Supporting Information

Clarifying the Adsorption of Triphenylamine on Au(111): Filling the HOMO-LUMO Gap

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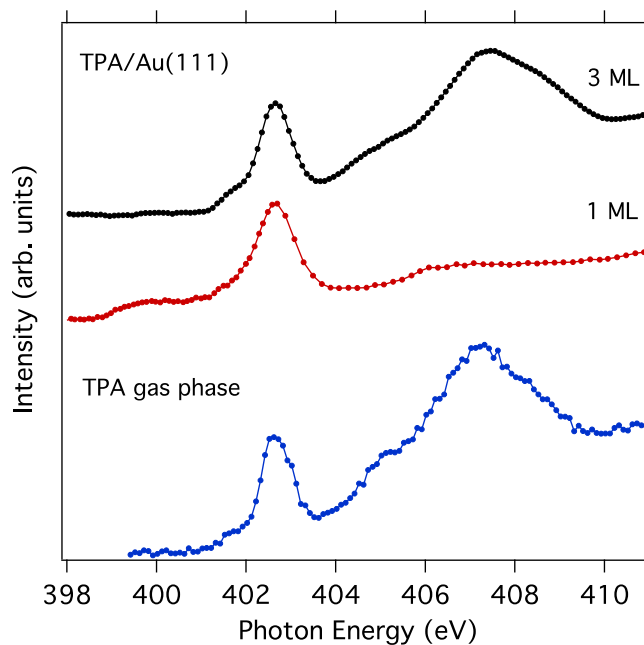**N Kedge NEXAFS for different coverages of TPA/Au(111)**

Figure S1 N K-edge NEXAFS spectra of TPA in gas-phase, of one monolayer (1 ML) and three layers (3 ML) of TPA adsorbed on Au(111). The pre-edge feature is clearly visible in the 1 ML spectrum but disappears in the 3 ML spectrum, indicating that it is the result of the interaction between the molecules and the surface.

C 1s and N 1s Photoelectron Spectroscopy

In Figure S2(a), we can observe a main peak at a BE of 283.82 eV and a weaker peak at the higher BE of 285.02 eV. In our previous study of gas-phase TPA,[1] we could attribute the lower intensity peak, that in gas-phase was located at 290.94 eV BE, to the C-*ipso,* while the main peak at the lower BE of 289.85 eV, to all the other C atoms (C-*ortho*, C-*meta* and C-*para* atoms). The adsorbed TPA spectrum profile is very similar to the gas-phase one. The general broadening of the adsorbate spectrum represents the main difference due to solid state effects,[2-3] therefore we maintain here the same assignment. The red and black arrows in the Figure S2(a) point to the shake-up features of TPA in gas-phase and /Au(111), respectively.
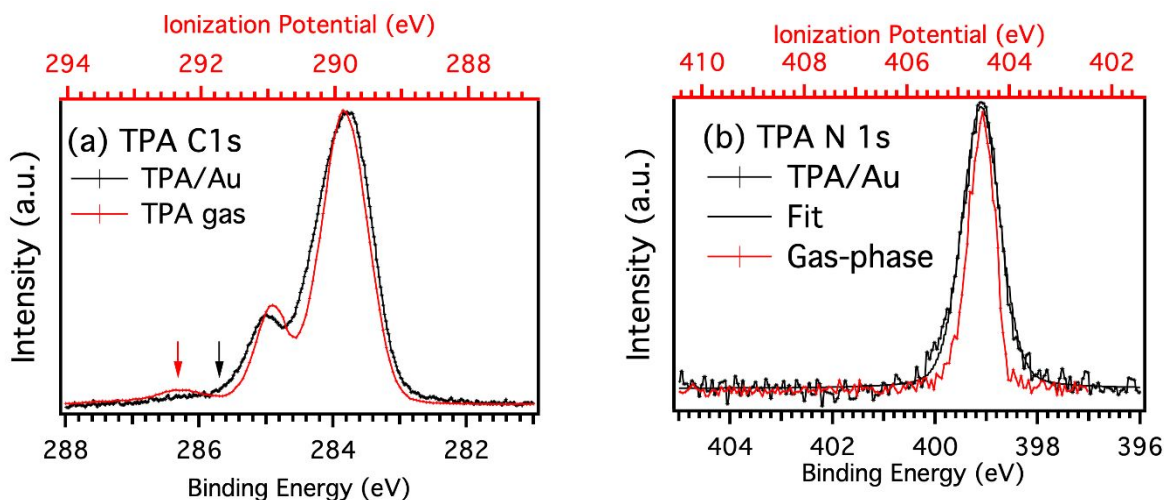
Figure S2: The (a) C 1s and (b) N 1s photoemission spectra showing comparison between gas-phase and 1 ML TPA/Au(111). Red and black arrows in (a) point to the shake-up in gas-phase and the C 1s tail in TPA/Au(111).

In Figure S2(b) we present the N 1s PE spectrum of 1 ML TPA/Au(111) in comparison to our previous gas-phase result.[1] The spectrum can be fitted by only one spectral component found at 399.11 eV. As for the C 1s PE spectrum and for similar reasons, the N 1s shows a broadening compared to the gas-phase results (FWHM 0.88 *vs* 0.56 eV) and a small asymmetry on the higher binding energy side of the peak.
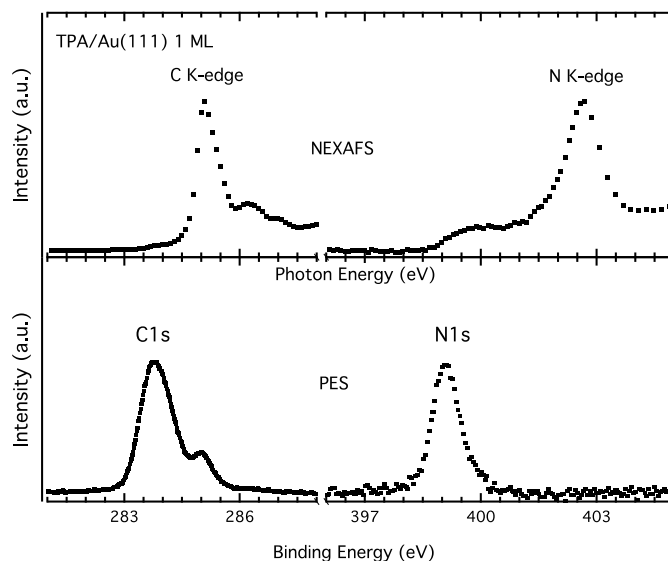

Figure S3: C1s and N1s core lines in (top) photoabsorption and (bottom) photoemission for 1 ML TPA/Au(111).

Adsorption Energy of TPA/Au(111)

The adsorption energy was computed as the difference between the total energy of the adsorbed system (TPA+surface) and the sum of the total energies of the molecule and of the surface and results in -2.00 eV. Since we do not have an experimental reference and, moreover, the calculated adsorption energy strongly depends on the choice of the DFT functionals and of the van der Waals descriptions,[4] this result is not a reliable parameter to evaluate the strength of the bonding of the molecule on the surface.

The propeller-like conformation of the TPA does not allow to simply evaluate the binding energy per each C atom. As the molecule has a non-flat geometry, there are six C atoms which are near the Au surface, with distances around 3.1 Å from their closest Au atoms. This would give a maximum value of 330 meV per each of these atoms, which would be rather high. However, this excludes all the other C atoms that are in the molecule, so in principle the binding energy for the C atoms closer to the surface could be lower.

Individual C contributions to C1s NEXAFS

Figure S4 shows the individual contributions in-plane and out-of-plane to the C K-edge NEXAFS in the HOL2 configuration of each C atom separately: C_{ipso}, C_{ortho} , C_{meta} (where *far* and *close* indicate the C_{ortho} or C_{meta} atoms closer or farther from the Au surface) and C_{para}.

shift=282.89 eV

- C-ipso$_{out of plane}$
- C-ipso$_{in plane}$
- C-ortho$_{out of plane}$ close
- C-ortho$_{in plane}$ close
- C-ortho$_{out of plane}$ far
- C-ortho$_{in plane}$ far
- C-meta$_{out of plane}$ close
- C-meta$_{in plane}$ close
- C-meta$_{out of plane}$ far
- C-meta$_{in plane}$ far
- C-para$_{out of plane}$
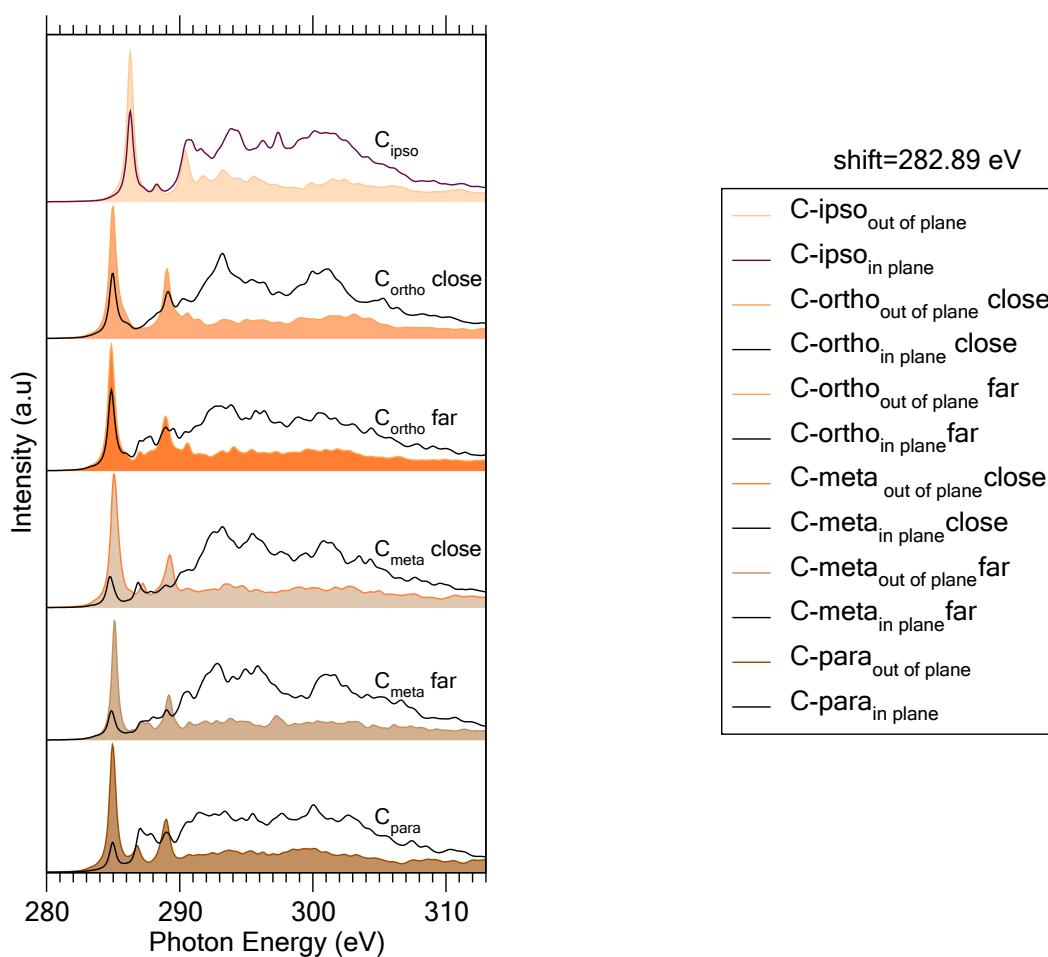- C-para$_{in plane}$

Figure S4: Individual contributions to the C K edge NEXAFS in the HOL2 configuration of each C atom separately.

References

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2.   Bidermane, I., et al., Characterization of Gas Phase Iron Phthalocyanine with X-Ray Photoelectron and Absorption Spectroscopies. *physica status solidi (b)* **2015**, *252*, 1259-1265.

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