SUPPORTING INFORMATION

FOR

Probing the role of surface termination in the adsorption of azupyrene on copper

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1. Alternate fit to the soft X-ray photoelectron spectroscopy (SXPS)

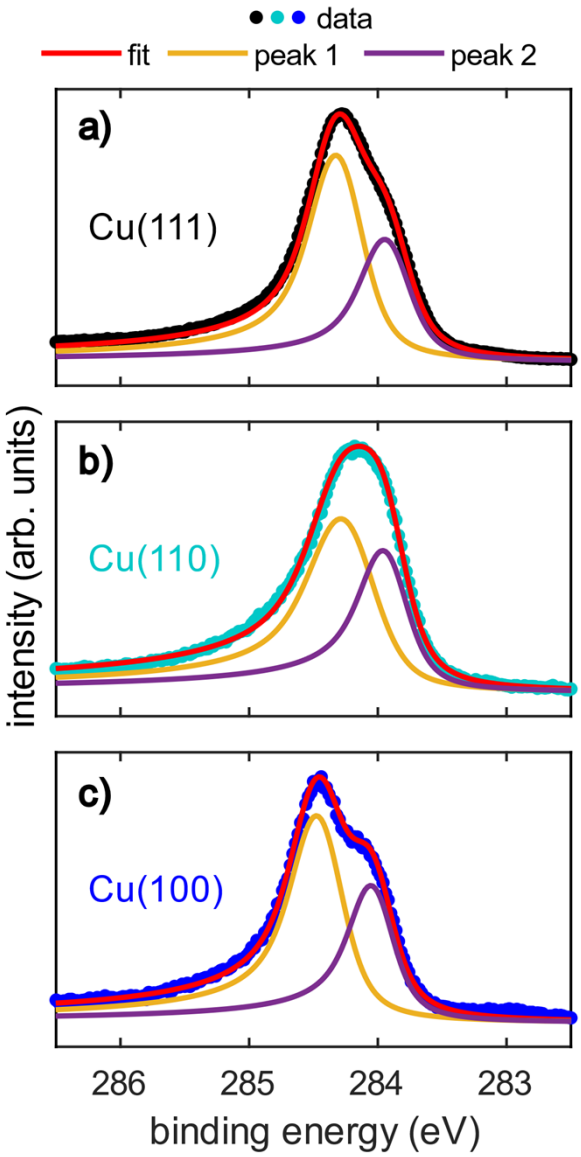

Figure S1: (a-c) Soft X-ray photoelectron spectroscopy (SXPS) of azupyrene adsorbed on (a) Cu(111), (b) Cu(110), and (c) Cu(100). The data were acquired at a photon energy of 430 eV, the binding energy scale was corrected using a subsequent measurement of the Cu Fermi edge at the same photon energy. Nb. the fitting is not unique and is presented here for illustrative purposes. Here the relative area of peak 2 was constrained to be identical (53%) on all three samples.

2. Hard X-ray photoelectron spectroscopy (HAXPES)

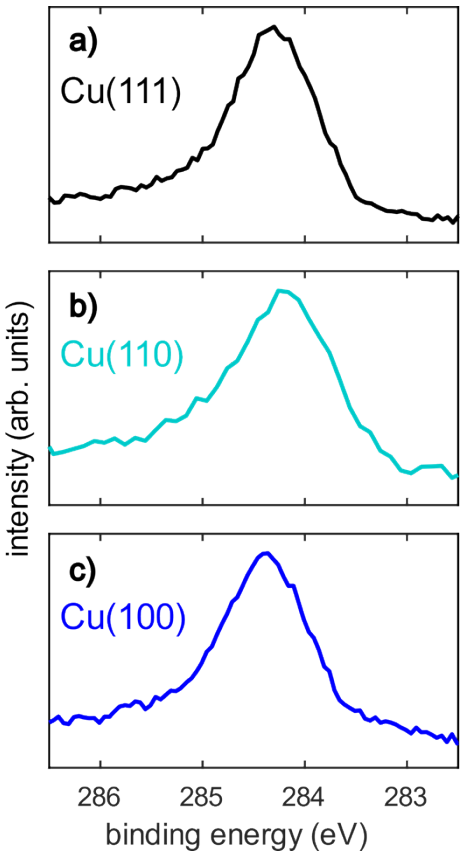

Figure S2: C 1s HAXPES data of azupyrene adsorbed on a) Cu(111), b) Cu(110) and c) Cu(100). The data were acquired at a) 2960 eV, b) 4820 eV and c) 3410 eV, close to the normal incidence Bragg energy of the (111), (220) and (200) reflection, respectively, and have had their binding energy scale corrected by rigidly shifting the data to share the same centroid as the corresponding SXPS data (shown in Figure 2 in the main article).

3. Determination of the Cu lattice constants

The copper lattice constants were determined by performing Birch-Murnaghan fits; this resulted in a lattice constant of 3.597 Å for both PBE+MBD-NL and HSE06+MBD-NL as seen in Figure S3.

For the PBE+MBD-NL Birch-Murnaghan fit, an initial lattice parameter of 3.6 was chosen for the Cu primitive lattice unit cell, and 10 total energy calculations were performed from 95% to 105% either side of this value. The lattice constants were plotted as a function of the total energy, and a fit was then applied to this data. The calculations were performed with a k-grid of 24×24×24, atomic ZORA scalar relativity, a β value for the MBD-NL correction of 0.81, and a tight basis set in FHI-aims. The minimum of the curve was at 3.597 Å and used as the lattice parameter for the creation of supercells for the bulk structure, from which the different Cu facets were created from using the atomic simulation environment (ASE).

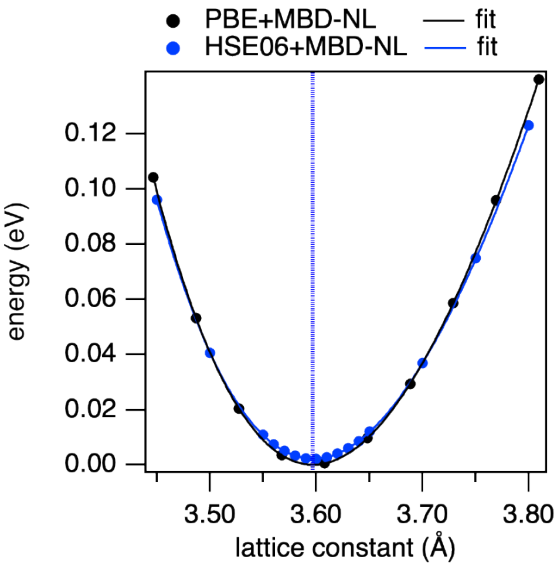

Figure S3: Birch fit results for PBE+MBD-NL and HSE06+MBD-NL resulting in lattice constants (represented by vertical dashed lines) of 3.597 Å for both functionals. Energies were shifted up by the minimum fit energy for each of the functionals. The raw energy values are represented by circular markers and the fits by solid lines.

The Birch-Murnaghan equations of state equation is expressed below:[1]

$$E(\eta) = E_0 + \frac{9B_0V_0}{16}(\eta^2-1)^2\left(6 + B_0^{'}(\eta^2-1) - 4\eta^2\right) \;\; and \;\; \eta = \left(\frac{V_0}{V}\right)^{\frac{1}{3}}, \qquad (1)$$

where V is the volume, V_0 is the volume at 0 pressure, B_0 is the bulk modulus at 0 pressure, and $B_0^{'}$ is its pressure derivative.[2]

4. Determination of the best adsorption site for azupyrene on Cu(111), Cu(110) and Cu(100)

An adsorption site search was performed to determine the most likely adsorption sites for azupyrene on each of the Cu facets. Each of the investigated adsorption sites are shown in Figure S4 for the (111) surface, Figure S5 for the (110) surface, and Figure S6 for the (100) surface. These were initially performed by roughly creating the structures at each of the adsorption sites in ASE before performing a geometry optimisation with PBE+MBD-NL. From here, the adsorption energies were compared and those with the lowest energies were selected for a geometry optimization with HSE06+MBD-NL. The individual values for adsorption heights, adsorption energies, and the final adsorption sites are shown in Tables S1, S2, and S3. The most energetically stable adsorption sites for each substrate are discussed in the main text and are shown in Figure 5 and Figure 6 in the main article.

The adsorption energy calculations were performed as follows:

$$E_{ads} = E_{interface} - \left(E_{adsorbate} + E_{surface}\right), \qquad (2)$$

where $E_{interface}$, $E_{adsorbate}$, and $E_{surface}$ are zero-broadening corrected energies from of the relaxed azupyrene-surface interface system, the relaxed free molecule, and the clean Cu surface (bottom 4 layers constrained).

The adsorption heights calculated in this section are the centre-of-mass (COM) heights and are calculated as follows:

$$\frac{1}{M_r}\left[\sum_i^N\left(A_{r_i}\cdot\sum_j^n z_{i_j}\right)-h_{Cu_1}\right], \quad (3)$$

here M_r is the relative molecular mass of the adsorbate (202.256 amu for azupyrene), N is the number of elements, A_{r_i} is the relative atomic mass of the i-th element, n is the number of atoms of the i-th element, z is the z-coordinate of the j-th atom of the i-th element, and h_{Cu_1} is the average height of the first Cu layer.

Table S1. PBE+MBD-NL optimised adsorption sites of azupyrene on Cu(111). For each adsorption site, the corresponding adsorption energy (E_{ads}), COM adsorption height (h_{COM}) with respect to the bulk spacing and resulting adsorption site after optimisation are shown. The table is sorted by increasing E_{ads}; the structure with the lowest adsorption energy was used for the HSE06+MBD-NL calculations for the Cu(111) surface, shown in the main article. The structural model for the starting adsorption sites can be found in Figure S4. The structural model for the final adsorption site "Close to bridge parallel 60°" can be found in Figure 5c,f and Figure 6c,f in the main manuscript.

starting adsorption site	E_{ads} (eV)	h_{COM}(Å)	final adsorption site
Hollow 30	-1.833	2.236	Close to bridge parallel 60
Bridge parallel 0	-1.825	2.236	Bridge parallel 30
Hollow 0	-1.825	2.236	Bridge parallel 30
Bridge ortho 30	-1.824	2.236	Bridge parallel 30
Bridge parallel 30	-1.814	2.233	Bridge parallel 30
Top 0	-1.643	2.285	Close to Top 0
Top 30	-1.504	2.312	Top 30

Table S2**.** Summary of PBE+MBD-NL optimised adsorption sites of azupyrene on Cu(110). For each adsorption site, the adsorption energy (E_{ads}), COM adsorption height (h_{COM}) with respect to the bulk truncated height and resulting adsorption site after optimisation are shown. The short bridge is the bridge site along the $[1\bar{1}0]$ direction, the long bridge is the bridge site along the $[001]$ direction. The table is sorted by increasing E_{ads}; the structure with the lowest adsorption energy was used for the HSE06+MBD-NL calculations for the Cu(110) surface, shown in the main article. The structural model for the starting adsorption sites can be found in Figure S5.

starting adsorption site	E_{ads} (eV)	h_{COM}(Å)	final adsorption site
Long bridge 45	-3.239	2.146	Long bridge 45
Hollow 45	-3.239	2.146	Long bridge 45
Short Bridge 0	-3.108	2.095	Short bridge 0
Short bridge 45	-3.095	2.217	Hollow 45/ top45
Top 0	-3.019	2.158	Top 0
Long Bridge 0	-3.007	2.13	Short bridge 0/ top 0
Top 45	-2.92	2.151	Top 45
Top 90	-2.873	2.152	Top 90
Short bridge 90	-2.837	2.2	Long bridge 90/ hollow 90
Long bridge 90	-2.77	2.207	Long bridge 90
Hollow 90	-2.749	2.205	Hollow 90
Hollow 0	-2.533	2.183	Hollow 0

Table S3. Summary of PBE+MBD-NL optimised adsorption sites of azupyrene on Cu(100). For each adsorption site, the adsorption energy (E_{ads}), COM adsorption height (h_{COM}) with respect to the bulk spacing and resulting adsorption site after optimisation are shown. The table is sorted by increasing E_{ads}; the structure with the lowest adsorption energy was used for the HSE06+MBD-NL calculations for the Cu(100) surface, shown in the main article. The structural model for the starting adsorption sites can be found in Figure S4.

starting adsorption site	E_{ads} (eV)	h_{COM}(Å)	final adsorption site
Top 45	-3.549	2.173	Top 45
Hollow 45	-3.549	2.173	Top 45
Bridge 45	-3.549	2.173	Top 45
Hollow 0	-2.785	2.213	Bridge 90/hollow 0
Bridge 0	-2.782	2.212	Bridge 90/hollow 0
Bridge 90	-2.717	2.251	Bridge 90
Top 0	-2.239	2.294	Top 0

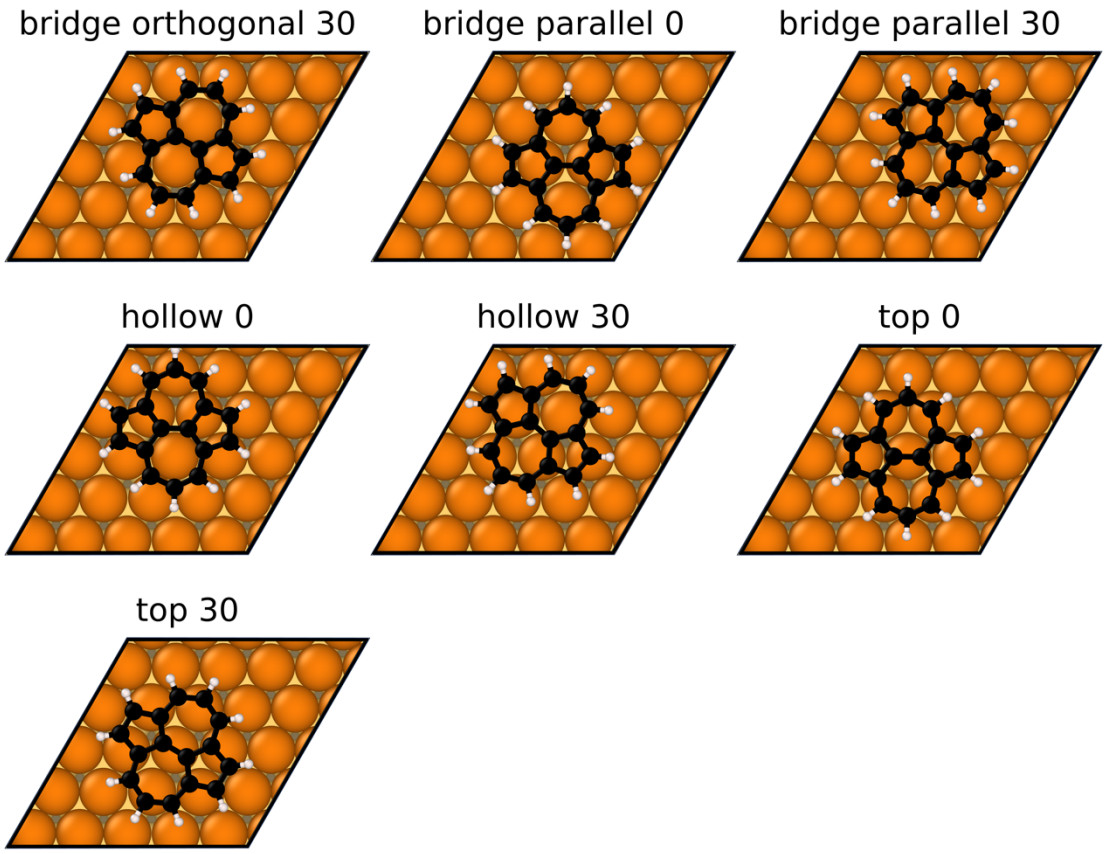

Figure S4: Schematics of the different starting adsorption sites for the adsorption site search of azupyrene on Cu(111) with the PBE+MBD-NL functional. The black spheres represent C atoms, white spheres represent H atoms, copper spheres the top layer of Cu atoms, yellow spheres the second layer Cu atoms and grey spheres the third layer Cu atoms.

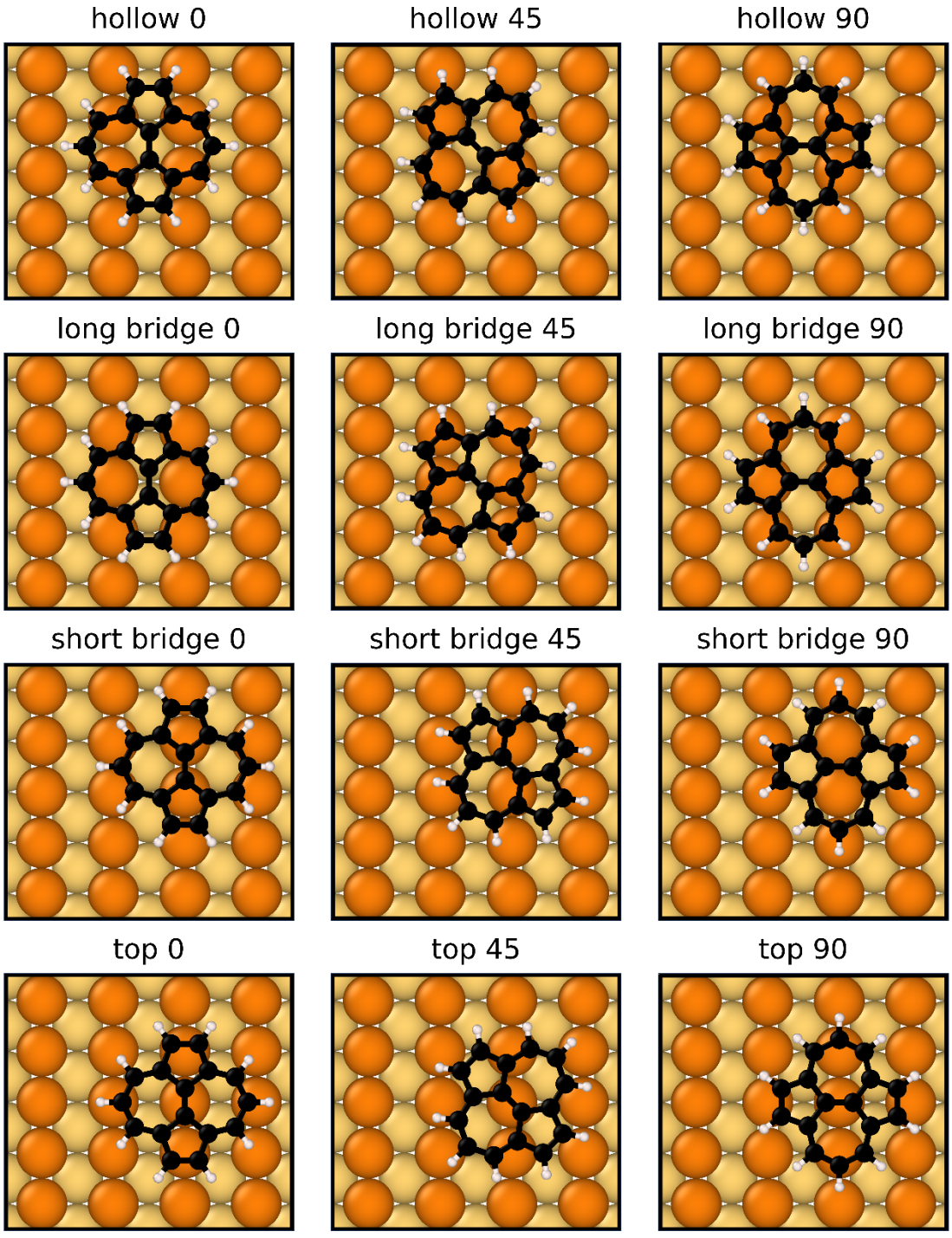

Figure S5: Schematics of the different starting adsorption sites for the adsorption site search of azupyrene on Cu(110) with the PBE+MBD-NL functional. The black spheres represent C atoms, white spheres represent H atoms, copper spheres the top layer of Cu atoms, yellow spheres the second layer Cu atoms.

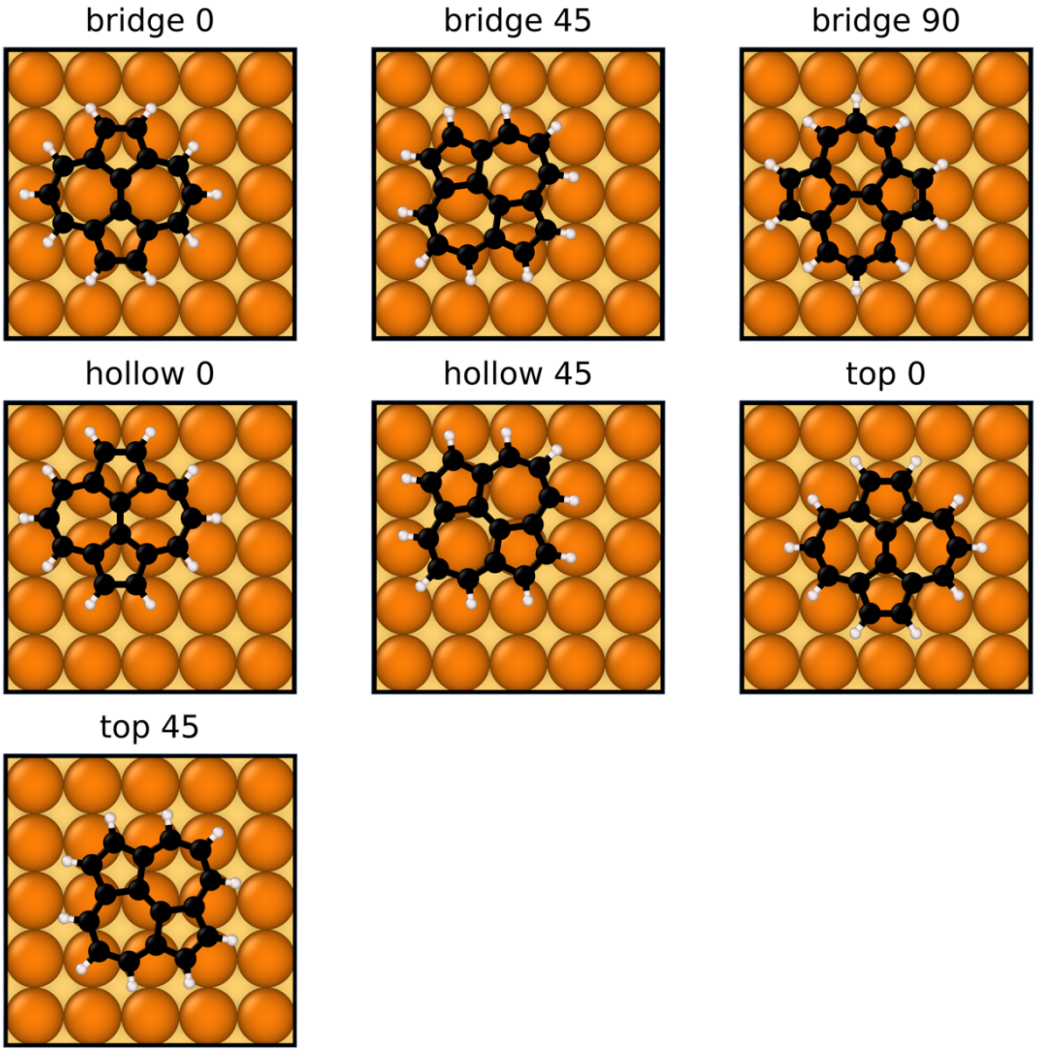

Figure S6: Schematics of the different starting adsorption sites for the adsorption site search of azupyrene on Cu(100) with the PBE+MBD-NL functional. The black spheres represent C atoms, white spheres represent H atoms, copper spheres the top layer of Cu atoms, yellow spheres the second layer Cu atoms.

5. Comparison of coverages for azupyrene on Cu(111)

In order to establish the effect of surface coverage of the adsorbate, HSE06+MBD-NL calculations were performed for Cu(111) in both a 4×4 and a 5×5 supercell structure of azupyrene adsorbed on Cu. The same parameters were used in these calculations as is outlined in section 2 of the ESI, and the results from this are shown in Table S4.

Table S4. Summary of the NIXSW and DFT data of azupyrene on Cu(111), Cu(110), and Cu(100). Coherent fraction (f_H), coherent position (p_H) and the corresponding mean adsorption height above a bulk projected surface termination (h_H) were obtained from fitting the C 1s NIXSW data, shown in Figure 4. The results from the DFT calculations are the average adsorption height of the carbon atoms with respect to the bulk projected termination (directly comparable to the NIXSW data), the vertical adsorption height of the centre-of-mass (COM) with respect to the average position of the relaxed surface Cu atoms in the first layer (h_{COM}), and the adsorption energy per molecule (E_{ads}), and the adsorption energy per surface atom ($E_{ads/Cu}$). The DFT calculations were performed using HSE06+MBD-NL.

	Experiment			Theory				
Cu facet	f_H	p_H	h_H (Å)	Unit cell	h_H (Å)	h_{COM}(Å)	E_{ads} (eV)	$E_{ads/Cu}$ (eV/Cu)
Cu(111)	0.72(3)	0.07(1)	2.24(3)	4×4	2.23	2.28	-2.72	-0.17
				5×5	2.19	2.23	-2.92	-0.12
Cu(110)	0.74(4)	0.71(2)	2.18(3)	4×5	2.07	2.13	-3.36	-0.17
Cu(100)	0.70(5)	0.24(2)	2.23(4)	5×5	2.18	2.20	-3.46	-0.14

References

1. F. Birch, *Physical Review*, 1947, **71**, 809-824.
2. M. Hebbache and M. Zemzemi, *Physical Review B*, 2004, **70**, 224107.