Supplementary Information for

Hybridization at the organic-metal interface: a surface-scientific analogue of Hückel's rule?

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Experimental Methods

The experiments were performed in ultrahigh vacuum (UHV) using a commercial lowtemperature STM (Createc LT-STM) operated at 5.5 K. The Au(111), Ag(100) and Cu(100) single-crystal substrates were cleaned by standard sputter-annealing procedures and then transferred *in situ* into the cold STM. Owing to its high vapour pressure, COT (Sigma Aldrich, 98% purity) was injected into the UHV system as a pure gas through a leak valve. The molecules were deposited onto the cold sample inside the STM by opening the cryostat shutter for about 60 seconds. During this process, the partial pressure was about 10^{-8} to 10^{-7} mbar and the sample temperature always stayed below 20 K. The bias voltage in STM acquisition is referred to the sample, i.e., at positive (negative) voltages electrons tunnel from the tip (sample) to the sample (tip) thus probing the unoccupied (occupied) local density of states of the sample.

Theoretical Methods

Density functional theory (DFT) calculations were performed with the VASP code using the projector augmented wave (PAW) pseudopotential method with a plane-wave cut-off energy of 500 eV.^{S1-S4} The exchange correlation (xc) effects were described by the Perdew-Burke-Ernzerhof (PBE) functional.^{S5} The influence of long-range dispersion interactions, that are not correctly taken into account by the local or semi-local exchange-correlation functionals,⁸ has been investigated using the semi-empirical DFT-D3 approach.^{S6} For all three surfaces, the molecule-substrate system was modelled in a slab geometry consisting of six metal layers with the molecule adsorbed on one side of the slab. The ground state was obtained by relaxing the molecule as well as the upper three metal layers until forces were smaller than 0.002 eV/Å. STM images have been simulated within the Tersoff-Hamann model.^{S7}

Details of DFT calculations

Table S1 summarizes calculated bond lengths, molecule-surface distances, and adsorption energies for COT on the three noble-metal surfaces. The binding (adsorption) energy E_{ads} is defined as the difference between the total energy of the relaxed molecule-surface system E_{sys} and those of the molecule in the gas phase E_{molec} and the clean surface E_{surf} , i.e., $E_{ads} = E_{sys} - (E_{molec} + E_{surf})$.

Table S1. Calculated C–C single and C=C double bond lengths as well as DFT and DFT-D3 molecule-surface equilibrium distances (d_{eq}) and corresponding adsorption energies E_{ads} of COT on Au(111), Ag(100), and Cu(100). d_{eq} is defined as the distance between plane spanned by the substrate's surface atoms underneath the molecules and that spanned by the lowest molecular atoms (which is hydrogens in case of Au and carbons in case of Ag and Cu).

Surface	CC (Å)	C=C (Å)	$d_{\rm eq}({\rm \AA})$		$E_{\rm ads}({\rm eV})$	
			DFT	DFT-D3	DFT	DFT-D3
Au(111)	1.474	1.349	2.86	2.71	-0.162	-0.679
Ag(100)	1.436	1.416	2.39	2.39	-1.614	-2.174
Cu(100)	1.443	1.418	2.10	2.10	-2.636	-3.389



Figure S1. Overview images of COT adsorption on the three different noble-metal surfaces. Imaging parameters: (a) 1 V, 90 pA; (b) 1 V, 160 pA; (c) 1 mV, 1 nA

STM overview images

Fig. S1 displays large-scale images of COT on Au(111), Ag(100), and Cu(100), respectively. On Au(111), all molecules are clustered, despite the low deposition temperature of $T_{dep} < 20$ K. For the study of a single COT, we pulled out molecules from a cluster via lateral STM manipulation.^{S8} On Ag(100), only few clusters with a c(4x4) arrangement are found on Ag(100), while most molecules are isolated. On Cu(100), all COT molecules are isolated, i.e., no cluster has been found anywhere on the surface.



Figure S2. Lateral control of COT conformation on Au(111). (a) COT molecules adsorbed at elbow dislocations of the herringbone reconstruction exhibit a flat round protrusion different from the tub conformation. (b) A highly-resolved image of COT at an elbow dislocation (left) reveals a cross-like shape indicative of a planar conformation. (c) A tub-shaped COT is moved to an exposed elbow dislocation (arrow) (d) The molecule has changed to a planar conformation. Tunneling parameters: (a) 1 V, 80 pA; (b) 0.36 V, 0.4 nA; (c,d) 0.5 V, 1 pA.

Further results on Au(111)

In order to corroborate the general concept that the degree of hybridization determines the COT conformation, we can directly compare its properties on a surface with locally varying reactivity. Here we make use of the Au(111) herringbone reconstruction that can be seen as faint stripes in all our STM images on Au(111). The elbows (bends of the stripes) of the so-called *x*-type discommensuration lines exhibit point dislocations that are more reactive than other parts of the surface, often serving as nucleation sites for atoms and molecules. ^{11,S9–S12} Indeed, we also found that initial adsorption of COT on Au(111) starts by occupying the dislocation sites with a single molecule, respectively (cf. Fig. S1(a) and Fig. S2). Each COT appears as round protrusion with an apparent height of about 1.0 Å, i.e., much lower than the elongated COT on other parts of the Au surface. Highly resolved images reveal a cross-like pattern with fourfold symmetry (Fig. S2(b)) reminiscent of COT on Ag(100). These observations are clear evidence for a change of molecular conformation from tub to planar geometry upon adsorption of COT at Au(111) dislocation sites.

Going a step further, the conformation of COT can even be altered by means of STM manipulation.^{S8} Fig. S2(c) shows an STM image with two COT molecules in the tub conformation (left side and top right corner), a molecule in planar conformation adsorbed at an elbow dislocation (bottom left), and a free elbow site (bottom right). As indicated by the arrow in (c), one of the tub-shaped COT was moved to the dislocation (typical manipulation parameters: 50 mV, 0.5 nA). The image after this manipulation (Fig. S2(d)) shows that the molecule is now adsorbed at the dislocation and has changed its shape. It is now identical to that of the other elbow-adsorbed COT, i.e., it has changed from tub to planar conformation.

Bias dependence of apparent heights

Fig. S3 summarizes the apparent height of COT molecules on the three noble metals as a function of sample bias. There is virtually no bias dependence for Au(111). The apparent heights on Ag(100) and Cu(100) behave almost identical, and we observed a slight decrease for increasing sample voltages. The lack of significant bias dependent variations in the apparent height indicate that no sharp molecular resonances are present in the observed energy window ± 1 eV around E_F . Also simulated STM images show no significant voltage dependence. We note that for a particular set bias measured heights vary by several 0.1 Å. This is due to different set-point currents but also due to the influence of different STM tips.



Figure S3. Apparent height vs. sample bias of COT molecules on Au(111), Ag(100), and Cu(100). The observed bias dependence is relatively weak.

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