

Electronic Supplementary Information (ESI)

## **Analysis of intermolecular interactions of *n*-perfluoroalkanes with circumcoronene using dispersion-corrected DFT calculations: Comparison with those of *n*-alkanes**

Yoshihiro Kikkawa\*<sup>a</sup> and Seiji Tsuzuki \*<sup>b</sup>

<sup>a</sup> *National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba Central 5, 1-1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan*

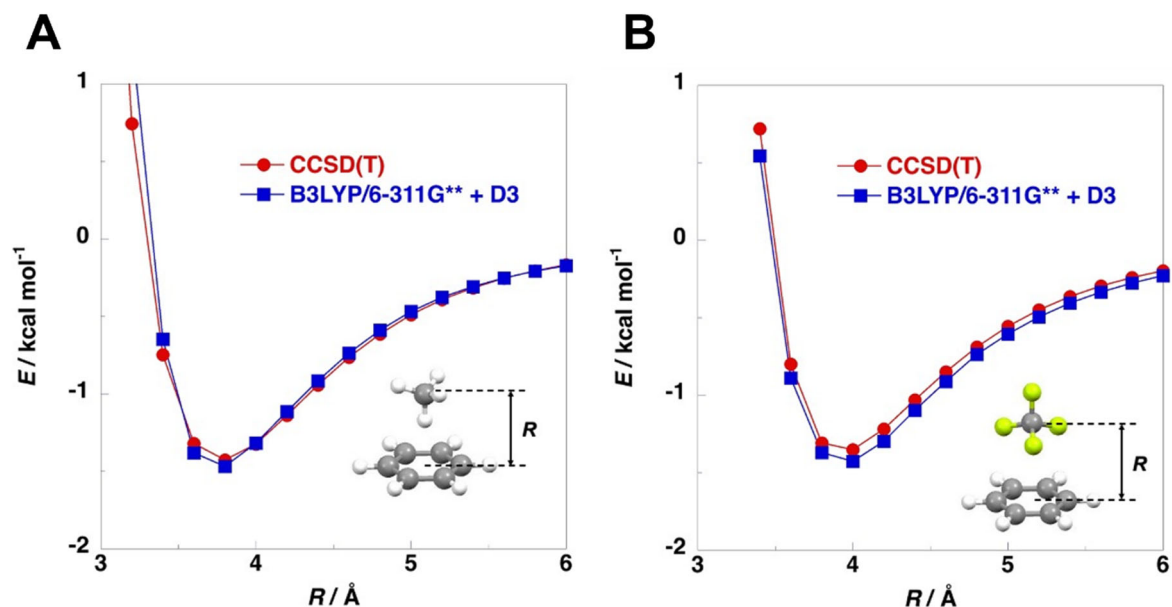
<sup>b</sup> *Department of Applied Physics, The University of Tokyo, Tokyo 113-8656, Japan*

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## 1. CCSD(T) calculations of interaction energy potential for C<sub>6</sub>H<sub>6</sub>-CF<sub>4</sub> complex and adsorption energies of *n*-alkanes on coronene

### 1.1 CCSD(T) calculations of C<sub>6</sub>H<sub>6</sub>-CF<sub>4</sub> complex

The interaction energy potentials calculated for the C<sub>6</sub>H<sub>6</sub>-CH<sub>4</sub> and C<sub>6</sub>H<sub>6</sub>-CF<sub>4</sub> complex by the DFT method used for this work were compared with the CCSD(T) level potentials at the basis set limit to confirm the accuracy of the DFT calculations. Interaction energy potentials calculated for C<sub>6</sub>H<sub>6</sub>-CH<sub>4</sub> and C<sub>6</sub>H<sub>6</sub>-CF<sub>4</sub> complexes are shown in Fig. S1. The procedure for calculating the CCSD(T) level interaction energy potential for the C<sub>6</sub>H<sub>6</sub>-CF<sub>4</sub> complex is shown below. Geometry optimisations were carried out at the MP2/cc-pVTZ level. The optimised geometries of isolated molecules were used for the calculations of the intermolecular interaction energies without further geometry optimisations. The BSSE was corrected by the counterpoise method. The MP2 level interaction energy at the basis set limit [ $E_{\text{MP2}(\text{limit})}$ ] was estimated from the interaction energies calculated at the MP2/aug-cc-pVDZ and MP2/aug-cc-pVTZ levels. The CCSD(T) level interaction energy at the basis set limit [ $E_{\text{CCSD(T)}(\text{limit})}$ ] was calculated from the  $E_{\text{MP2}(\text{limit})}$  and estimated CCSD(T) correction term [ $\Delta\text{CCSD(T)}$ ] at the basis set limit ( $\Delta\text{CCSD(T)}(\text{limit})$ ). The  $\Delta\text{CCSD(T)}$  is the difference between the calculated CCSD(T) and MP2 level interaction energies. The  $\Delta\text{CCSD(T)}(\text{limit})$  was estimated using the CCSD(T)/6-31G\* level calculations. The details of the estimation procedures of the  $E_{\text{MP2}(\text{limit})}$  and  $E_{\text{CCSD(T)}(\text{limit})}$  are explained below.



**Fig. S1** The interaction energy potentials calculated for the  $C_6H_6-CH_4$  and  $C_6H_6-CF_4$  complexes at the B3LYP/6-311G\*\* level with Grimme's D3 dispersion correction and estimated CCSD(T) interaction energy potentials at the basis set limit: (A)  $C_6H_6-CH_4$ ; (B)  $C_6H_6-CF_4$ . The  $C_6H_6-CH_4$  and  $C_6H_6-CF_4$  complexes have  $C_{3v}$  symmetry. The CCSD(T) level potential for the  $C_6H_6-CH_4$  complex was taken from ref. S1.

S1 S. Tsuzuki, T. Uchamaru, *Phys. Chem. Chem. Phys.*, 2020, **22**, 22508-22519.

## 1.2 CCSD(T) calculations of adsorption energies on coronene

The adsorption energies of methane, ethane and propane on coronene obtained by the DFT method used for this work were compared with those obtained by the CCSD(T) calculations to confirm the accuracy of the adsorption energies obtained by the DFT calculations. The procedure for calculating adsorption energies at the CCSD(T) level is shown below. Geometry optimisations were carried out at the MP2/cc-pVDZ level. The optimised geometry of isolated coronene was used for the calculations of the adsorption energies. Only the geometries of adsorbed molecules were optimised.

The BSSE was corrected by the counterpoise method in the calculations of the complexes. The adsorption energy ( $E_{\text{ad}}$ ) was calculated as the sum of the intermolecular interaction energy ( $E_{\text{int}}$ ) and the deformation energy ( $E_{\text{def}}$ ), which is the increase in energy of adsorbed molecule due to the deformation associated with the adsorption. The  $E_{\text{def}}$  was calculated at the MP2/cc-pVDZ level. The MP2 level interaction energy at the basis set limit [ $E_{\text{MP2}(\text{limit})}$ ] was estimated from the interaction energies calculated at the MP2/cc-pVDZ and MP2/cc-pVTZ levels. The CCSD(T) level interaction energy at the basis set limit [ $E_{\text{CCSD(T)}(\text{limit})}$ ] was calculated from the  $E_{\text{MP2}(\text{limit})}$  and estimated CCSD(T) correction term [ $\Delta\text{CCSD(T)}$ ] at the basis set limit ( $\Delta\text{CCSD(T)}(\text{limit})$ ). The  $\Delta\text{CCSD(T)}(\text{limit})$  was estimated using the CCSD(T)/6-31G\* level calculations. The estimated CCSD(T) level interaction energy at the basis set limit ( $E_{\text{CCSD(T)}(\text{limit})}$ ) was used as  $E_{\text{int}}$ . The  $E_{\text{ad}}$  was calculated from  $E_{\text{int}}$  and  $E_{\text{def}}$  ( $E_{\text{ad}} = E_{\text{int}} + E_{\text{def}}$ ).

The  $E_{\text{MP2}(\text{limit})}$  was estimated from the interaction energies calculated at the MP2/cc-pVDZ and MP2/cc-pVTZ levels. The  $E_{\text{CCSD(T)}(\text{limit})}$  was calculated from the  $E_{\text{MP2}(\text{limit})}$  and  $\Delta\text{CCSD(T)}(\text{limit})$ . The  $\Delta\text{CCSD(T)}(\text{limit})$  was estimated using the CCSD(T)/6-31G\* level calculations. The details of the estimation procedures of the  $E_{\text{MP2}(\text{limit})}$  and  $E_{\text{CCSD(T)}(\text{limit})}$  are explained below. The calculated  $E_{\text{MP2}(\text{limit})}$ ,  $E_{\text{CCSD(T)}(\text{limit})}$ ,  $E_{\text{def}}$  and  $E_{\text{ad}}$  for adsorption of methane, ethane, propane on coronene are summarized in Table S1. In addition, comparison between the  $E_{\text{ad}}$  of *n*-alkanes on coronene obtained by CCSD(T) and that of dispersion corrected DFT calculations is shown in Table S2.

**Table S1** Interaction energies ( $E_{\text{int}}$ ), deformation energies ( $E_{\text{def}}$ ) and adsorption energies ( $E_{\text{ad}}$ ) calculated for adsorbed methane, ethane and propane on coronene<sup>a</sup>

Complex <sup>b</sup>	$E_{\text{int}}$							$E_{\text{def}}^{\text{c}}$	$E_{\text{ad}}^{\text{d}}$
	MP2/ cc-pVDZ	MP2/ cc-pVTZ	MP2 (limit) <sup>e</sup>	HF/ 6-31G*	MP2/ 6-31G*	CCSD(T)/ 6-31G*	CCSD(T) (limit) <sup>f</sup>		
coronene-CH <sub>4</sub> A	1.170	-2.449	-2.830	1.191	-1.000	-0.469	-1.861	0.000	-1.860
coronene-CH <sub>4</sub> B	1.367	-3.107	-3.618	1.485	-1.084	-0.502	-2.488	0.005	-2.483
coronene-CH <sub>4</sub> C	1.469	-3.262	-3.804	1.580	-1.133	-0.510	-2.594	0.004	-2.590
coronene-C <sub>2</sub> H <sub>6</sub> D	2.493	-5.204	-5.948	2.561	-2.240	-1.082	-3.913	0.004	-3.910
coronene-C <sub>3</sub> H <sub>8</sub> E	3.576	-7.449	-8.454	3.636	-3.397	-1.658	-5.480	0.018	-5.462

<sup>a</sup> Energy in kcal mol<sup>-1</sup>.

<sup>b</sup> Geometries of complexes are shown in Fig. S2.

<sup>c</sup> Deformation energy of alkanes associated with adsorption.

<sup>d</sup> Adsorption energy ( $E_{\text{ad}} = E_{\text{int}} + E_{\text{def}}$ ).

<sup>e</sup> Estimated MP2 level interaction energy at the basis set limit.

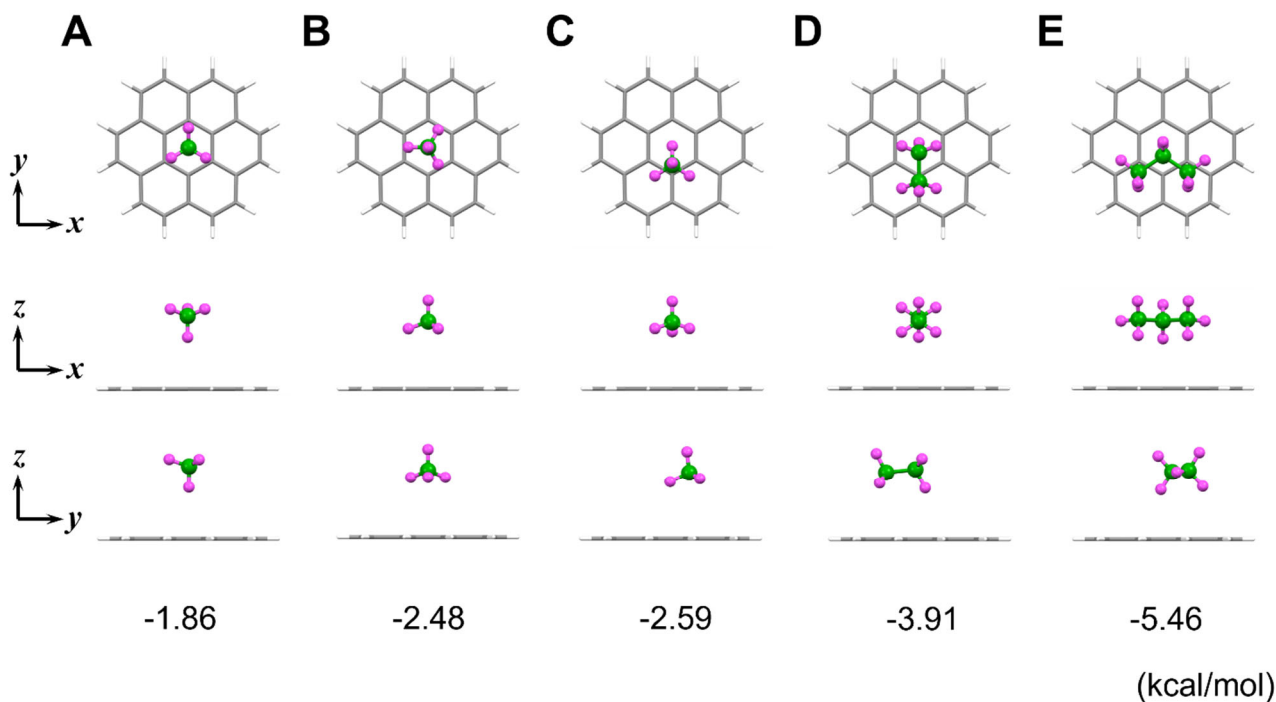
<sup>f</sup> Estimated CCSD(T) level interaction energy at the basis set limit.

**Table S2** Adsorption energies of alkanes on coronene obtained by CCSD(T) and dispersion corrected DFT calculations<sup>a</sup>

Complex	CCSD(T) <sup>b</sup>	B3LYP/6-311G** + D3
coronene-CH <sub>4</sub> A	-1.86	-2.29
coronene-CH <sub>4</sub> B	-2.48	-2.92
coronene-CH <sub>4</sub> C	-2.59	-2.91
coronene-C <sub>2</sub> H <sub>6</sub> D	-3.91	-4.50
coronene-C <sub>3</sub> H <sub>8</sub> E	-5.46	-6.26

<sup>a</sup> Energy in kcal mol<sup>-1</sup>.

<sup>b</sup> CCSD(T) level interaction energy at the basis set limit.



**Fig. S2** Optimised geometries of alkanes on coronene obtained by MP2 calculations and their estimated CCSD(T) level adsorption energies ( $E_{ad}$ ) at the basis set limit: (A, B, C) methane; (D) ethane; (E) propane. The carbon and hydrogen atoms in adsorbed alkanes are coloured in green and pink, respectively.

### 1.3 Estimation of CCSD(T) level interaction energies at the basis set limit.

The MP2 level interaction energy at the basis set limit [ $E_{MP2(\text{limit})}$ ] for the complex was obtained by Helgaker et al.'s method (ref. S2) from the MP2 interaction energies ( $E_{MP2}$ ) obtained using the cc-pVDZ and cc-pVTZ (or aug-cc-pVDZ and aug-cc-pVTZ) basis sets. In Helgaker et al.'s method the calculated  $E_{MP2}$  were fitted to a form  $a + b X^{-3}$  (where  $X$  is 2 for cc-pVDZ and 3 for cc-pVTZ). The  $E_{MP2(\text{limit})}$  was then calculated by an extrapolation. Helgaker et al.'s method was originally proposed for calculating the electron correlation contribution at the basis set limit. But we used this method to calculate the  $E_{MP2(\text{limit})}$ , since the basis set dependence of HF level interaction energy ( $E_{HF}$ ) is small.

The CCSD(T) level interaction energy at the basis set limit [ $E_{\text{CCSD(T)}(\text{limit})}$ ] for the complex was obtained according to equation (1)

$$E_{\text{CCSD(T)}(\text{limit})} = E_{\text{MP2}(\text{limit})} + \Delta\text{CCSD(T)}(\text{limit}) \quad (1)$$

where  $\Delta\text{CCSD(T)}(\text{limit})$  denotes the CCSD(T) correction term [ $\Delta\text{CCSD(T)}$ ] at the basis set limit. The  $\Delta\text{CCSD(T)}$  [=  $E_{\text{CCSD(T)}} - E_{\text{MP2}}$ ] is the difference between the CCSD(T) level interaction energy [ $E_{\text{CCSD(T)}}$ ] and the MP2 level interaction energy ( $E_{\text{MP2}}$ ). The  $\Delta\text{CCSD(T)}(\text{limit})$  was obtained by equation (2)

$$\Delta\text{CCSD(T)}(\text{limit}) = \Delta\text{CCSD(T)}(\text{M}) + \Delta(\text{M})\Delta\text{CCSD(T)}, \quad (2)$$

where  $\Delta\text{CCSD(T)}(\text{M})$  denotes  $\Delta\text{CCSD(T)}$  obtained using a Medium size basis set. The 6-31G\* basis set was used for the Medium size basis set in this work. The  $\Delta\text{CCSD(T)}$  has a weak basis set dependence.  $\Delta(\text{M})\Delta\text{CCSD(T)}$  is a correction term for slight underestimation of the  $\Delta\text{CCSD(T)}$  by the Medium size basis set. The  $\Delta(\text{M})\Delta\text{CCSD(T)}$  corresponds to a difference between the  $\Delta\text{CCSD(T)}(\text{limit})$  and  $\Delta\text{CCSD(T)}(\text{M})$ .

We can calculate the  $\Delta(\text{M})\Delta\text{CCSD(T)}$ , if we know the value of  $F_{\text{corr}(\text{M})}$ , which is defined by equation (3)

$$F_{\text{corr}(\text{M})} = \Delta\text{CCSD(T)}(\text{M})/\Delta\text{CCSD(T)}(\text{limit}) \quad (3).$$

From equations (2) and (3) we can obtain equation (4)

$$\Delta(\text{M})\Delta\text{CCSD(T)} = \Delta\text{CCSD(T)}(\text{M}) \times (1 - F_{\text{corr}(\text{M})})/F_{\text{corr}(\text{M})} \quad (4).$$

We calculated the  $F_{\text{corr(M)}}$  value by equation (5) in this work

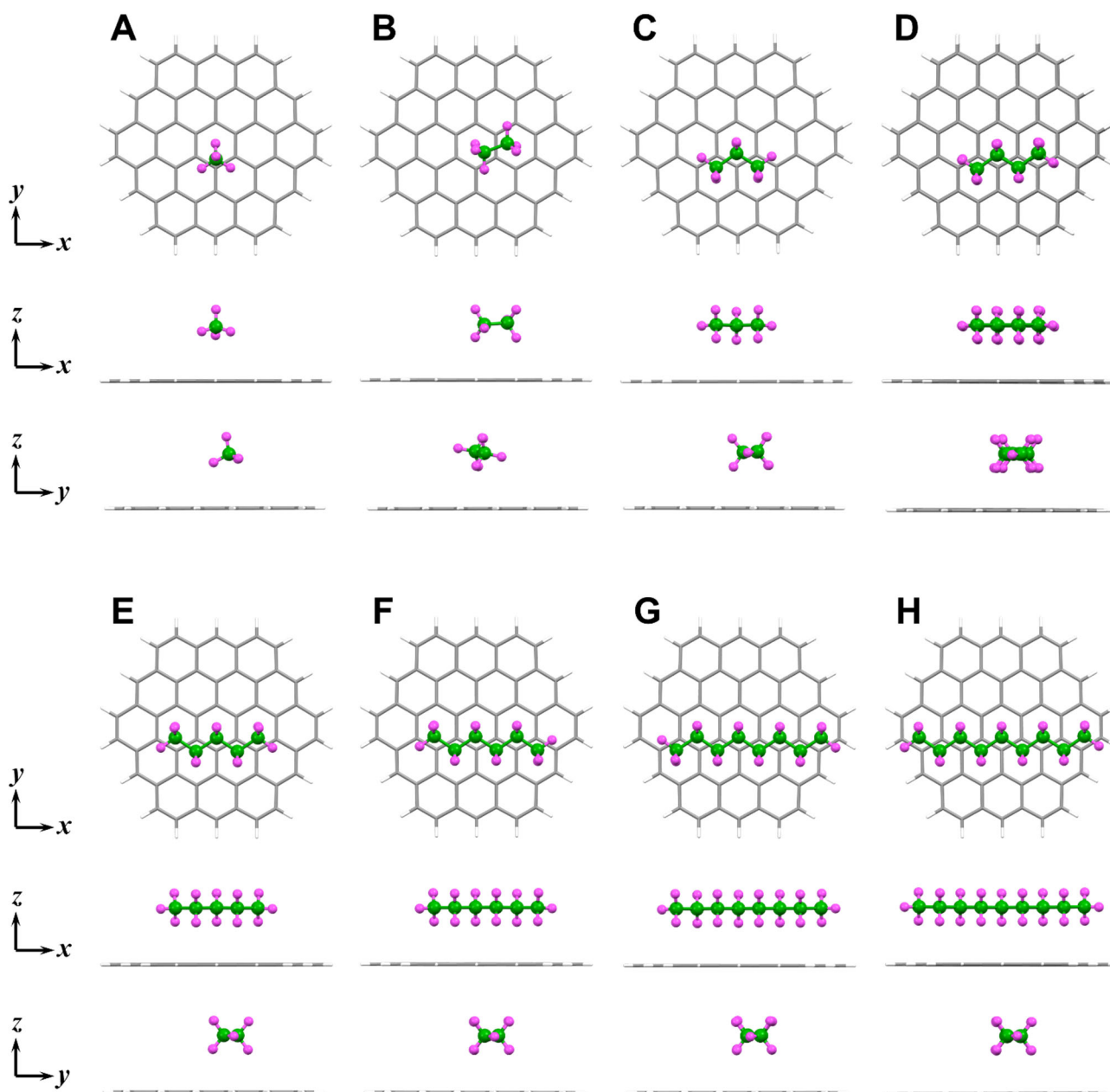
$$F_{\text{corr(M)}} = E_{\text{corr(MP2)(M)}}/E_{\text{corr(MP2)(limit)}} \quad (5),$$

where the  $E_{\text{corr(MP2)(M)}}$  denotes the MP2 level electron correlation effect on the calculated interaction energy ( $E_{\text{corr(MP2)}} = E_{\text{MP2}} - E_{\text{HF}}$ ) using the medium size basis set. The  $E_{\text{corr(MP2)(limit)}}$  denotes the MP2 level electron correlation effect at the basis set limit ( $= E_{\text{MP2(limit)}} - E_{\text{HF(limit)}}$ ). We can obtain sufficiently accurate  $F_{\text{corr(M)}}$  value by equation (5), if the basis set dependence of the CCSD(T) level electron correlation effect is close to that of  $E_{\text{corr(MP2)}}$ . The  $E_{\text{HF}}$  calculated using the cc-pVTZ basis set was used as the  $E_{\text{HF(limit)}}$ , since the basis set dependence of the  $E_{\text{HF}}$  beyond the cc-pVTZ basis set is small.

S2 T. Helgaker, W. Klopper, H. Koch, J. Noga, *J. Chem. Phys.*, 1997, **106**, 9639-9646.



## 2. Optimised geometries of *n*-alkanes on circumcoronene



**Fig. S3** Optimised geometries of *n*-alkanes on circumcoronene: (A) methane; (B) ethane; (C) propane; (D) *n*-butane; (E) *n*-pentane; (F) *n*-hexane; (G) *n*-octane; and (H) *n*-nonane. The carbon and hydrogen atoms in adsorbed *n*-alkanes are coloured in green and pink, respectively.

### 3. Numerical data of adsorption and interaction energies<sup>a</sup>

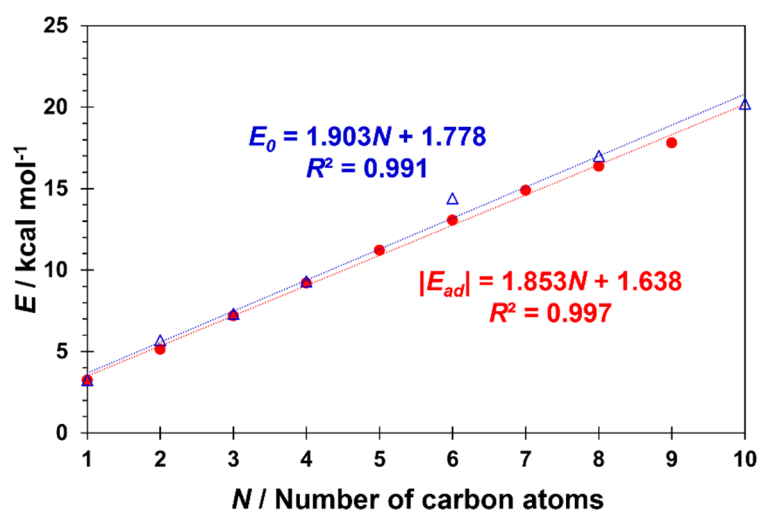
**Table S3** Adsorption energies ( $E_{\text{ad}}$ ) of single  $n$ -alkane and  $n$ -perfluoroalkane, and interaction energies between two adsorbed molecules ( $E_{\text{dim}}$ )

		$N$ / Number of carbon atoms								
		1	2	3	4	5	6	7	8	9
$n$ -alkane	$E_{\text{ad}}$	-3.25	-5.15	-7.19	-9.20	-11.22	-13.06	-14.90	-16.37	-17.80
	$E_{\text{dim}}$	-0.41	-1.17	-1.34	-1.86	-2.41	-2.98	-3.53		
$n$ -perfluoroalkane	$E_{\text{ad}}$	-3.55	-4.46	-5.71	-7.15	-8.20	-9.05	-9.75	-10.21	-10.84
	$E_{\text{dim}}$	-0.43	-1.00	-1.28	-1.79	-2.39	-2.96	-3.36		

<sup>a</sup> Energy in kcal mol<sup>-1</sup>.

#### 4. Comparison between the adsorption/desorption energies by DFT calculations and TPD experiments

Tait et al.<sup>S3</sup> studied the desorption of *n*-alkanes from graphene surface by TPD measurements. The original experimental data ( $E_{des}$ ) was converted to the desorption energy ( $E_0$ ) of an isolated *n*-alkanes from the surface of defect-free graphene. Since the present DFT calculation of  $E_{ad}$  was performed on isolated *n*-alkanes and circumcoronene without defect, the  $E_0$  and absolute value of  $E_{ad}$  was compared. Fig. S4 shows the plots of the  $E_0$  and  $E_{ad}$  as a function of carbon numbers ( $N$ ) in the *n*-alkanes. The values of  $|E_{ad}|$  were very close to that of  $E_0$ , and the increase in  $E_{ad}$  per  $\text{CH}_2$  unit ( $\Delta|E_{ad}| = 1.85 \text{ kcal mol}^{-1}$ ) was almost identical to that in  $\Delta E_0$  ( $1.90 \text{ kcal mol}^{-1}$ ). Even in the original TPD data which include the effects of surface defect of graphene and intermolecular interactions between adsorbed molecules,  $E_{des}$  per  $\text{CH}_2$  unit ( $\Delta E_{des}$ ) is calculated to be  $2.03 \text{ kcal mol}^{-1}$ , referring to the Table III in ref. S3. The good agreement with the experiments indicates that the adsorption energies of *n*-alkanes on graphite obtained by our DFT calculations are reliable.

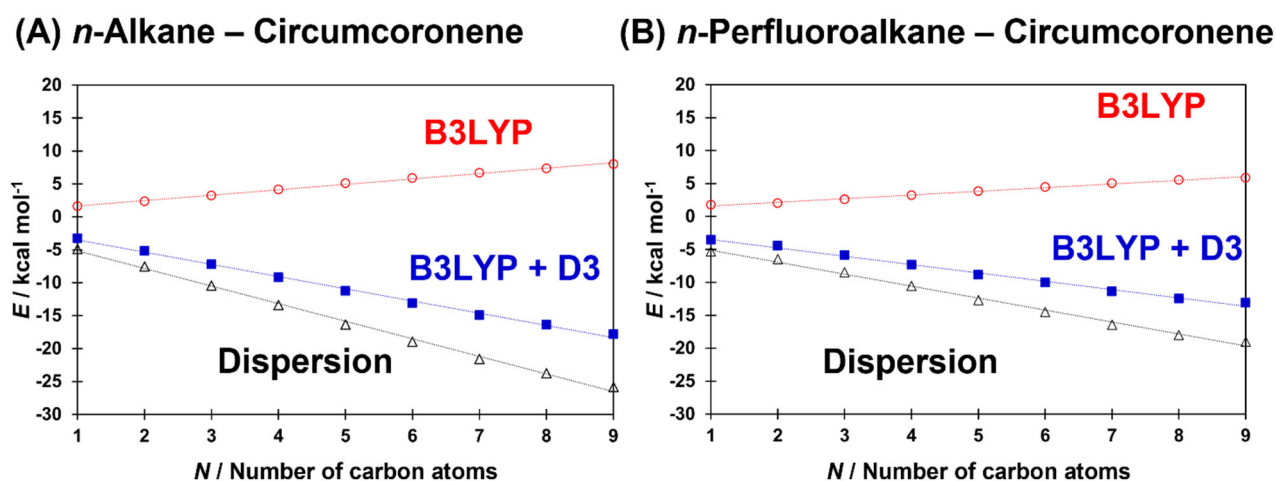


**Fig. S4** Plots of experimental  $E_0$  (blue triangles) and calculated  $|E_{ad}|$  (red circles) as a function of carbon numbers ( $N$ ) in the *n*-alkanes. The data of  $E_0$  was obtained from Table IV in ref. S3.

S3 S. L. Tait, Z. Dohnálek, C.T. Campbell, and B. D. Kay, *J. Chem. Phys.*, 2006, **125**, 234308-1-15.

## 5. Contribution of dispersion interactions to the stabilisation of the adsorbed molecules

In order to evaluate the contributions of dispersion interactions to the stabilisation of the adsorbed molecules, interaction energies of *n*-alkanes and *n*-perfluoroalkanes calculated with and without dispersion correction are compared. The calculated interaction energies for *n*-alkanes and *n*-perfluoroalkane are shown in Figs. S5A and S5B, respectively. The interaction energies calculated with dispersion correction are attractive, while those without dispersion correction are repulsive. Extremely large contributions of dispersion interactions (difference between the interaction energies calculated with and without dispersion correction) clearly shows that the dispersion interactions are mainly responsible for the stabilisation of adsorbed molecules.



**Fig. S5** Interaction energies between adsorbed molecules and circumcoronene ( $E_{\text{int}}$ ) calculated with (B3LYP + D3: blue squares) and without dispersion correction (B3LYP: red circles), and contributions of dispersion interactions (difference between the interaction energies calculated with and without dispersion correction: black triangles): (A) *n*-alkanes; (B) *n*-perfluoroalkanes.

The contribution of each energy term was further investigated for the optimised geometries of *n*-pentane/circumcoronene and *n*-perfluoropentane/circumcoronene complexes as summarized in Table 1. The electrostatic ( $E_{\text{es}}$ ) and induction ( $E_{\text{ind}}$ ) energies were calculated using the ORIENT version

3.2.<sup>S4</sup> The electrostatic energy of complex was calculated as interactions between distributed multipoles of molecules. Distributed multipoles<sup>S5, S6</sup> up to hexadecapole on all atoms were obtained from the B3LYP/6-311G\*\* wave functions of an isolated molecule using the GDMA program.<sup>S7</sup> The induction energy was calculated as interactions of polarizable sites with the electric field produced by the distributed multipoles of monomers.<sup>S8</sup> The atomic polarizabilities of carbon ( $a = 10$  au) and fluorine ( $a = 3$  au) were used for the calculations.<sup>S9</sup> Distributed multipoles were used only to estimate the electrostatic and induction energies. The B3LYP/6-311G\*\* level interaction energy without the dispersion correction ( $E_{b3lyp}$ ) is approximately the sum of the electrostatic, induction and the short-range (orbital-orbital) interaction energies ( $E_{short}$ ), since DFT calculations using the B3LYP functional cannot evaluate the dispersion interactions. The  $E_{short}$  was calculated according to equation ( $E_{short} = E_{b3lyp} - E_{es} - E_{ind}$ ). The dispersion energy ( $E_{disp}$ ) was calculated as the difference between the calculated interaction energy with the dispersion correction ( $E_{int}$ ) and that without the dispersion correction ( $E_{b3lyp}$ ) according to equation ( $E_{disp} = E_{int} - E_{b3lyp}$ ).

The dispersion interactions are the major source of the attraction in both complexes. The contributions of the electrostatic and induction interactions are negligible, despite the large bond dipole of C-F bonds in *n*-perfluoropentane.

S4 A. J. Stone, A. Dullweber, M. P. Hodges, P. L. A. Popelier, D. J. Wales, *Orient: a program for studying interactions between molecules version 3.2*. University of Cambridge, **1995**.

S5 A. J. Stone, M. Alderton, *Mol. Phys.* **1985**, *56*, 1047-1064.

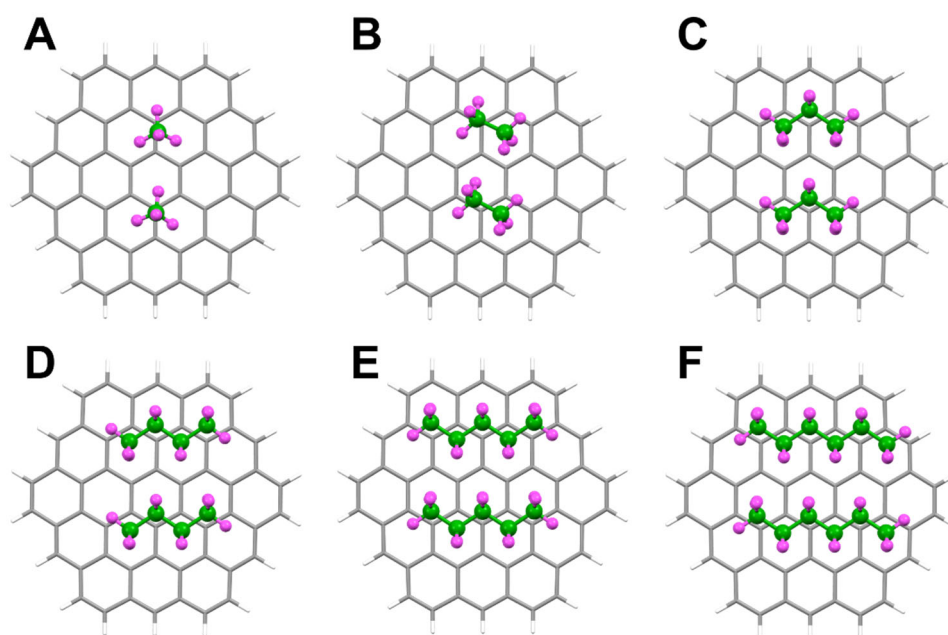
S6 A. J. Stone, *The theory of intermolecular forces*, second edition; Oxford University Press: Oxford, **2013**.

S7 A. J. Stone, *J. Chem. Theory Comput.* **2005**, *1*, 1128-1132.

S8 A. J. Stone, *Mol. Phys.* **1985**, *56*, 1065-1082.

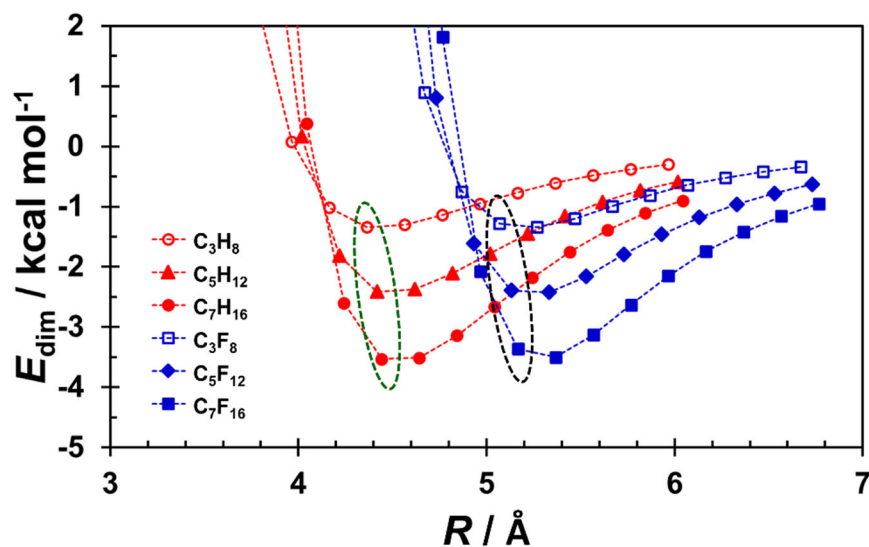
S9 P. T. van Duijnen, M. Swart, *J. Phys. Chem. A* **1998**, *102*, 2399-2407.

## 6. Optimised geometries of *n*-alkane dimers on circumcoronene



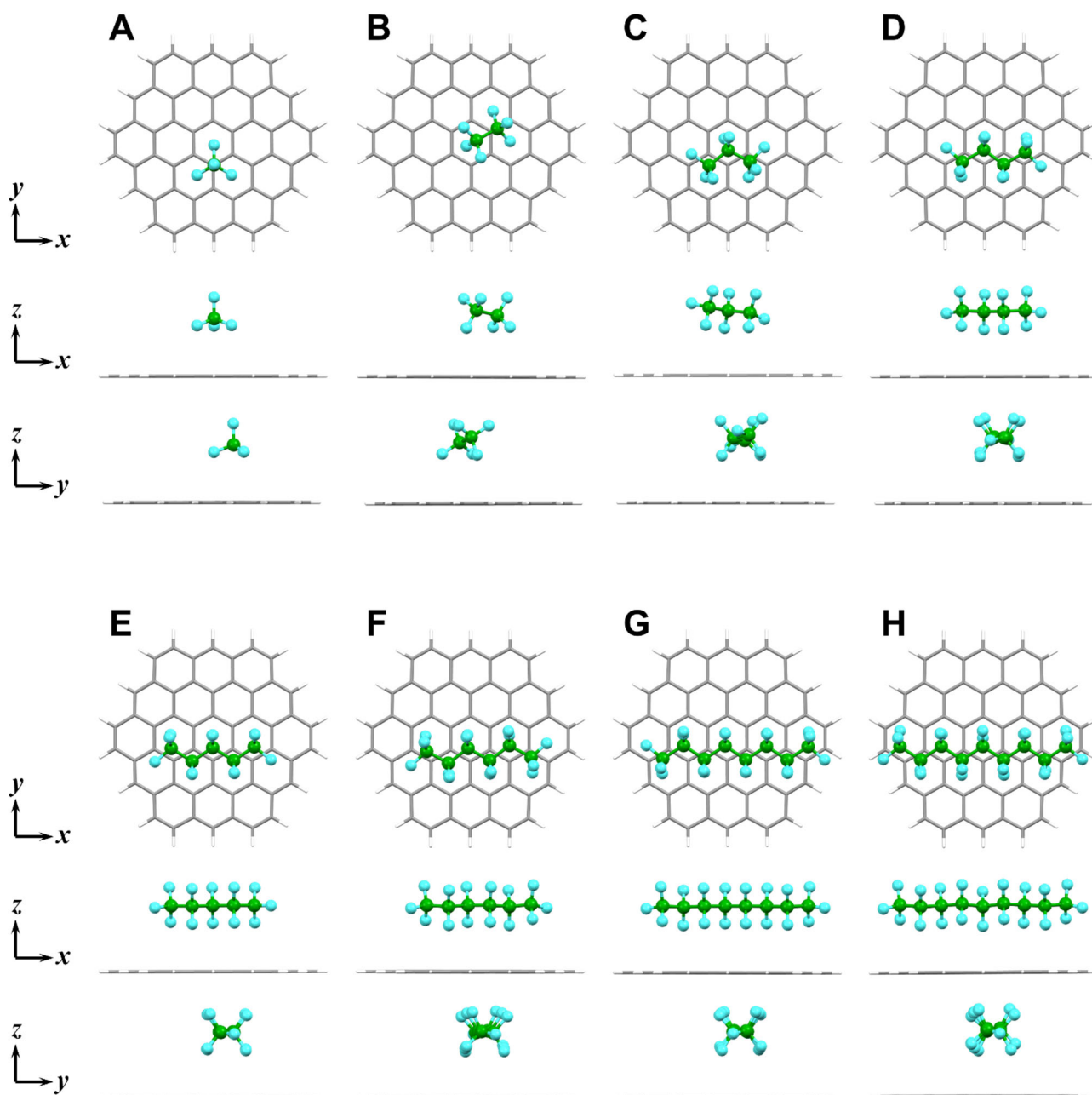
**Fig. S6** Optimised geometries of *n*-alkane dimers on circumcoronene: (A) methane; (B) ethane; (C) propane; (D) butane; (E) pentane; and (F) hexane. The carbon and hydrogen atoms in adsorbed *n*-alkanes are coloured in green and pink, respectively.

## 7. Intermolecular interaction energies between two *n*-alkanes and *n*-fluoroalkanes



**Fig. S7** Intermolecular interaction energies ( $E_{\text{dim}}$ ) between two *n*-alkanes (red) and *n*-fluoroalkanes (blue) calculated by changing the intermolecular distances of the adsorbed dimer geometries.  $R$  is the distance from the plane of circumcoronene. The distances between the two *n*-alkanes adsorbed on circumcoronene are in green circle ( $\sim 4.4$  Å), whereas those between the *n*-fluoroalkanes are in black circle ( $\sim 5.1$  Å).

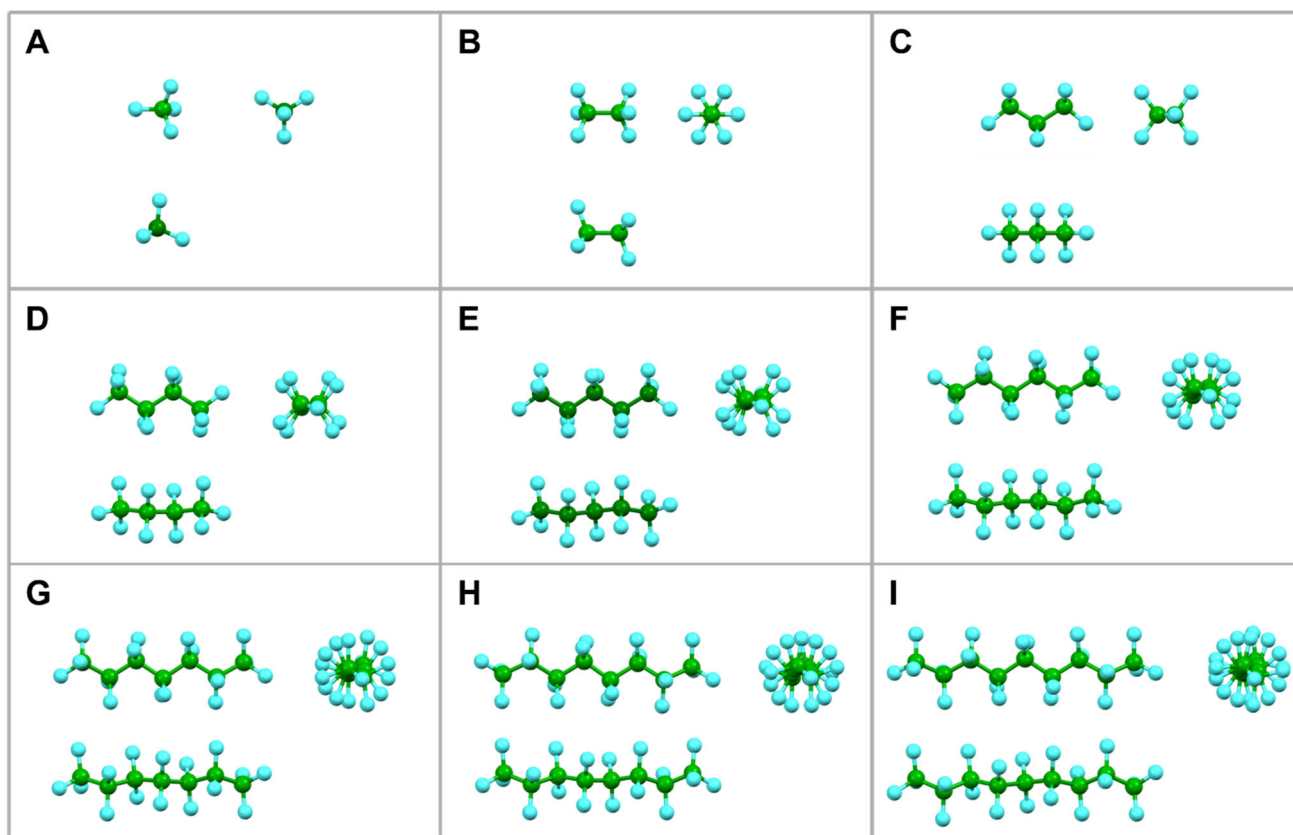
## 8. Optimised geometries of *n*-perfluoroalkanes on circumcoronene



**Fig. S8** Optimised geometries of *n*-perfluoroalkanes on circumcoronene: (A) perfluoromethane; (B) perfluoroethane; (C) perfluoropropane; (D) *n*-perfluorobutane; (E) *n*-perfluoropentane; (F) *n*-perfluorohexane; (G) *n*-perfluorooctane; and (H) *n*-perfluorononane. The carbon and fluorine atoms in adsorbed *n*-perfluoroheptane are coloured in green and cyan, respectively.



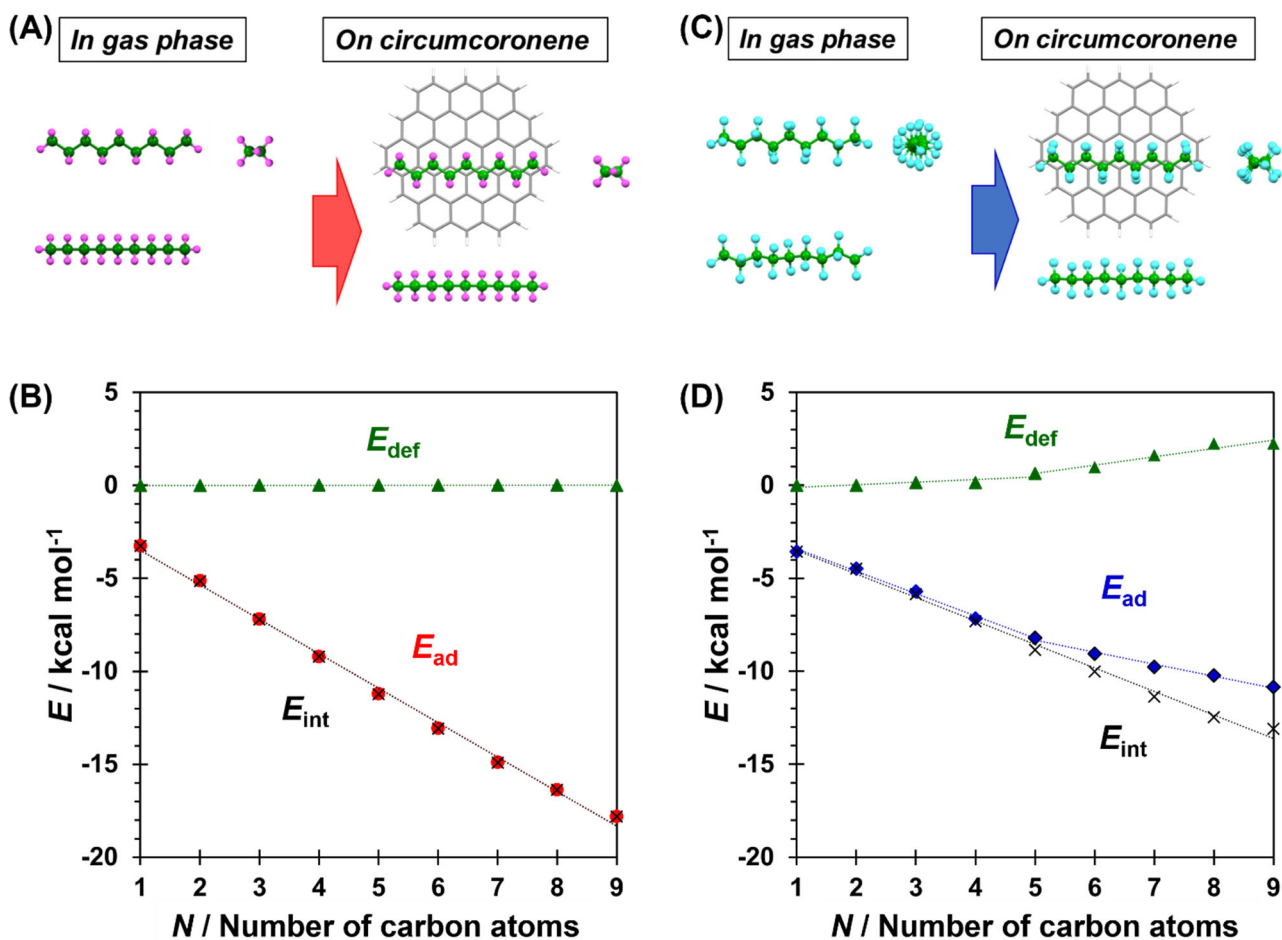
## 9. Optimised geometries of isolated *n*-perfluoroalkanes



**Fig. S9** Optimised geometries of isolated *n*-perfluoroalkanes: (A) perfluoromethane; (B) perfluoroethane; (C) perfluoropropane; (D) *n*-perfluorobutane; (E) *n*-perfluoropentane; (F) *n*-perfluorohexane; (G) *n*-perfluoroheptane; (H) *n*-perfluorooctane; and (I) *n*-perfluorononane. The carbon and fluorine atoms in adsorbed *n*-perfluoroheptane are coloured in green and cyan, respectively.

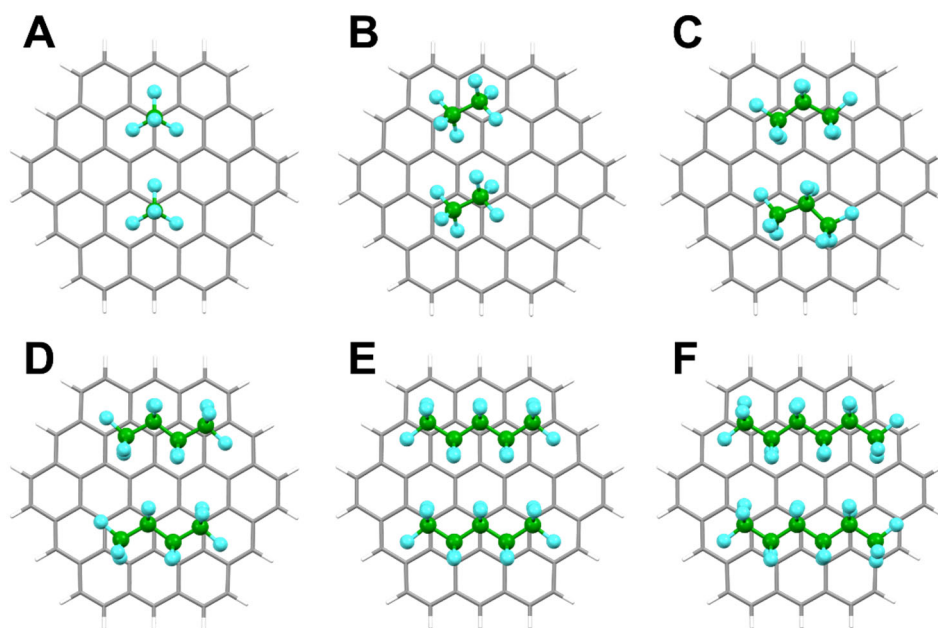
## 10. Effect of molecular deformation on the adsorption energies

Optimised geometries of isolated *n*-nonane and optimised geometries of *n*-nonane adsorbed on circumcoronene (Fig. S10A) indicate that the conformation does not largely change associated with the adsorption. This is also the case for the other *n*-alkanes, indicating that the deformation energy ( $E_{\text{def}}$ , the difference between  $E_{\text{int}}$  and  $E_{\text{ad}}$ ) calculated for *n*-alkanes are negligible (Fig. S10B). In contrast, the conformation of *n*-perfluorononane significantly changes associated with the adsorption. Optimised geometry of isolated *n*-perfluorononane has helical conformation, while that adsorbed on circumcoronene is nearly planar (Fig. S10C). Similar conformational changes are observed associated with the adsorption when the number of carbon atoms ( $N$ ) of *n*-perfluoroalkanes are 5-9 (see. Figs. S8 and S9). Owing to the large conformational changes, long *n*-perfluoroalkanes ( $N = 5-9$ ) have large  $E_{\text{def}}$ . Therefore, the slope of  $E_{\text{ad}}$  (sum of  $E_{\text{int}}$  and  $E_{\text{def}}$ ) for long *n*-perfluoroalkanes ( $N = 5-9$ ) is different from that for short *n*-perfluoroalkanes ( $N = 1-5$ ), although  $E_{\text{int}}$  becomes larger (more negative) linearly (Fig. S10D).



**Fig. S10** Optimised geometries of isolated *n*-nonane and *n*-perfluorononane, optimised geometries of *n*-nonane and *n*-perfluorononane adsorbed on circumcoronene, interaction energies ( $E_{\text{int}}$ ) between adsorbed molecule and circumcoronene, adsorption energies ( $E_{\text{ad}}$ ) of *n*-nonane and *n*-perfluorononane, and deformation energies ( $E_{\text{def}}$ ) of adsorbed molecules: (A) Optimised geometries of *n*-nonane; (B)  $E_{\text{int}}$  (cross),  $E_{\text{ad}}$  (red circle) and  $E_{\text{def}}$  (green triangle) calculated for *n*-alkanes; (C) Optimised geometries of *n*-perfluorononane; (D)  $E_{\text{int}}$  (cross),  $E_{\text{ad}}$  (blue rhombus) and  $E_{\text{def}}$  (green triangle) calculated for *n*-perfluoroalkanes.

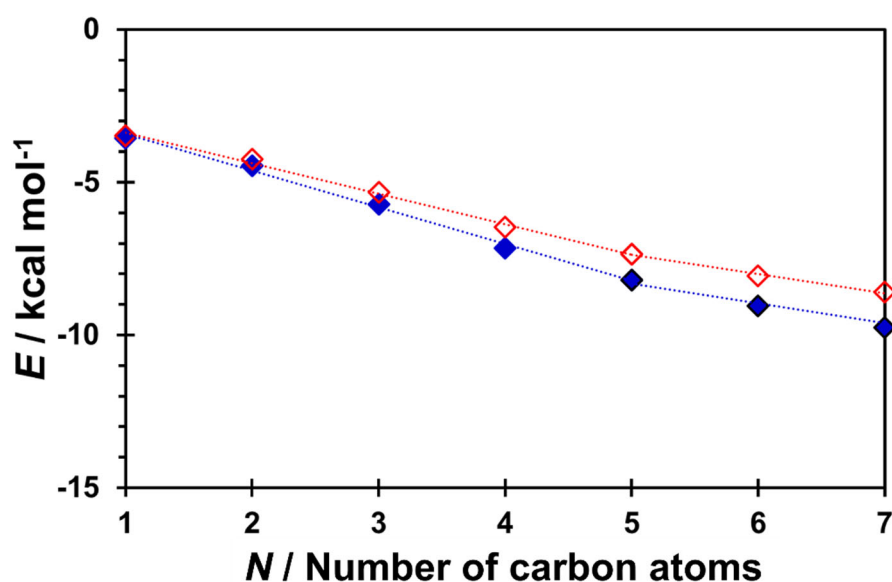
## 11. Optimised geometries of *n*-perfluoroalkane dimers on circumcoronene



**Fig. S11** Optimised geometries of *n*-perfluoroalkane dimers on circumcoronene: (A) perfluoromethane; (B) perfluoroethane; (C) perfluoropropane; (D) *n*-perfluorobutane; (E) *n*-perfluoropentane; and (F) *n*-perfluorohexane. The carbon and fluorine atoms in adsorbed *n*-perfluoroheptane are coloured in green and cyan, respectively.

## 12. Adsorption energies of *n*-perfluoroalkanes calculated using optimised geometries of adsorbed single molecules and those of adsorbed dimers

The adsorption energies calculated for one of adsorbed molecules using optimised geometries of adsorbed *n*-perfluoroalkane dimers are smaller (less negative) than those calculated using the optimised geometries of adsorbed single molecules. The longer the chain length, the greater the difference. The intermolecular distance between two adsorbed *n*-perfluoroalkane in the optimised structures ( $\sim 5.1$  Å) is longer than the width of two units of benzene in circumcoronene (4.3 Å). Apparently, the lattice mismatch destabilizes the adsorbed *n*-perfluoroalkane dimers.



**Fig. S12** Adsorption energies calculated for *n*-perfluoroalkanes using optimised geometries of single *n*-perfluoroalkanes adsorbed on circumcoronene (blue rhombi), and those calculated for one of adsorbed molecules (near the centre of circumcoronene) using optimised geometries of adsorbed *n*-perfluoroalkane dimers (red rhombi). The geometries of adsorbed dimers are shown in Figs. 3B and S11.