

Supporting Information

Size Effect in the Ionization Energy of PAH Clusters

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I- On the dissociative ionization of PAH clusters

We have stated in the experimental methodology of the main text that the spectra shown in Figure 2 are not affected by dissociative ionization, as verified by ion imaging experiments, performed in coincidence (in-situ) in the case of pyrene clusters, and on a separate experiment (not coincident with the electron information) in the case of coronene clusters. The fragmentation of cationic PAH clusters is out of the scope of the current article and will be the subject of a future article. Nevertheless we elaborate here a bit further on the experimental methodology. Figure S1 shows an example of the ion image recorded for the pyrene tetramer at a photon energy of 7.2 eV with the DELICIOUS 3 spectrometer (see Ref. 26 of main text). From the lateral displacement of the ions, the velocity of the molecular beam is measured at about 650 m/sec. The same value is extracted for the argon carrier gas mass-selected ion image, which is consistent with a beam temperature of about 100K. Even though the mean velocity is the same for all species in the molecular beam, the same cannot be said for the translational temperature, or velocity spread. Indeed, evaporation processes occurring in the molecular beam $M_N \rightarrow M_{N-1} + M$ lead to a temperature gradient in which the larger clusters possess translational temperatures close to the carrier gas, while the smaller clusters are expected to be translationally hotter. Indeed, from the kinetic energy release distribution (KERD) shown in Fig. S1 below, a temperature of ~ 140 K is deduced for the tetramer, already slightly hotter than that of the carrier gas. Upon interaction of the clusters with VUV photons, dissociative ionization processes can occur, in particular the loss of a monomer unit following ionization: $M_N \xrightarrow{h\nu} M_N^{+*} \rightarrow M_{N-1}^+ + M$. That will lead to a positive change in temperature of the KERD of M_{N-1}^+ since the produced fragment is expected to be translationally hotter relative to the other M_{N-1}^+ ions. The onset of dissociation can then be traced by recording the ion KERD as a function of the photon energy. In Fig. S1 we show that, on increasing the photon energy from 7.2 to 7.5 eV, the KERDs are identical and no dissociative ionization is thus occurring between these energies. The same study has been performed in the 7.2 to 12 eV range for all clusters and we can confirm that

dissociative ionization kicks in well above the photon energy range presented in Fig. 2 of the main text, with the exact values being the subject of a future publication.

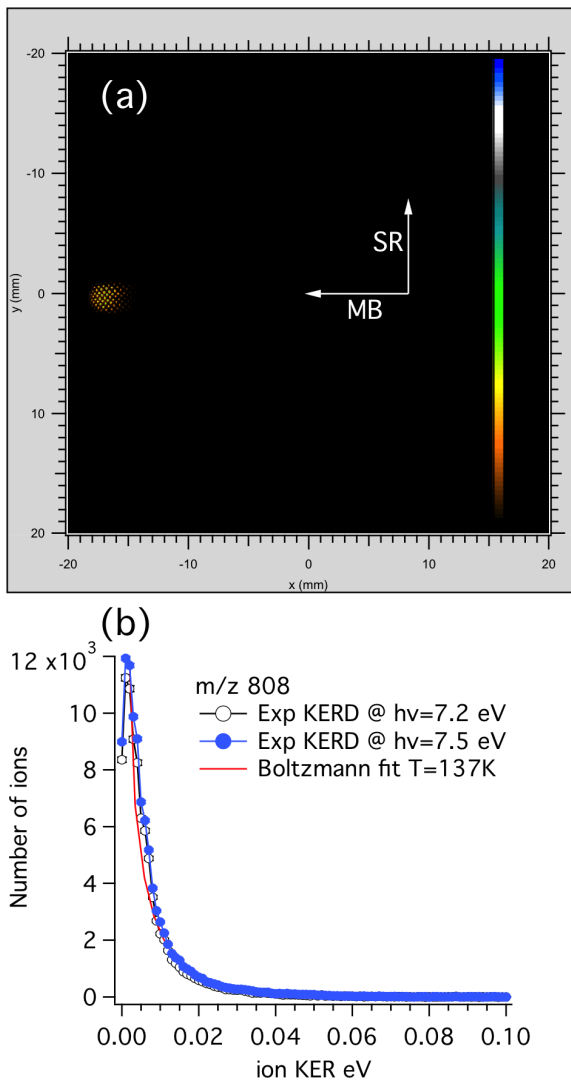


Figure S1: (a) Mass-selected ion image recorded for the tetramer of pyrene at $h\nu=7.2$ eV. The molecular beam (MB) travels from right to left, while the synchrotron radiation (SR) propagates from south to north of the image. (b) The black curve represents the ion KERD extracted from (a). Also added are the ion KERD recorded at 7.5 eV (blue curve), and a Boltzmann fit (red curve) to (b) yielding a translational temperature of 137 K.

II- Theoretical ionization spectra for finite temperatures

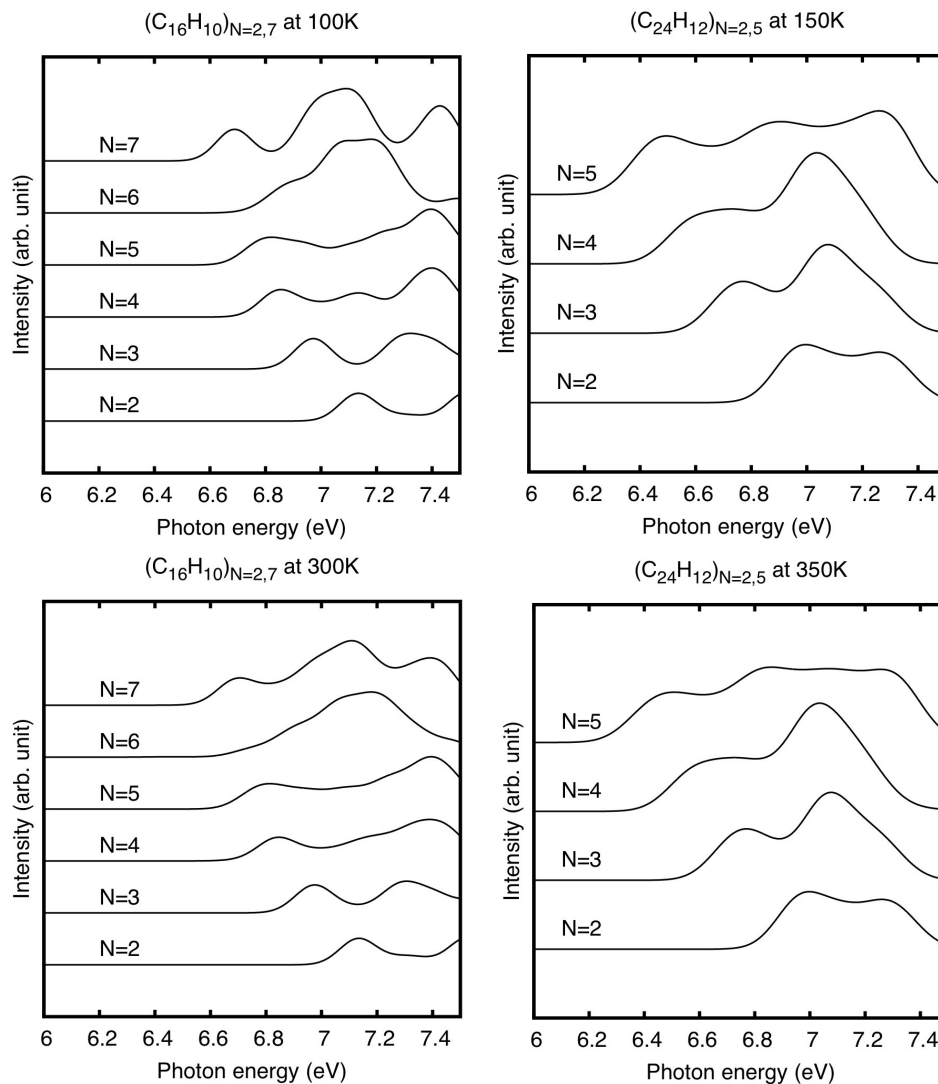


Figure S2: Computed ionization spectra at finite temperatures for pyrene and coronene clusters. These spectra were used to derive the ionization energies as described and shown (Fig. 3) in the main text.

III- Computed energetics and structural properties of PAH clusters

PAH clusters

Pyrene clusters

In Figures S3 to S8, the isomers are listed according to the energetics properties reported in Table S1 (ΔE relative to the lowest-energy isomer, vertical ionization potentials IP_v and, for a few cases, adiabatic ionization potentials IP_a). In cationic states, molecules in green carry the charge and molecules in grey are mostly neutral.

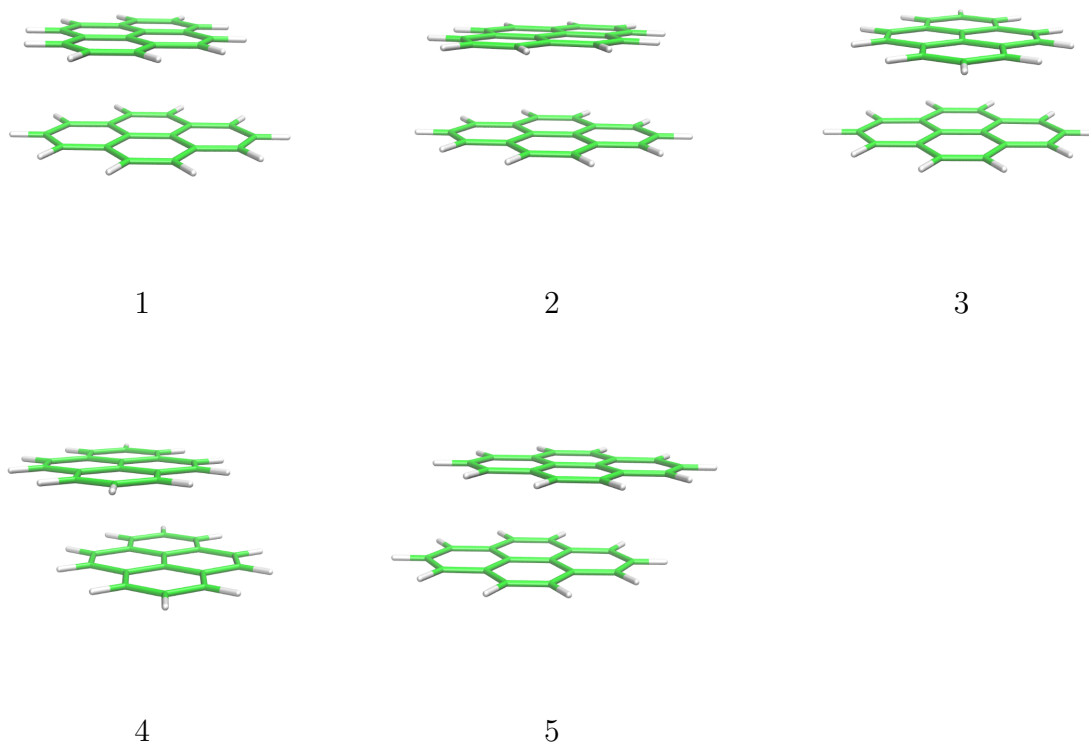


Figure S3: Most stable structures obtained for neutral $(C_{16}H_{10})_2$.

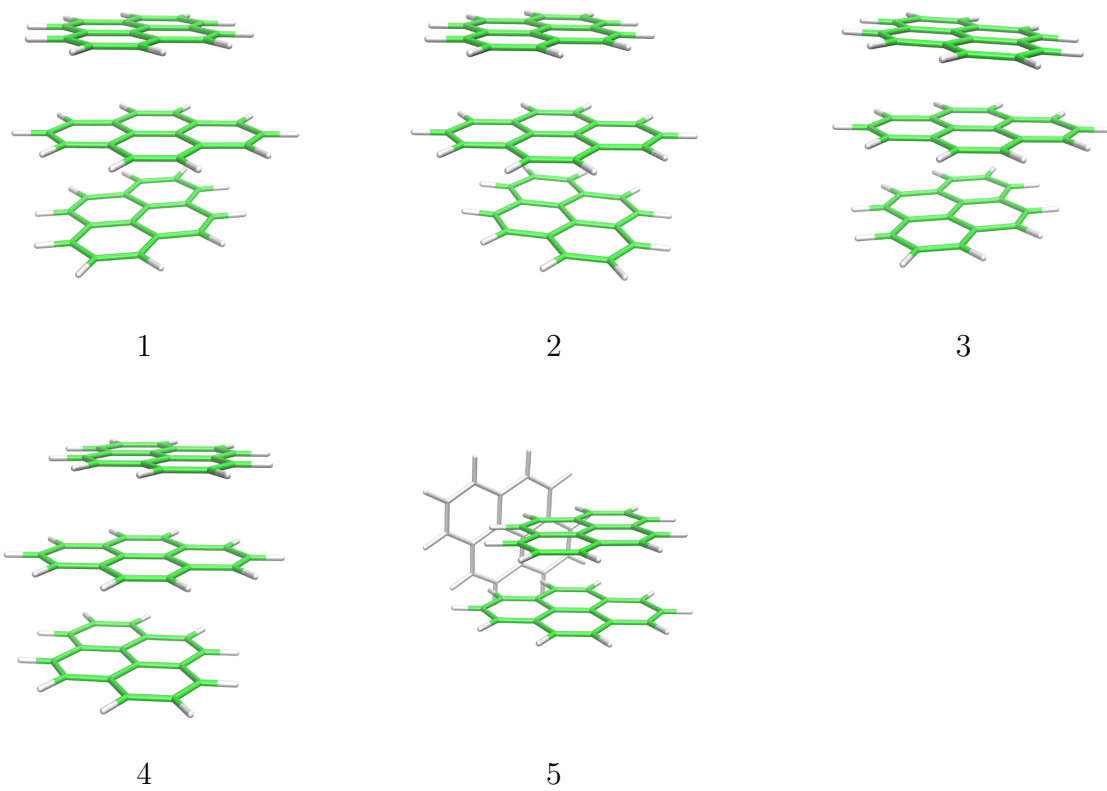


Figure S4: Most stable structures obtained for neutral $(C_{16}H_{10})_3$.

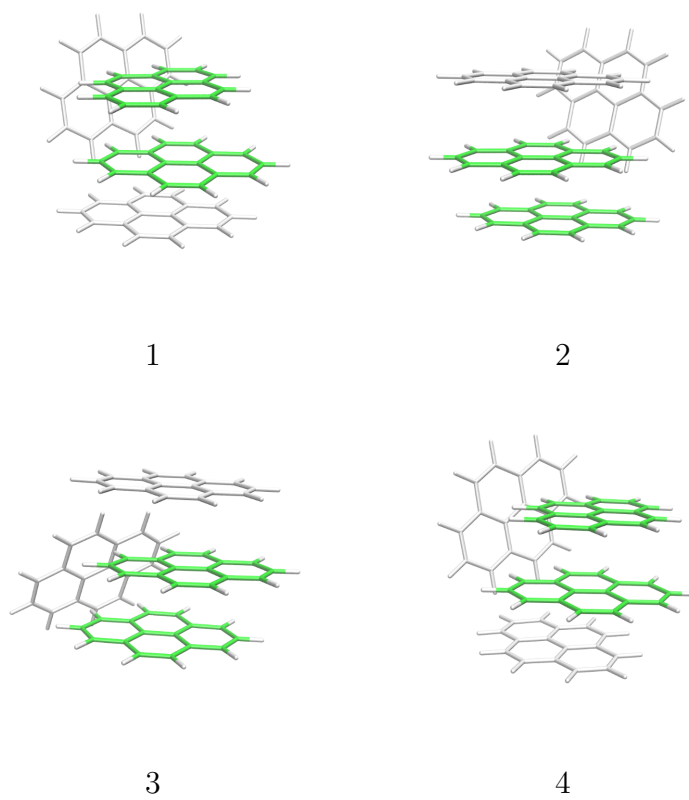
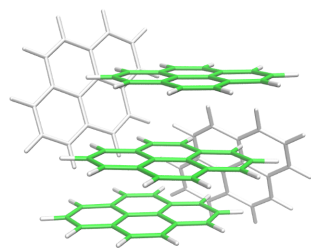
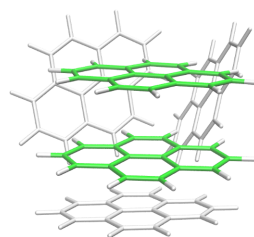


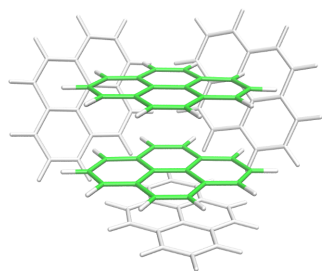
Figure S5: Most stable structures obtained for neutral $(C_{16}H_{10})_4$.



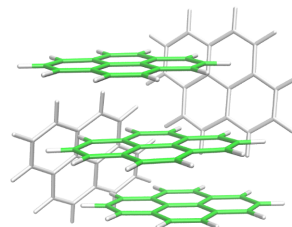
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Figure S6: Most stable structures obtained for neutral $(C_{16}H_{10})_5$.

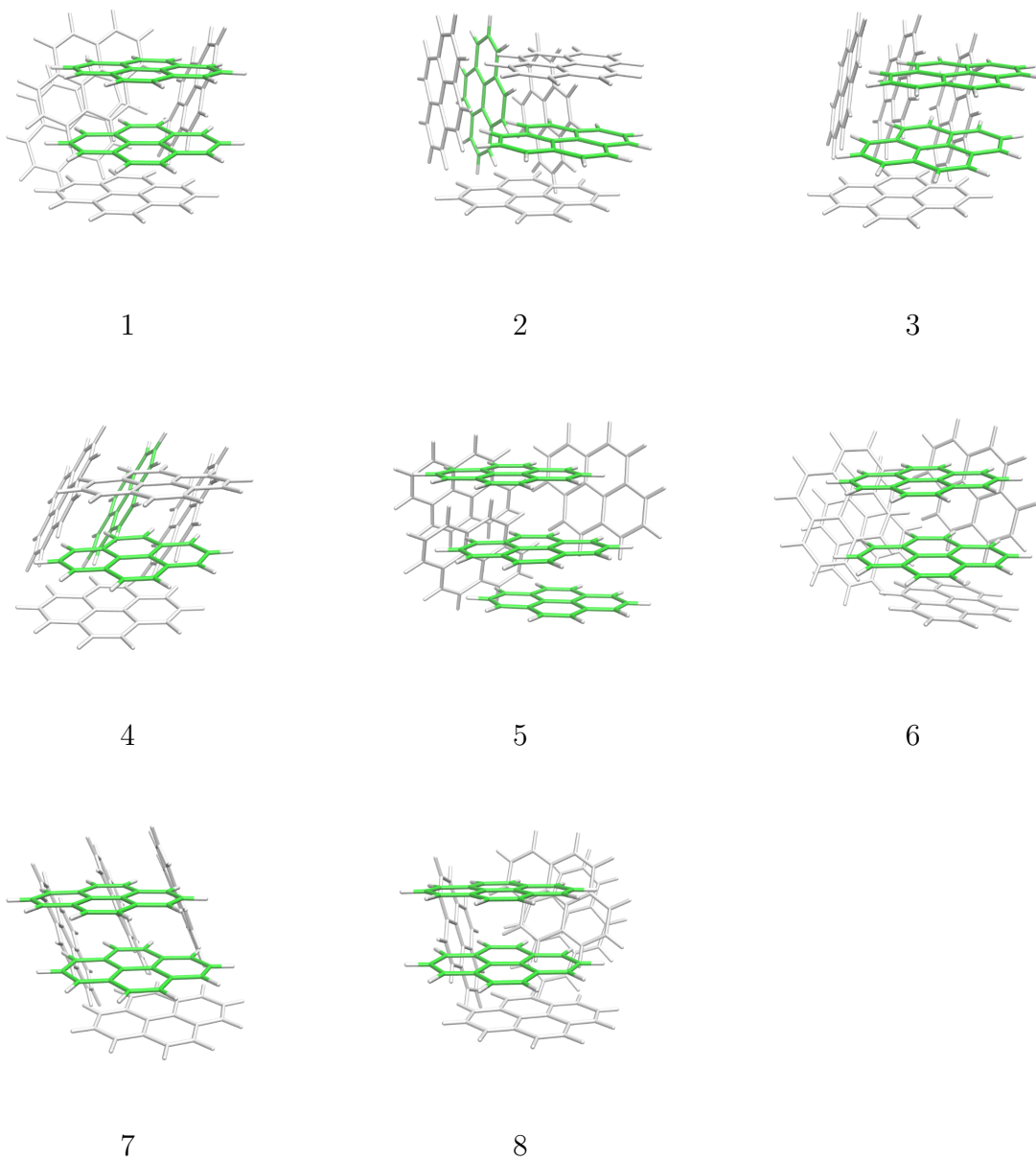


Figure S7: Most stable structures obtained for neutral $(C_{16}H_{10})_6$.

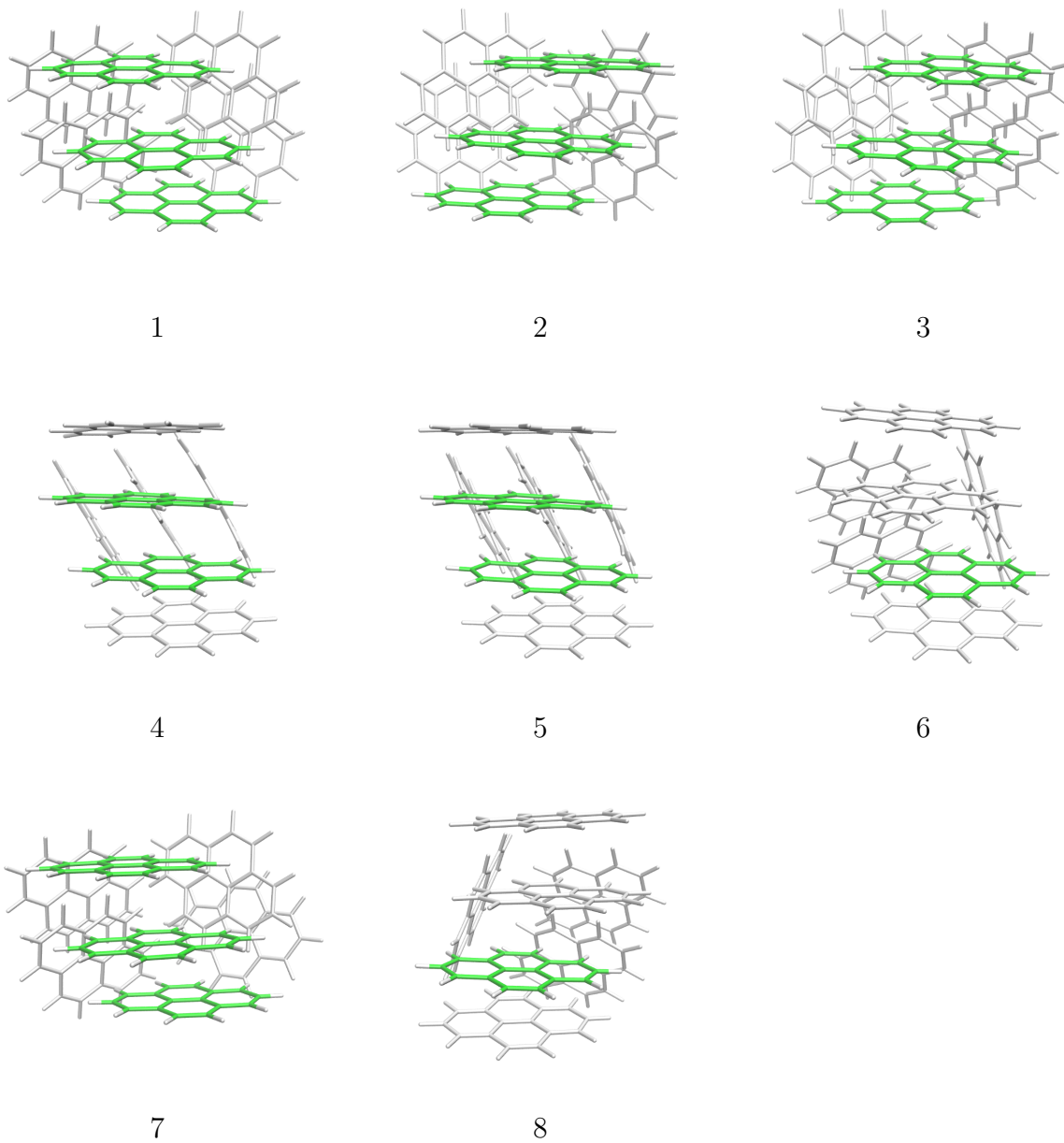


Figure S8: Most stable structures obtained for neutral $(C_{16}H_{10})_7$.

Table S1: Relative energies for neutral isomers of $(C_{16}H_{10})_{N=2,7}$ and corresponding vertical and adiabatic (for $N=2-4$) ionization potentials.

Isomer	ΔE (eV)	IPv (eV)	IPa (eV)
$(C_{16}H_{10})_2$			
1	0.000	7.187	6.90
2	0.005	7.128	
3	0.010	7.315	
4	0.012	7.294	
5	0.012	7.182	
$(C_{16}H_{10})_3$			
1	0.000	6.982	6.62
2	0.001	6.967	
3	0.002	6.978	
4	0.003	6.963	
5	0.009	6.924	
$(C_{16}H_{10})_4$			
1	0.000	6.845	6.56
2	0.006	6.936	
3	0.012	6.838	
4	0.017	6.848	
$(C_{16}H_{10})_5$			
1	0.000	6.790	
2	0.002	6.864	
3	0.010	6.742	
4	0.018	6.791	
$(C_{16}H_{10})_6$			
1	0.000	6.840	
2	0.002	7.061	
3	0.008	6.929	
4	0.016	6.911	
5	0.028	6.737	
6	0.031	6.738	
7	0.038	6.943	
8	0.039	6.842	
$(C_{16}H_{10})_7$			
1	0.000	6.686	
2	0.007	6.689	
3	0.027	6.669	
4	0.027	6.754	
5	0.028	6.736	
6	0.033	6.816	
7	0.044	6.690	
8	0.044	6.814	

Coronene clusters

In Figures S9 to S12, the isomers are listed according to the energetics properties reported in Table S2 (ΔE relative to the lowest-energy isomer and vertical ionization potentials IP_v). In cationic states, molecules in green carry the charge and molecules in grey are mostly neutral.

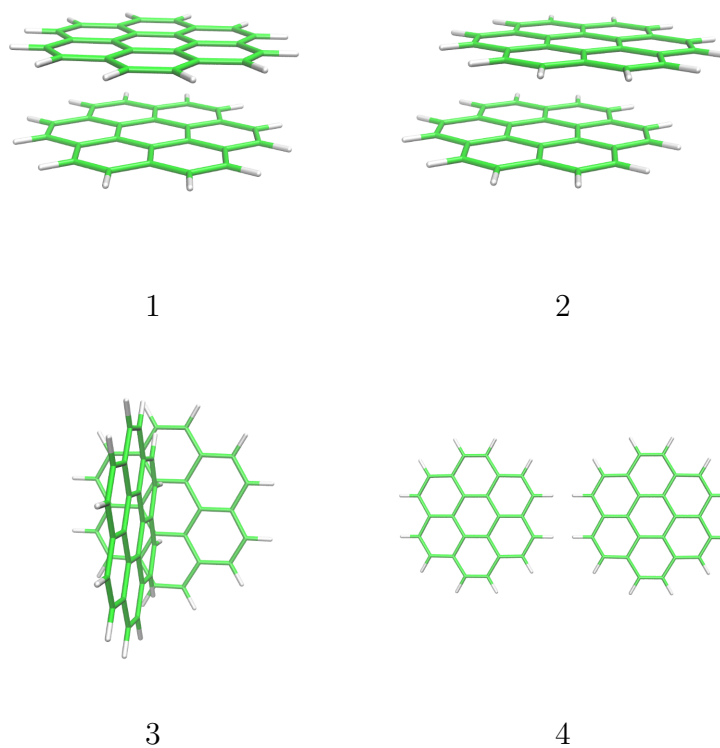
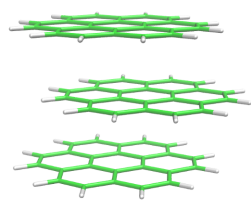
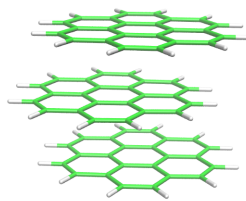


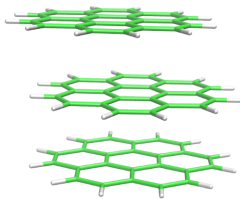
Figure S9: Most stable structures obtained for neutral $(C_{24}H_{12})_2$.



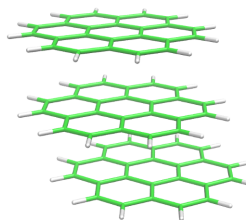
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Figure S10: Most stable structures obtained for neutral $(C_{24}H_{12})_3$.

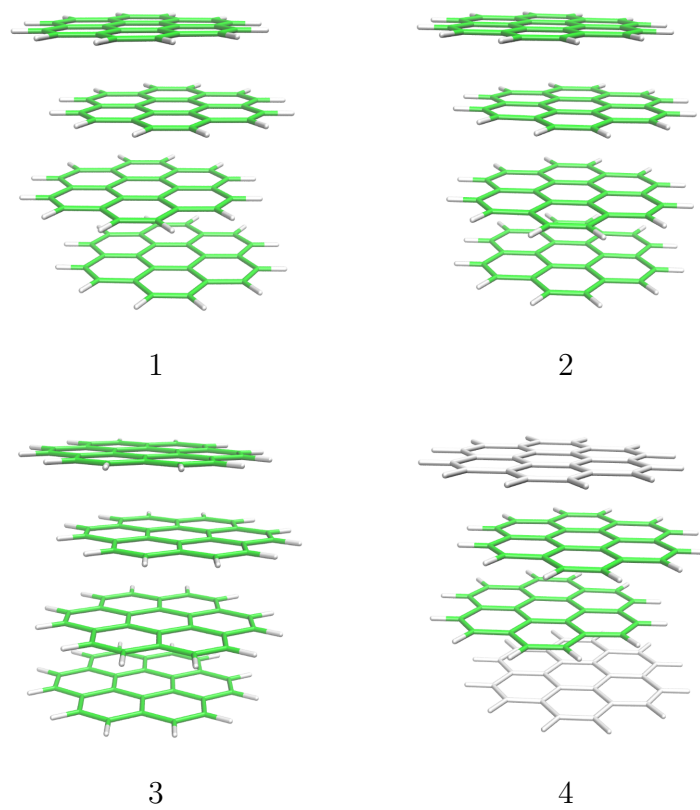


Figure S11: Most stable structures obtained for neutral $(C_{24}H_{12})_4$.

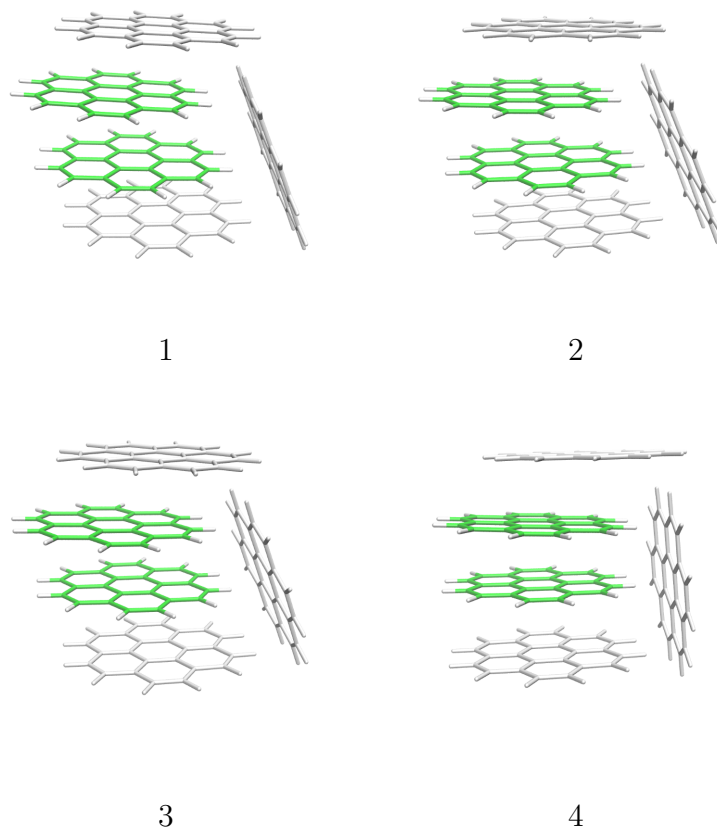


Figure S12: Most stable structures obtained for neutral $(C_{24}H_{12})_5$.

Table S2: Relative energies for neutral isomers of $(C_{24}H_{12})_{N=2,5}$ and corresponding vertical ionization potentials.

Isomer	ΔE (eV)	IPv (eV)
$(C_{24}H_{12})_2$		
1	0.000	6.971
2	0.001	6.950
3	0.511	7.088
4	0.582	7.288
$(C_{24}H_{12})_3$		
1	0.000	6.712
2	0.001	6.725
3	0.003	6.716
4	0.005	6.757
$(C_{24}H_{12})_4$		
1	0.000	6.552
2	0.001	6.558
3	0.001	6.570
4	0.002	6.572
$(C_{24}H_{12})_5$		
1	0.000	6.428
2	0.022	6.418
3	0.023	6.437
4	0.048	6.398