## **Supporting Information**

# Lateral Interactions and Order-Disorder Phase Transitions of Metal Phthalocyanines on Ag(111)

Laura Fernández<sup>a,b,c</sup>, Sebastian Thussing<sup>a</sup>, Anton X. Brión-Ríos<sup>c,d</sup>, Daniel Sánchez-Portal<sup>c,d</sup> and Peter Jakob<sup>a</sup>

<sup>a</sup> Fachbereich Physik und Wissenschaftliches Zentrum für Materialwissenschaften, Philipps-Universität Marburg, Renthof 5, 35032 Marburg, Germany

<sup>b</sup> Universidad del País Vasco UPV/EHU, Dpto. Física Aplicada, 20018 San Sebastián, Spain.

<sup>c</sup> Centro de Física de Materiales CSIC-UPV/EHU, Paseo Manuel de Lardizabal 5, 20018 San Sebastián, Spain

<sup>d</sup> Donostia International Physics Center (DIPC), Paseo Manuel de Lardizabal 4, 20018 San Sebastián, Spain

### 1. Adsorption geometries for CuPc/Ag(111)

Several adsorption geometries have been calculated for CuPc/Ag(111) in the low coverage regime, namely a single CuPc molecule adsorbed on a ( $7 \times 4\sqrt{3}$ ) supercell (area 405 Å<sup>2</sup>). In Table S1, the calculated quantities for the different adsorption geometries are listed: adsorption energies E<sub>ads</sub> (eV), magnetization per molecule S ( $\mu_B$ ), metal ion positions with respect to the molecular plane h<sub>1</sub> (Å), and the distance between the topmost Ag-layer and the molecular plane h<sub>2</sub> (Å). To aid comparison, the respective values for TiOPc/Ag(111) [1] in the bridge<sub>+</sub> configuration have been included at the bottom (see Ref. [1] for TiOPc in other adsorption configurations).

Configuration	<sup>a</sup> E <sub>ads</sub> (eV)	<sup>b</sup> S (µв)	<sup>c</sup> h1 (Å)	<sup>d</sup> h2 (Å)
CuPc gas-phase	-	0.94	0.00	-
CuPc fccx	3.86	0.83	- 0.16	3.22
CuPc top <sub>x</sub>	3.84	0.85	- 0.11	3.22
CuPc top+	3.71	0.87	- 0.12	3.30
CuPc bridgex	3.87	0.87	- 0.08	3.29
CuPc bridge+	3.95	0.84	- 0.16	3.20
TiOPc bridge+	3.74	-	0.65	3.29

<sup>a</sup>E<sub>ads</sub>: adsorption energy per molecule in eV; <sup>b</sup>S: magnetization per molecule in Bohr magnetons; <sup>c</sup>h<sub>1</sub>: height difference between the central metal atom and the Pc molecular plane (aromatic backbone) in Å; <sup>d</sup>h<sub>2</sub>: distance between the Ag(111) surface and the Pc molecular plane in Å.

**Table S1:** Calculated quantities for different adsorption geometries of CuPc/Ag(111) in the low coverage regime, namely a single CuPc molecule adsorbed on a ( $7 \times 4\sqrt{3}$ ) supercell (area 405 Å<sup>2</sup>) in a fcc<sub>x</sub>, top<sub>x</sub>, top<sub>+</sub>, bridge<sub>x</sub>, and a bridge<sub>+</sub> configuration. To aid comparison, the respective values for TiOPc/Ag(111) [1] and CuPc in the gas phase have been included.

We have considered different positions of the metal center on the substrate: top, bridge and fcc. We have also considered two different geometries regarding the azimuthal angle: (i) with two of the inner-ring N atoms aligned along the <-110> high symmetry direction of Ag(111), in the following referred to as top<sub>+</sub> and bridge<sub>+</sub> and (ii) a 45° rotated geometry with respect to the <-110> direction of the surface. These last configurations are labelled as fcc<sub>x</sub>, top<sub>x</sub> and bridge<sub>x</sub>.

### 2. Dipole moment for CuPc/Ag(111)

The dipole moments for different adsorption geometries of CuPc on Ag(111) have been calculated and the results are summarized in Table S2. In general, only minor variations in the total dipole moments of CuPc/Ag(111) due to the specific adsorption configuration are found. Comparison to gas-phase CuPc reveals that the interaction with the surface leaves the molecular dipole  $d_{mol}$  virtually unchanged but imposes a strong induced dipole moment  $d_{ind}$  in the normal direction.

Configuration	<sup>a</sup> d <sub>mol</sub> (e·Å)	<sup>b</sup> dind (e·Å)
CuPc gas-phase	0.00	-
CuPc fccx	-0.05	1.50
CuPc top <sub>x</sub>	-0.02	1.53
CuPc top+	-0.04	1.36
CuPc bridgex	-0.07	1.46
CuPc bridge+	-0.01	1.49
TiOPc bridge+	-0.63	0.91

<sup>a</sup>d<sub>mol</sub> (molecular dipole) corresponds to the dipole of the (free) molecule computed using the molecular geometry obtained after adsorption. <sup>b</sup>d<sub>ind</sub> denotes the induced dipole computed using charge density distributions equivalent to those in Fig. 3(c) in the main text.

**Table S2:** Calculated vertical dipole moments ( $e \cdot Å$ ) of CuPc adsorbed on Ag(111), consistent with the results in Table S1. To aid comparison, the respective values for TiOPc/Ag(111) [1] have been included at the bottom.

#### 3. Highly symmetric molecular configurations

In order to compute the intermolecular interaction potentials we have used three different highly symmetric configurations where pairs of molecules are located in close proximity. They are denoted as ××, ×+ and ++. The respective intermolecular potentials computed for these configurations reveal that the most plausible ones are ×× and ×+ (see Fig. S1 and Fig. S2), while we disregard the ++ configuration (see Fig. S3). The latter yielded the smallest binding energies and it becomes very unfavorable at short distances (<17 Å). The respective effective intermolecular potential has been computed for both TiOPc (solid red line) and CuPc (solid black line).

In the case of CuPc a barrier potential is found at short range distances that is much more pronounced than in the case of TiOPc. For comparison, the computed effective intermolecular potential that considers the effect of the total point dipole only, e.g. without considering ab-initio Coulomb interactions, is additionally displayed (dashed lines). As expected, both potentials behave very similar at large distances. At intermediate distances, however, the potentials that merely include the effect of the dipolar interactions severely underestimate the electrostatic repulsion.



**Figure S1:** Effective intermolecular potential computed for the configuration ×× for CuPc (black line) and TiOPc (red line) Continuous lines represent the effective potential calculated considering ab initio Coulomb interactions. The dashed lines represent effective potentials that only include the effect of the total point dipole.



**Figure S2:** Effective intermolecular potential computed for the configuration ×+ for CuPc (black line) and TiOPc (red line) Continuous lines represent the effective potential calculated considering ab initio Coulomb interactions. The dashed lines represent effective potentials that only include the effect of the total point dipole.



**Figure S3:** Effective intermolecular potential computed for the configuration ++ for CuPc (black line) and TiOPc (red line) Continuous lines represent the effective potential calculated considering ab initio Coulomb interactions. The dashed lines represent effective potentials that only include the effect of the total point dipole.

Fernández, L.; Thussing S.; Mänz, A.; Witte, G.; Brión-Ríos, A. X.; Cabrera-Sanfelix, P.;
Sánchez-Portal, D.; Jakob, P. Structural and Vibrational Properties of the TiOPc
Monolayer on Ag(111). *J. Phys. Chem. C* **2017**, 121, 1608-1617.