

Electronic Supplementary Information

Electron Beam Controlled Covalent Attachment of Small Organic Molecules to Graphene

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Simulations

Table S1 The PBE+D binding energies (E_b , in eV) and magnetic moments (M , μ_B) for radicals of several polycyclic aromatic hydrocarbons chemisorbed on graphene.

radical	alignment on graphene	M , μ_B	E_b , eV
zigzag edge on radical			
phenyl, C_6H_5	N/A	1	0.99
1,8- $C_{10}H_6$ bi-radical 1,2-bonding	armchair	0	2.95
1,8- $C_{10}H_6$ bi-radical 1,4-bonding	armchair	0	2.80
1,8- $C_{10}H_6$ bi-radical 1,3-bonding	zigzag	2	1.94
1,8,9- $C_{14}H_7$ tri-radical 1,4-bonding	armchair	1	4.46
1,8,9- $C_{14}H_7$ tri-radical 1,3-bonding	zigzag	3	2.92
armchair edge on radical			
C_6H_4 bi-radical 1,2-bonding	armchair	0	1.15
C_6H_4 bi-radical 1,4-bonding	armchair	0	1.13
C_6H_4 bi-radical 1,3-bonding	zigzag	2	0.29
3,4,5,6- $C_{14}H_6$ tetra-radical 1,2-bonding	armchair	0	2.66
3,4,5,6- $C_{14}H_6$ tetra-radical 1,4-bonding	armchair	0	3.18

Additional details of MD simulations

It has been found that a structural optimization of the $C_{24}H_{10}$ radical bonded along 1,4-direction with the AIREBO^{S1} potential results in slight bending of the molecule as shown in Fig. S1. This bending also occurs in the MD simulations and suppress the oscillating motion of the radical described in the main text (see Figure 3 and accompanying text), so that the molecule is constantly inclined to one side for the whole time of the simulation (10 ns). No such bending, however, remains when the structure is reoptimized with DFT. It has been found that such bending only occurs when both the long-range interactions and the torsional term are present in the AIREBO potential. If one of these terms is switched off the bending of the molecule does not occur and the chemisorbed radical shows

oscillating behaviour similar to that described in the main text. In the case of the 1,2-bonding configuration oscillating motion of the radical has been observed for different combinations of the terms in the AIREBO potential, with no significant changes when one of the terms is switched off.

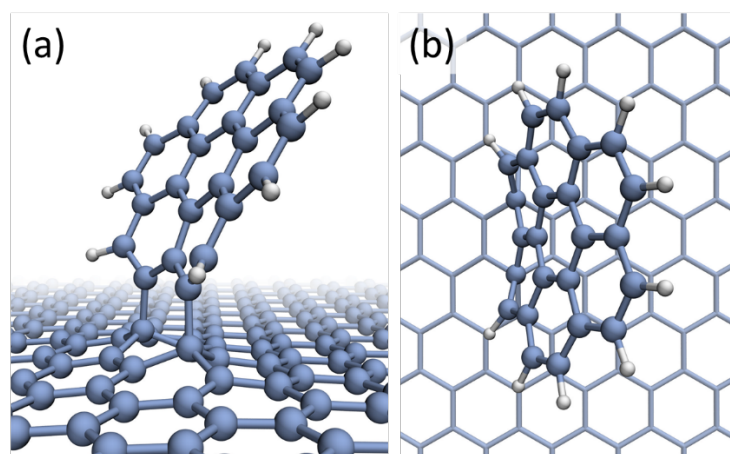


Fig. S1 Bending of the C₂₄H₁₀ radical in the 1,4-bonding configuration after geometry optimization with the AIREBO potential: a) side view and (b) top view.

Experiment

Coronene (> 95%) was purchased from TCI Europe and was used without further purification. The perchlorination of coronene was done following a literature protocol from Ballester, Molinet and Cast ner using sulfur monochloride (Aldrich, 98%), aluminum chloride (Aldrich, 99.99%) and sulfuryl chloride (Aldrich, 97%). The received product was washed with chloroform (VWR, p. A.) and filtered over a short silica column with hot chloroform (VWR, p. A.) to obtain pure, yellow PCC (yield ~ 90%).

Graphene was grown on 25 µm thin copper foils (99,8 %, Alfa Aesar GmbH & Co KG, Karlsruhe) using low-pressure chemical vapour deposition.^{S8,S9} Before growth the copper foils were rinsed with acetone then placed in acetic acid (p.a.) for 10 min and finally cleaned with water, acetone and isopropanol. Then the foils were dried under a nitrogen stream, put into a quartz tube and introduced into a furnace (Gero F40-200, Neuhausen). Pumping the tube to 1x10⁻³ mbar was followed by setting a H₂-flow of 50 sccm and subsequent heating to 1288 K in two steps (500K/h up to 1223 K, 100K/h up to 1288 K). After 3 h the H₂-flow was reduced to 10 sccm and a methane flow of 70 sccm was introduced for 15 min. Then the samples were cooled down to room temperature under the Ar/H₂ atmosphere. The grown graphene sheets were transferred onto TEM grids. To this end, poly(methyl methacrylate) was spun in two steps onto the graphene to stabilize it during the transfer process.^{S9,S10} First, a layer of low molecular weight PMMA (50k) and then a second layer of high molecular weight PMMA (950k) was spin-cast for 30 s at 4000 rpm onto the graphene. Then the back site of the copper foil was cleaned using O₂ plasma etching for 60 s, followed by etching away the copper using an ammonium persulfate solution (6.5 g ammonium persulfate/100 ml water) over night. After placing the graphene onto the Quantifoil TEM grid, the PMMA was dissolved in a critical point dryer. To additionally clean graphene the samples were introduced into ultra-high vacuum (4x10⁻⁹ mbar) and annealed for 2 h at 350° C.

C₂₄Cl₁₂ powder was introduced in a Knudsen cell (Kentax Evaporator TCE-BSC), put into ultra-high vacuum and was baked out over night at 473 K. The temperature was then further increased to 523

K and after 30 min of thermal equilibration the compound was evaporated for 30 minutes onto graphene.

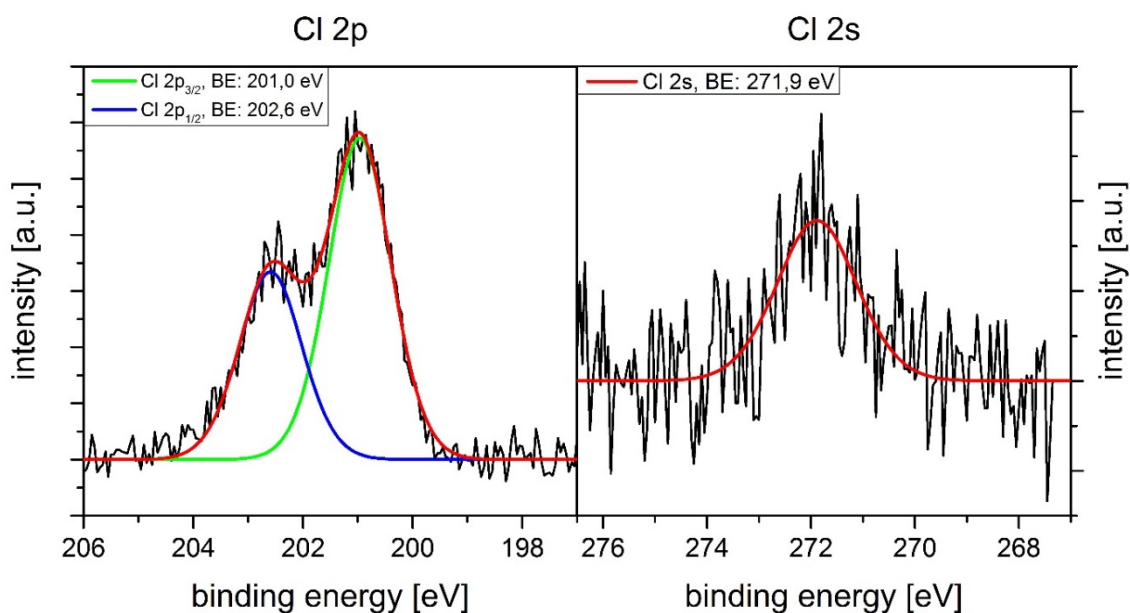


Fig. S2 *In situ* X-ray photoelectron spectra showing the presence of the characteristic Cl2s and Cl2p_{3/2}, _{1/2} peaks after deposition of C₂₄Cl₁₂ molecules on highly oriented pyrolytic graphite substrates. The Cl2p signal consists of a doublet with an intensity ratio between the components of I(2p_{3/2}):I(2p_{1/2})=2:1.

The X-ray photoelectron spectroscopy (Multiprobe, Omicron) characterization of samples prepared at similar conditions on highly oriented pyrolytic graphite substrates demonstrates the adsorption of C₂₄Cl₁₂ molecules by appearance of the characteristic Cl 2s and Cl 2p_{3/2,1/2} peaks (Fig. S2).

Fig. S2 shows that the Cl2p signal consists of a doublet with an intensity ratio between the components I(2p_{3/2}):I(2p_{1/2})=2:1. This intensity ratio is expected from the spin-orbit coupling if only one chemical species is present. The Cl2s signal also shows only one component, as expected for one chemical species. If the chemical decomposition would take place, then more than one doublet should be recognized in the Cl2p signal and additional components should be present in the Cl2s signal. Based on this analysis we can unambiguously exclude decomposition of C₂₄Cl₁₂ during the vapour deposition.

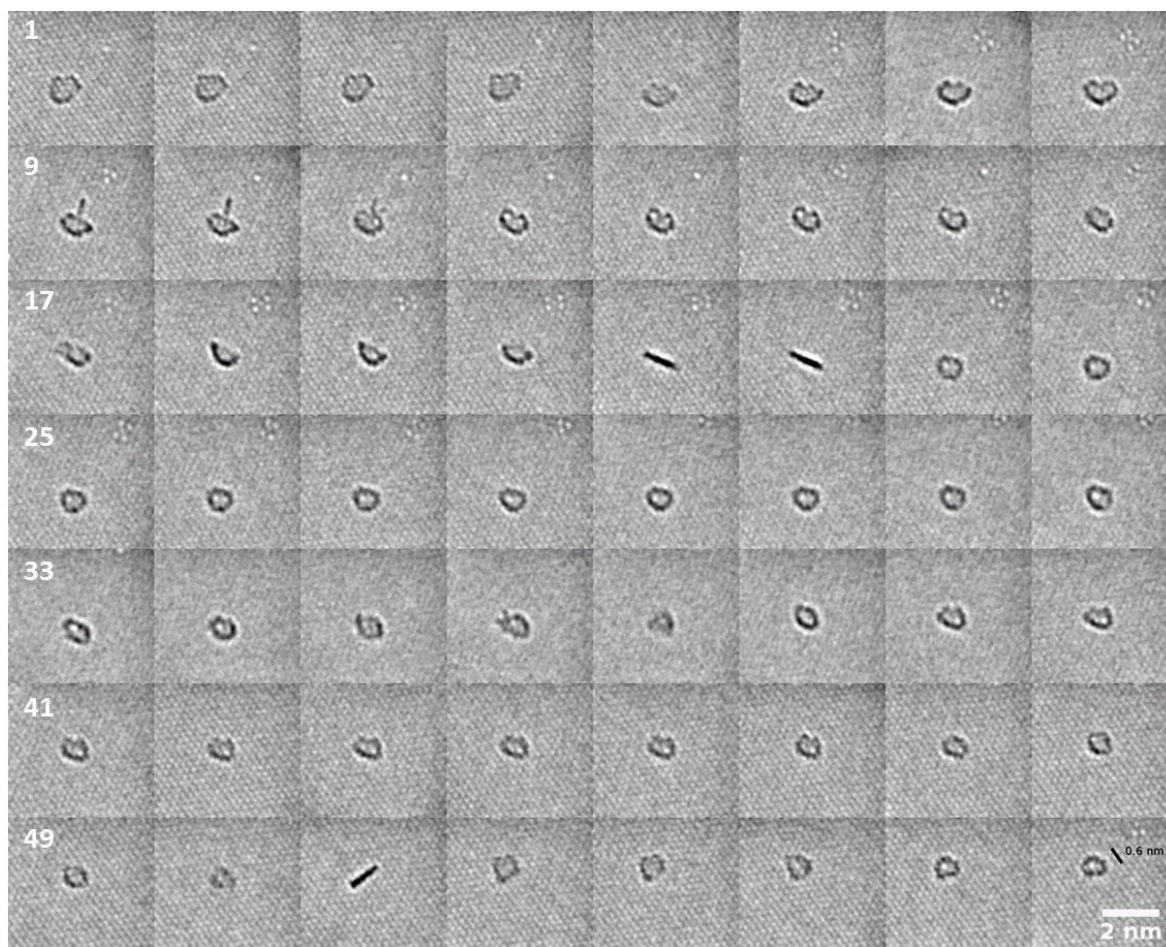


Fig. S3 Series of TEM images showing transformations of a $C_{24}Cl_{12}$ molecule on graphene under 80 keV electron beam. The molecule occasionally transforms between the circular and linear configurations. The size of the molecule tends to get smaller during imaging indicating gradual removal of atoms by the electron beam. The sequence numbers are shown for the first frame in each row.

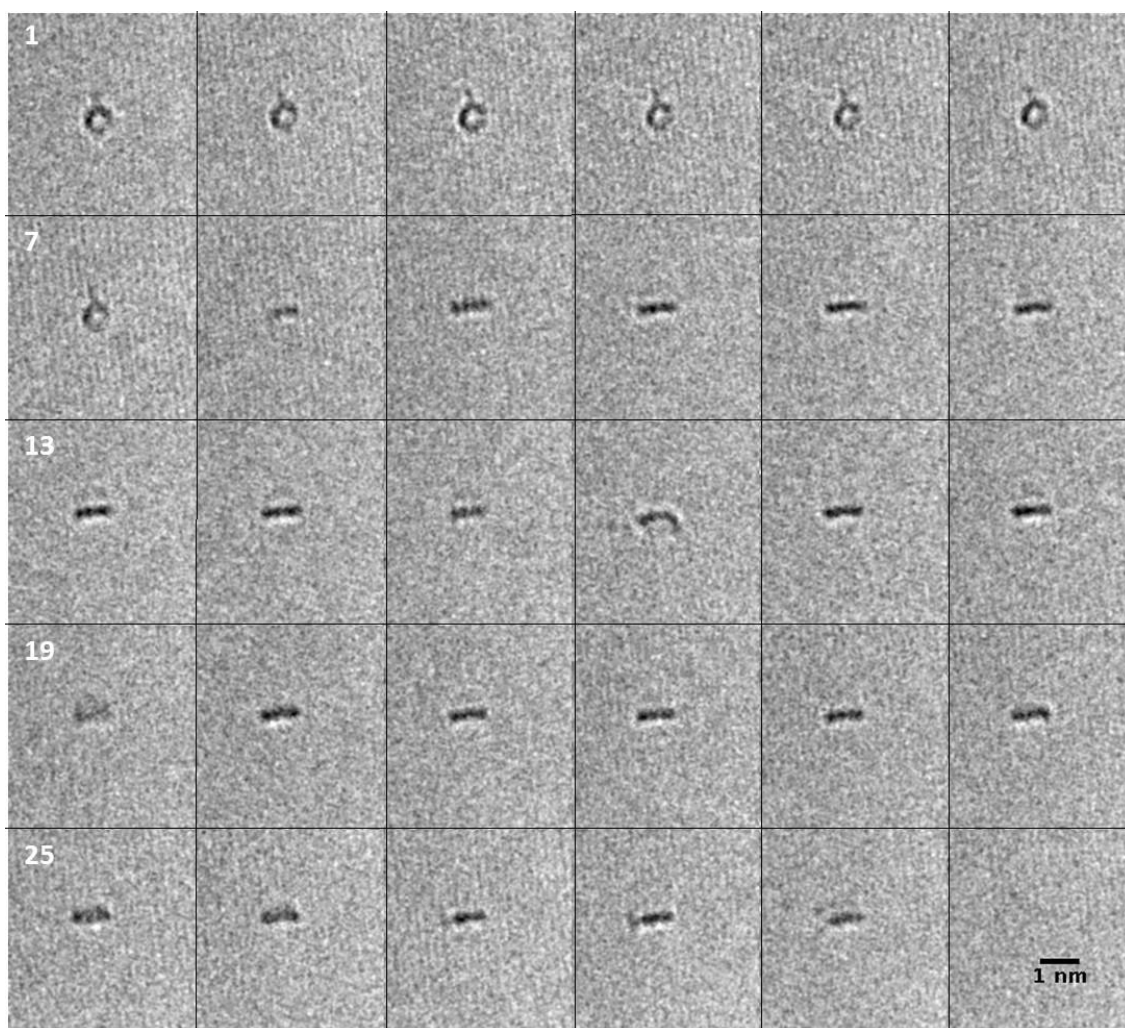


Fig. S4 Series of TEM images showing transformations of a $C_{24}Cl_{12}$ molecule on graphene under 80 keV electron beam. The sequence numbers are shown for the first frame in each row.

References

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