Supporting Information

Identical Binding Energies and Workfunctions for Distinct Adsorption Structures: Olympicenes on the Cu(111) Surface

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We explored the potential-energy surface of a single olympicene molecule by varying the orientation and position of the adsorbate on top of the Cu(111) surface, followed by geometry relaxation. For consistency, the *central* carbon ring of olympicenes was taken as reference in the molecule. We used a (6×6) unit cell to represent the periodic Cu(111) surface. The substrate was modeled by a slab with six atomic layers. The bottom four layers were constrained at their bulk positions, whilst the olympicene molecules and the uppermost two Cu layers were allowed to fully relax. Different slabs were separated by 30 Å of vacuum, to avoid the interaction between the adsorbate and the periodic images of the slab.

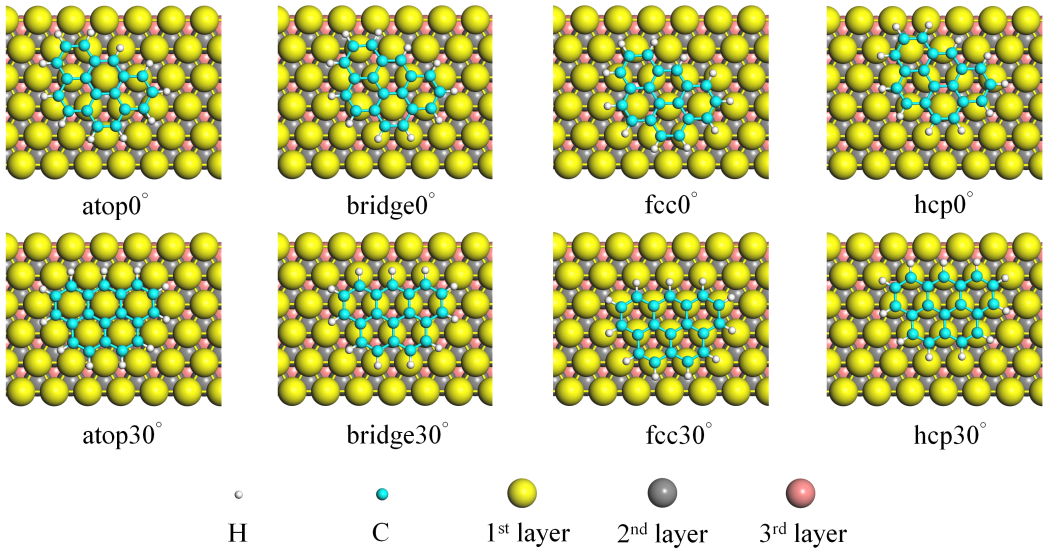

Figure S1: Illustration of the high-symmetry adsorption sites for the olympicene radical on the Cu(111) surface. Due to the face-centered cubic (fcc) structure of Cu, there are four possible adsorption sites (atop, bridge, fcc, and hcp) for the radical on the (111) metal surfaces. At each site, the radical has two orientations, i.e., 0° and 30°, referring to the angles of the C–C bond being rotated with respect to the neighbouring metal–metal bond. The olympicene molecule and its ketone derivative have similar starting geometries.

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Here we took the olympicene radical as an example to show adsorption sites on the metal substrate. As illustrated in Figure S1, the carbon rings are parallel to the metal substrate,[1] and there are in total eight high-symmetry adsorption sites for the radical/Cu(111) system. Specifically, the central carbon ring can adsorb at the so-called "atop", "bridge", "fcc", and "hcp" adsorption sites, and each site has two orientations of 0° and 30°. The orientation is referred to the angles of the C–C bond relative to the close-packed metal rows.[2,3] Similarly, we employed these starting adsorption geometries for the olympicene molecule and its ketone on the Cu(111) surface.

References

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