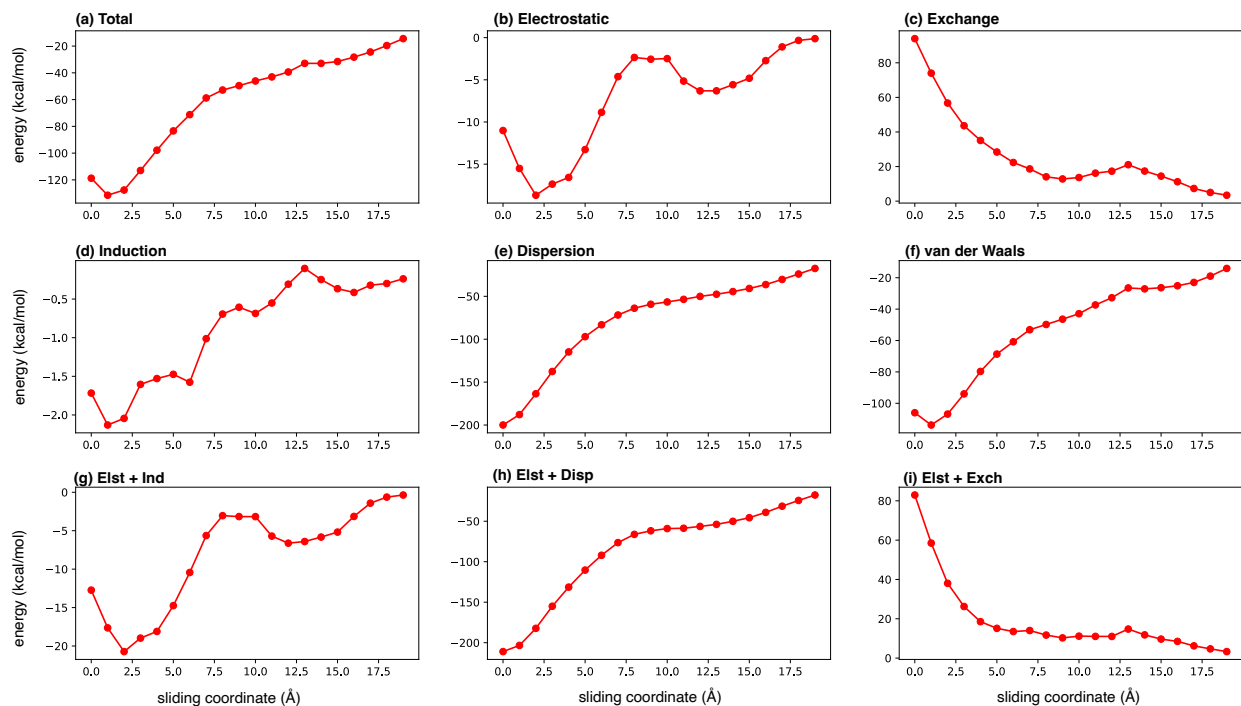


Fig. S5: Interaction potentials for $(\text{COF1})_2$ along a parallel-sliding coordinate at fixed face-to-face distance of 3.28 \AA , computed at the XSAPT+MBD/def2-SVP level of theory. These are the same plots as in Fig. S4 but computed here without diffuse basis functions.

S2 Two-Dimensional Contour Plots

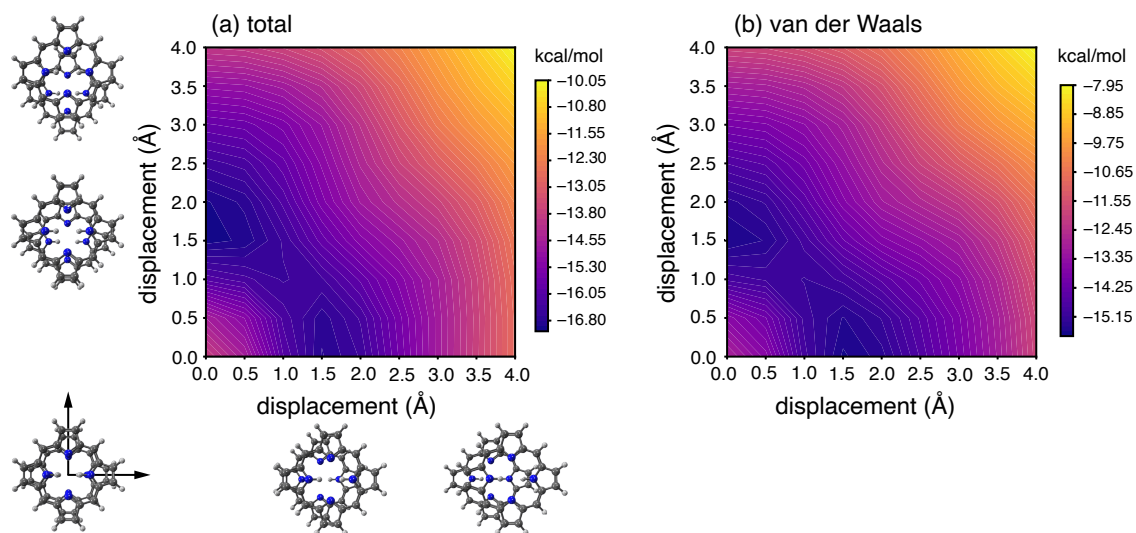


Fig. S6: Two-dimensional energy component surfaces for cofacial sliding of (porphyrin)₂ at a fixed face-to-face separation of 3.7 Å, computed at the XSAPT+MBD/def2-ma-TZVP level of theory: (a) total interaction energy and (b) vdW energy, E_{vdW} . The energy scale is different in either panel.

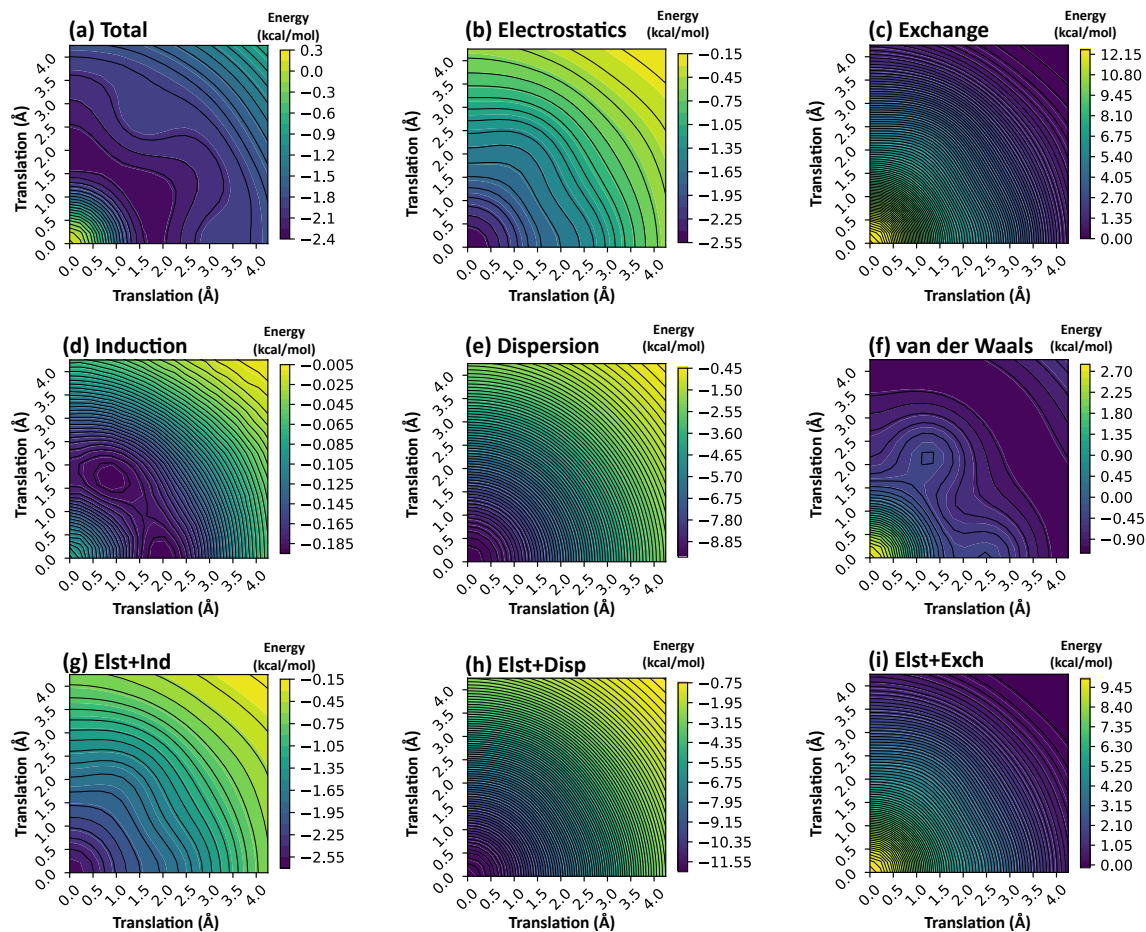


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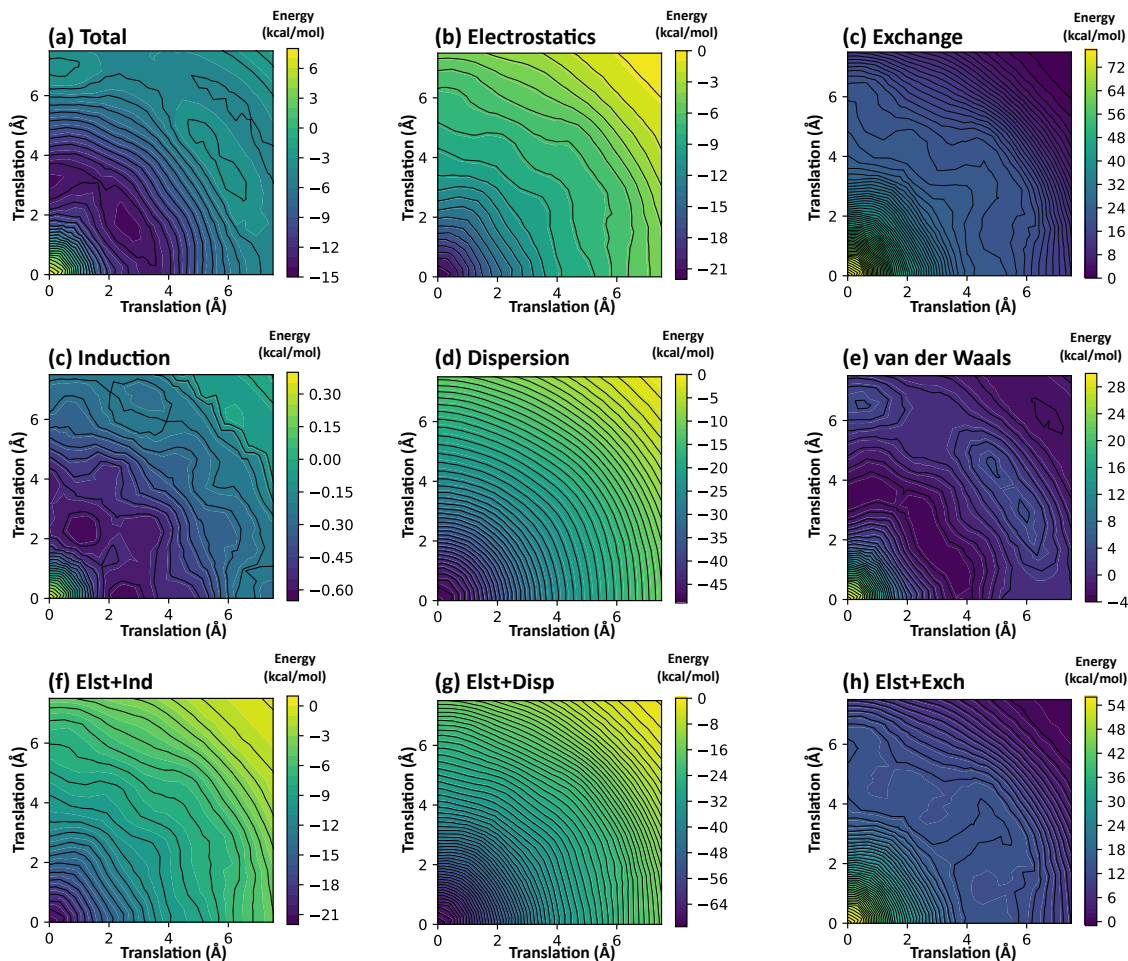


Fig. S8: Interaction potentials and energy components for [18]annulene dimer, computed at the XSAPT+MBD/def2-ma-TZVP level of theory at a fixed face-to-face separation of 3.2 Å. Potentials include (a) the total interaction energy potential, E_{int} , along with its components: (b) electrostatic energy, E_{elst} ; (c) exchange energy, E_{exch} ; (d) induction energy, E_{ind} ; and (e) dispersion energy, E_{disp} . Also plotted are (f) the van der Waals potential, $E_{\text{vdW}} = E_{\text{exch}} + E_{\text{disp}}$; (g) the sum $E_{\text{elst}} + E_{\text{ind}}$, sometimes called “polarized electrostatics”; (h) the sum $E_{\text{elst}} + E_{\text{disp}}$; and (i) the sum $E_{\text{elst}} + E_{\text{exch}}$. Coordinates represent translation of one monomer’s center of mass with respect to that of the other monomer, along the same two coordinates that are depicted in Fig. 7. Energy scales are different in each panel, with yellow representing less-favorable interactions (more positive) and blue representing more favorable interactions (more negative). Contours were constructed using a two-dimensional mesh of points with a spacing of 0.5 Å.

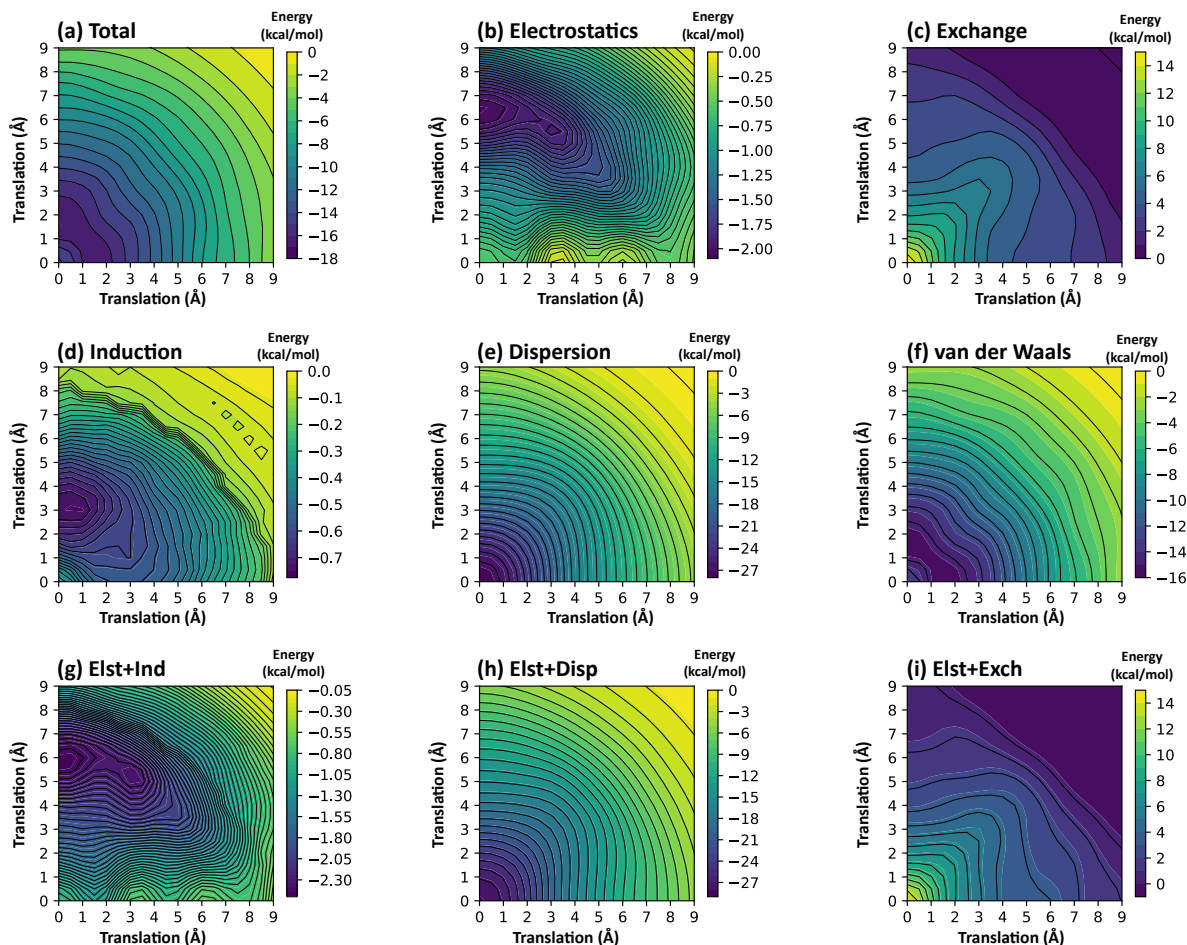


Fig. S9: Interaction potentials and energy components for (porphyrin)₂, computed at the XSAPT+MBD/def2-ma-TZVP level of theory at a fixed face-to-face separation of 3.7 Å. Potentials include (a) the total interaction energy potential, E_{int} , along with its components: (b) electrostatic energy, E_{elst} ; (c) exchange energy, E_{exch} ; (d) induction energy, E_{ind} ; and (e) dispersion energy, E_{disp} . Also plotted are (f) the van der Waals potential, $E_{\text{vdW}} = E_{\text{exch}} + E_{\text{disp}}$; (g) the sum $E_{\text{elst}} + E_{\text{ind}}$, sometimes called “polarized electrostatics”; (h) the sum $E_{\text{elst}} + E_{\text{disp}}$; and (i) the sum $E_{\text{elst}} + E_{\text{exch}}$. Coordinates represent translation of one monomer’s center of mass with respect to that of the other monomer, along the same two coordinates that are depicted in Fig. S6. Energy scales are different in each panel, with yellow representing less-favorable interactions (more positive) and blue representing more favorable interactions (more negative). Contours were constructed using a two-dimensional mesh of points with a spacing of 0.5 Å.

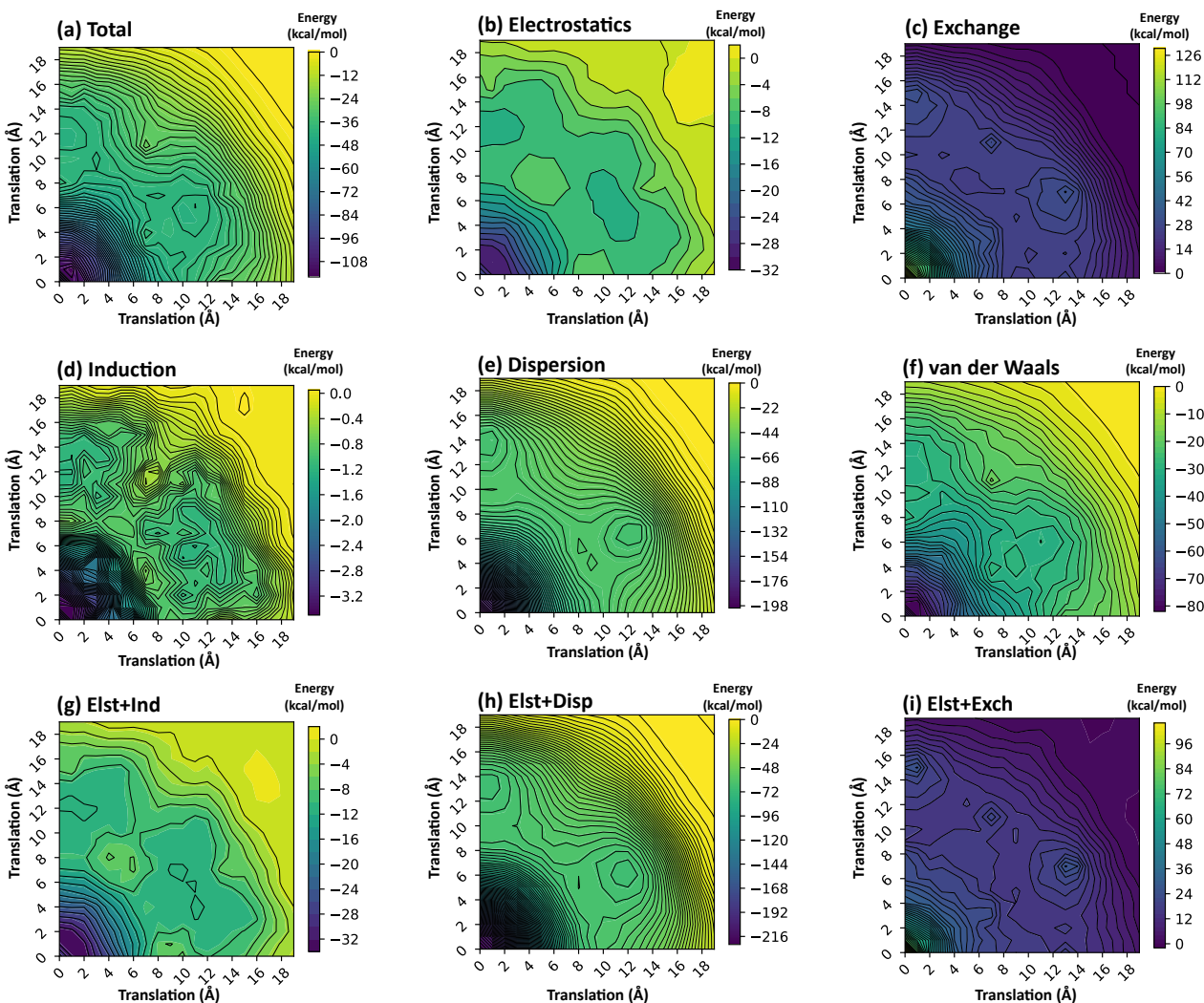


Fig. S10: Interaction potentials and energy components for $(\text{COF1})_2$, computed at the XSAPT+MBD/def2-SVPD level of theory at a fixed face-to-face separation of 3.28 \AA . Potentials include (a) the total interaction energy potential, E_{int} , along with its components: (b) electrostatic energy, E_{elst} ; (c) exchange energy, E_{exch} ; (d) induction energy, E_{ind} ; and (e) dispersion energy, E_{disp} . Also plotted are (f) the van der Waals potential, $E_{\text{vdW}} = E_{\text{exch}} + E_{\text{disp}}$; (g) the sum $E_{\text{elst}} + E_{\text{ind}}$, sometimes called “polarized electrostatics”; (h) the sum $E_{\text{elst}} + E_{\text{disp}}$; and (i) the sum $E_{\text{elst}} + E_{\text{exch}}$. Coordinates represent translation of one monomer’s center of mass with respect to that of the other monomer, along the same two coordinates that are depicted in Fig. 8. Energy scales are different in each panel, with yellow representing less-favorable interactions (more positive) and blue representing more favorable interactions (more negative). Contours were constructed using a two-dimensional mesh of points with a spacing of 1.0 \AA .

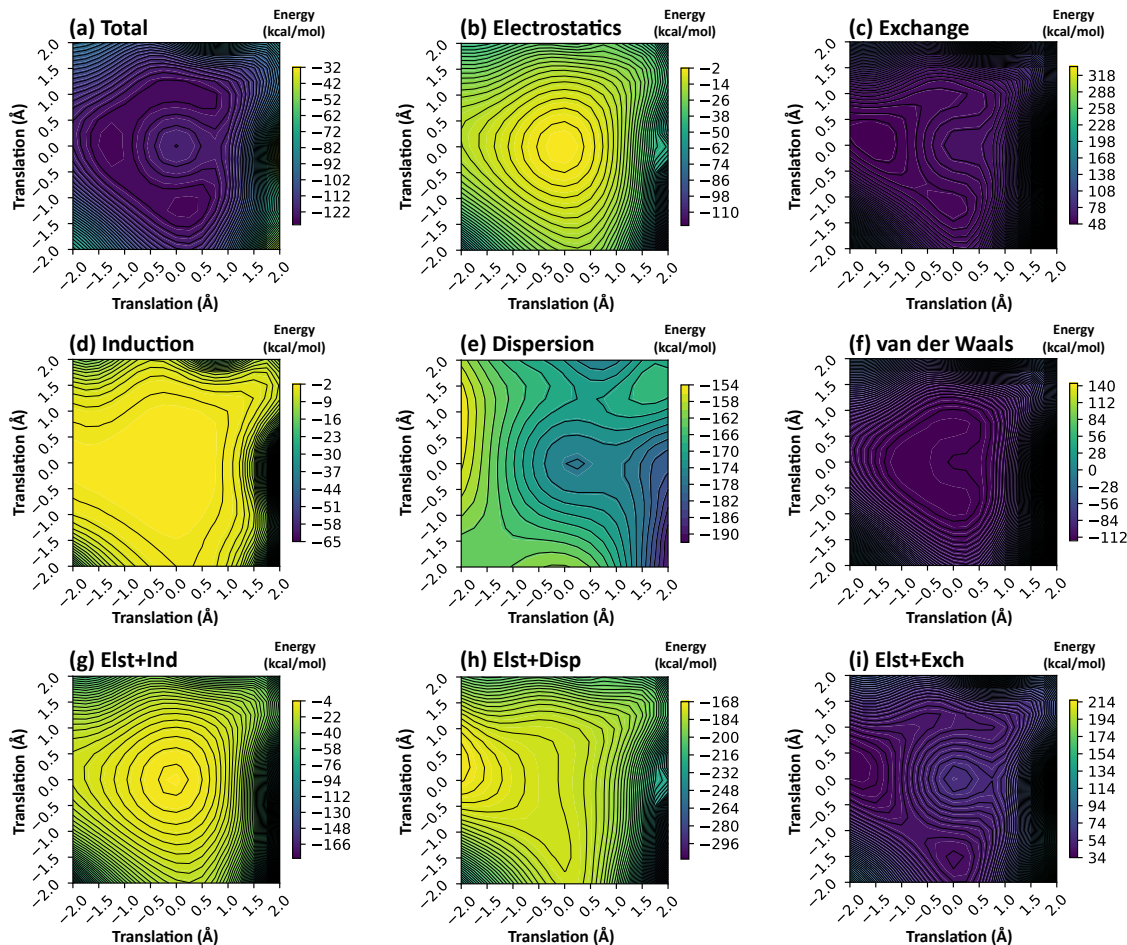


Fig. S11: Interaction potentials and energy components for $(\text{COF1})_2(\text{mesitylene})$, computed at the XSAPT+MBD/def2-SVP level of theory at a fixed face-to-face separation of 3.28 Å. Potentials include (a) the total interaction energy potential, E_{int} , along with its components: (b) electrostatic energy, E_{elst} ; (c) exchange energy, E_{exch} ; (d) induction energy, E_{ind} ; and (e) dispersion energy, E_{disp} . Also plotted are (f) the van der Waals potential, $E_{\text{vdW}} = E_{\text{exch}} + E_{\text{disp}}$; (g) the sum $E_{\text{elst}} + E_{\text{ind}}$, sometimes called “polarized electrostatics”; (h) the sum $E_{\text{elst}} + E_{\text{disp}}$; and (i) the sum $E_{\text{elst}} + E_{\text{exch}}$. Coordinates represent translation of one monomer’s center of mass with respect to that of the other monomer, along the same two coordinates that are depicted in Fig. 9. Energy scales are different in each panel, with yellow representing less-favorable interactions (more positive) and blue representing more favorable interactions (more negative). Contours were constructed using a two-dimensional mesh of points with a spacing of 0.25 Å.

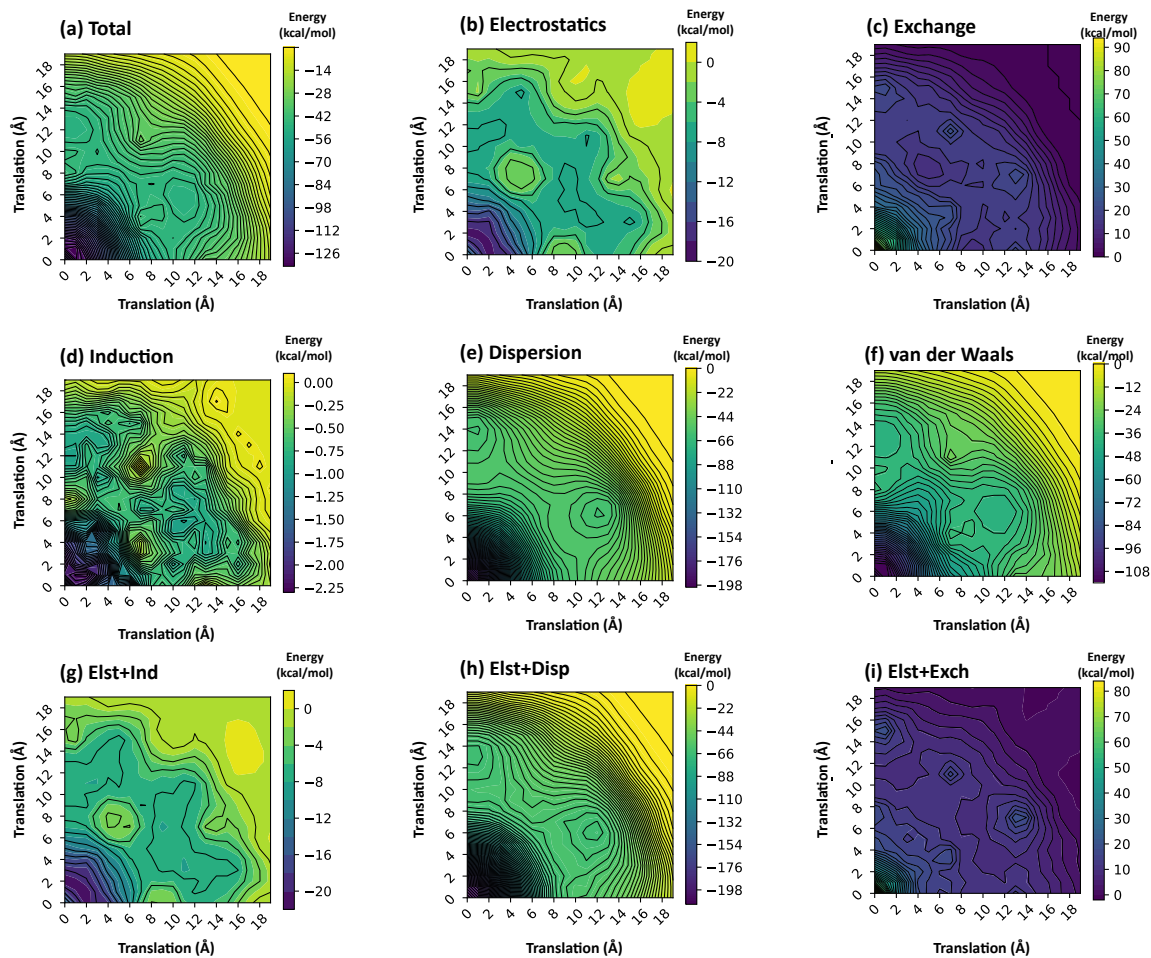


Fig. S12: Interaction potentials and energy components for $(\text{COF1})_2$, computed at the XSAPT+MBD/def2-SVP level of theory at a fixed face-to-face separation of 3.28 Å. These are the same plots as in Fig. S10 except that diffuse basis functions are omitted here.

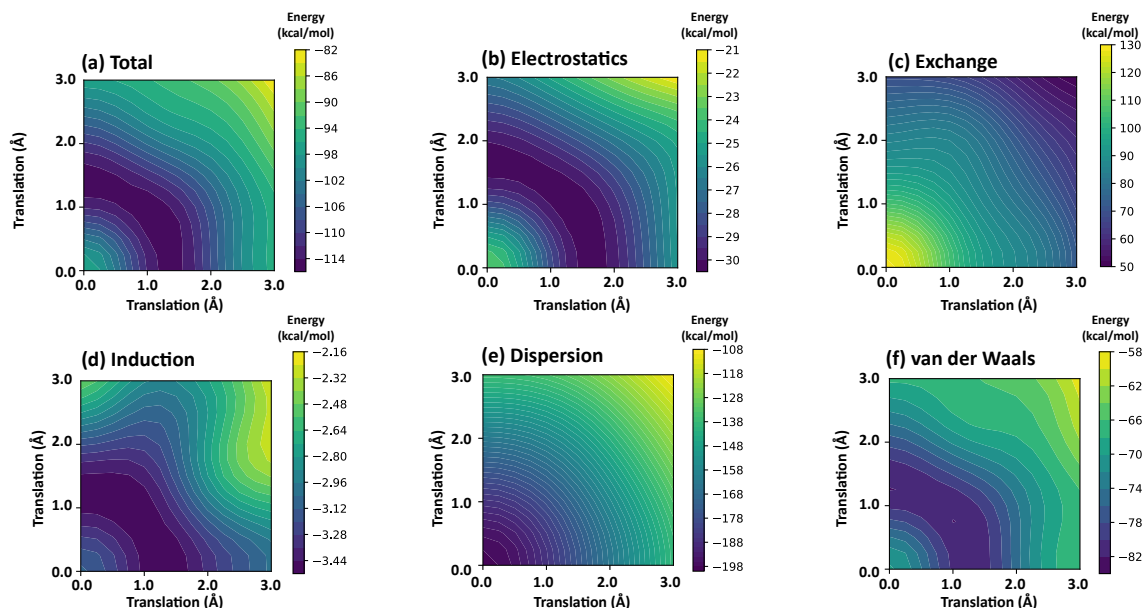


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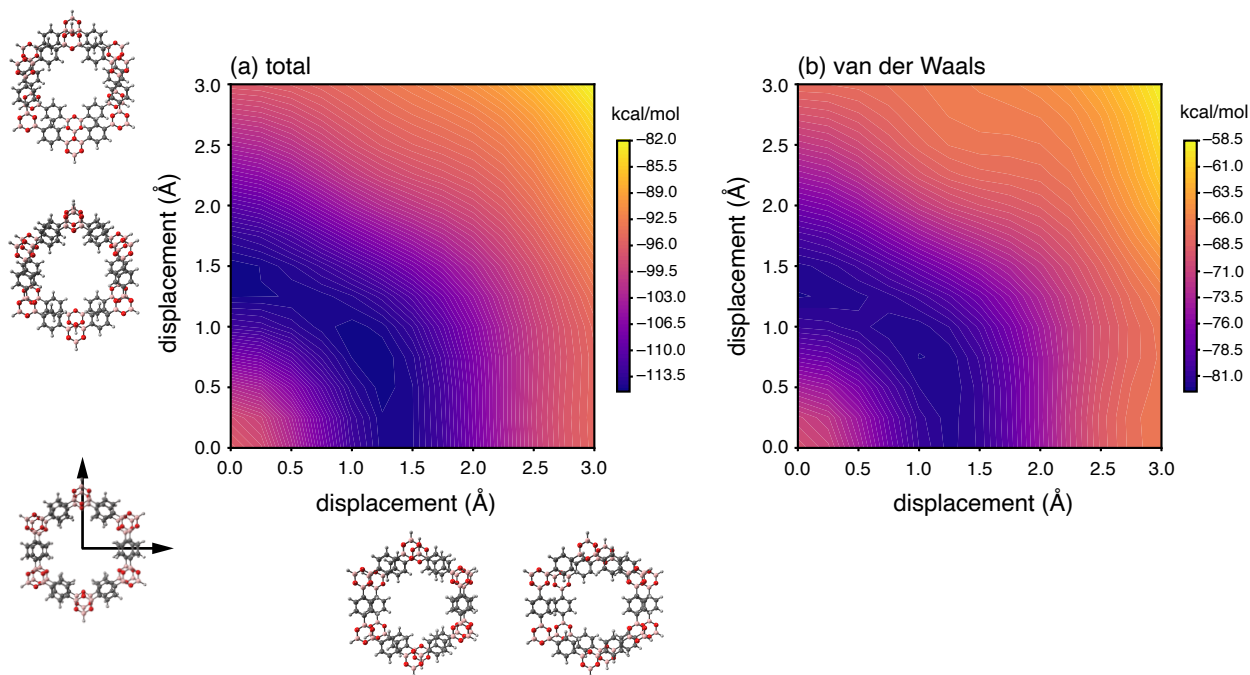


Fig. S14: Two-dimensional energy component surfaces for cofacial sliding of $(\text{COF1})_2$ at a fixed face-to-face separation of 3.28 Å: (a) total interaction energy E_{int} , and (b) vdW energy, E_{vdW} . (The two panels use different energy scales.) This is a close-up view of a part of the potential surface in Fig. 8. Contours were constructed using a two-dimensional mesh of points with a spacing of 0.25 Å.

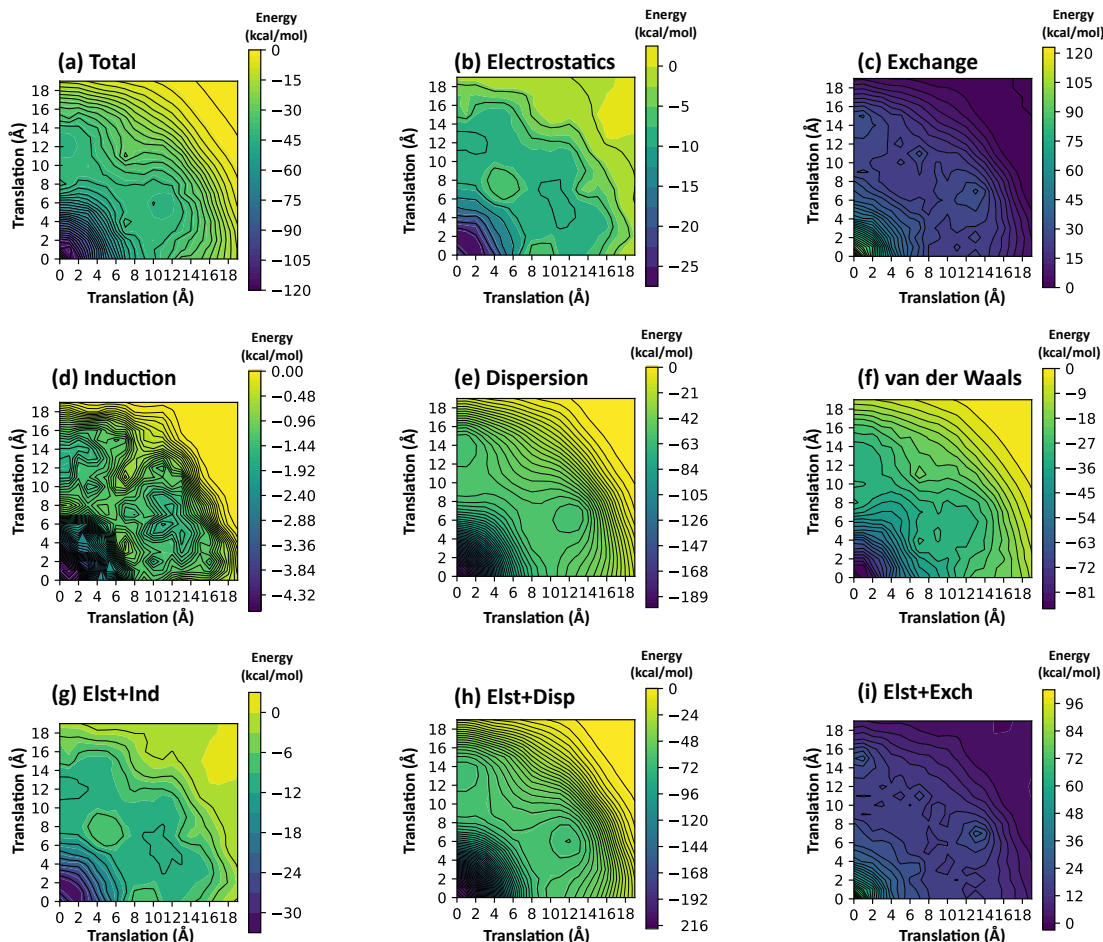


Fig. S15: Interaction potentials and energy components for $(\text{COF1})_2$, computed at the SAPT(PBE)+MBD/def2-SVP level of theory at a fixed face-to-face separation of 3.28 \AA . These are analogous to the plots in Fig. S10 but computed using the PBE functional within the SAPT(KS) formalism, so that E_{elst} represents quasi-classical electrostatics computed using a PBE description of the monomers.

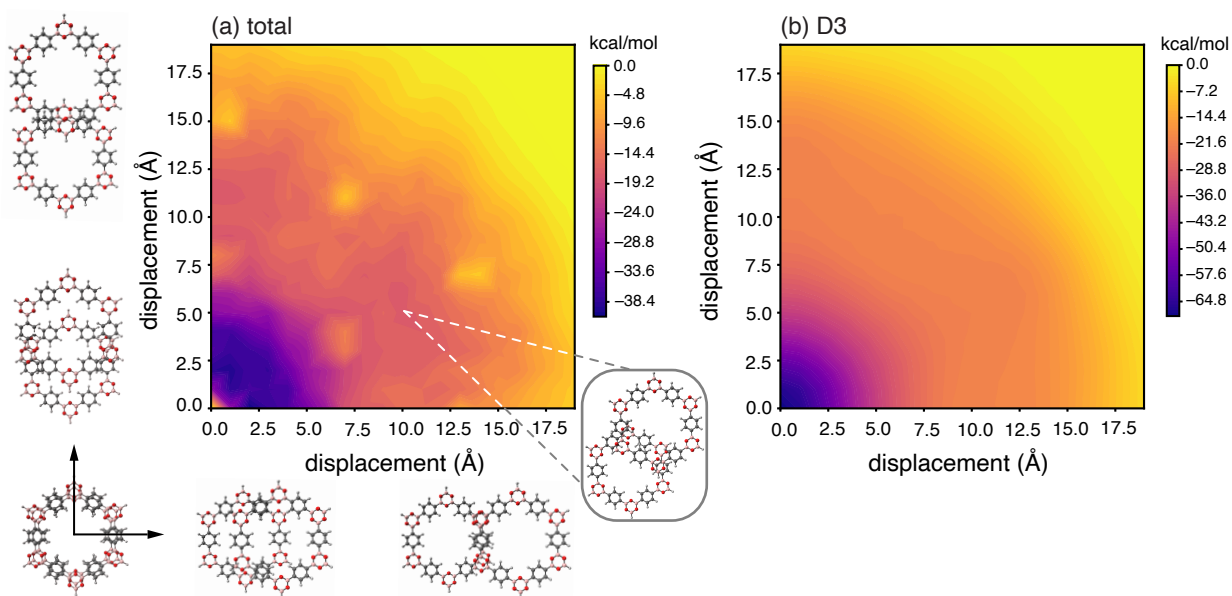


Fig. S16: Interaction potentials and energy components for $(\text{COF1})_2$, computed at the PBE+D3/def2-ma-SVP level of theory at a fixed face-to-face separation of 3.28 Å. (a) Total interaction energy computed by the supramolecular method ($E_{\text{int}} = E_{\text{AB}} - E_{\text{A}} - E_{\text{B}}$), including counterpoise correction. (b) Value of the D3 correction.

S3 Tables

Table S1: Interaction Energies (in kcal/mol) for dimer models of COF-1 without charge embedding.^a

Method	$(\Delta x, \Delta y)$ (Å)	(half-COF1) ₂		(COF1) ₂	
		E_{int}	relative	E_{int}	relative
SAPT0(LRC- ω PBE)+MBD	(0,0)	-38.7	0.0	-96.6	0.0
SAPT0(LRC- ω PBE)+MBD	(1,1)	-47.0	-8.4	-115.7	-19.0
SAPT0(LRC- ω PBE)+MBD	(5,5)	-21.7	+17.0	-50.2	+46.5
SAPT0(LRC- ω PBE)+MBD	(7,0)	-8.6	+30.0	-51.7	+45.0
SAPT0(LRC- ω PBE)+MBD	(0,7)	-20.6	+18.1	-45.5	+51.1
SAPT0(LRC- ω PBE)+MBD	(7,7)	-16.4	+22.3	-41.4	+55.3
XSAPT+MBD	(0,0)	-38.5	0.0	-96.2	0.0
XSAPT+MBD	(1,1)	-46.8	-8.3	-115.3	-19.1
XSAPT+MBD	(5,5)	-21.6	+16.9	-50.0	+46.2
XSAPT+MBD	(7,0)	-20.6	+17.9	-51.6	+44.6
XSAPT+MBD	(0,7)	-8.7	+29.8	-45.4	+50.8
XSAPT+MBD	(7,7)	-16.3	+22.2	-41.2	+55.0

^aThe def2-SVPD basis set was used for all calculations. XSAPT+MBD values include charge embedding and are the same as those in Table 1. The SAPT0(LRC- ω PBE)+MBD method does not include charge embedding but is otherwise the same.

Table S2: DFT supramolecular interaction energies (in kcal/mol) for (half-COF1)₂, computed using two different basis sets and several different functionals. All values include counterpoise correction.

$(\Delta x, \Delta y)$ (Å)	def2-ma-SVP			def2-TZVPD		
	PBE0+D4	PBE0+MBD	ω B97M-V	PBE0+D4	PBE0+MBD	ω B97M-V
(0,0)	-1.7	+1.4	-0.8	-2.7	+0.6	-3.4
(1,1)	-18.2	-16.8	-19.7	-19.7	-17.3	-21.4
(5,5)	-10.7	-9.7	-10.7	-10.9	-9.8	-11.0
(0,7)	-5.1	-5.2	-4.6	-5.2	-5.2	-4.6
(7,0)	-9.1	-7.9	-8.8	-9.5	-8.3	-9.3
(7,7)	-7.7	-6.8	-7.4	-8.0	-7.0	-7.8

Table S3: XSAPT+MBD interaction Energies (in kcal/mol) for (half-COF1)₂ using two different basis sets.

$(\Delta x, \Delta y)$ (Å)	def2-ma-SVP		def2-ma-TZVP	
	E_{int}	relative	E_{int}	relative
(0,0)	-38.6	0.0	-32.9	0.0
(1,1)	-46.4	-7.9	-42.9	-10.0
(5,5)	-21.7	+16.8	-18.8	+14.1
(0,7)	-20.5	+18.0	-19.0	+13.9
(7,0)	-8.4	+30.2	-7.9	+25.0
(7,7)	-16.4	+22.2	-15.2	+17.7