

# AlPc synthesis by spontaneous crossmetalation of ZnPc on Al(100)

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Central atoms in phthalocyanines (Pcs) take part in the interaction of the molecule with metal substrates and their specific role in such interaction is an important topic of investigation. Pcs, such as porphyrins, corrins and corroles can be synthesized with different metals in the center of the ring. In particular, the macrocycle of Pcs can host over 70 metal ions into its center [1].

However, as in the other porphyrins, if the central atom is trivalent, an axial substituent is necessary to stabilize the molecule. This is the reason why it is possible to buy a commercial CIAIPc, but AlPc is unstable in air. In recent years, AlPc has been synthesized via interface reactions. For example, it has been shown that, after the sequential deposition of H<sub>2</sub>Pc and Al atoms on Au(111), some of the H<sub>2</sub>Pcs spontaneously metalate, forming AlPc [2]. A different procedure consists in the dechlorination of CIAIPc deposited on Pb(100) by thermal annealing to 470 K [3]. Another interface reaction paths involving central atoms is the substitution of the central atoms with an atom from the substrate. In literature, it has been shown, for example, that AgPc can be obtained from H<sub>2</sub>Pc deposited on Ag(110) by spontaneous metalation [4], while on Ag(111) the process needs to be triggered by a scanning tunneling microscope (STM) tip [5]. However, the synthesis of AlPc by spontaneous crossmetalation with metal substrate atoms was never observed so far. Here, we demonstrate that AlPc is spontaneously formed by ZnPc when the latter is deposited on Al(100). Following a spontaneous crossmetalation path, Zn central atoms are in fact replaced with an Al atom from the substrate. We investigate this process by combining experimental results obtained by X-ray photoelectron spectroscopy (XPS) and low-temperature STM with ab-initio calculations. Density functional theory (DFT) indeed shows that the crossmetalation process occurs without any energy barrier, releasing 2 eV per molecule. Finally, we investigated the electronic properties of AlPc on Al(100) by ultra-violet photoelectron spectroscopy (UPS) and scanning tunneling spectroscopy (STS).

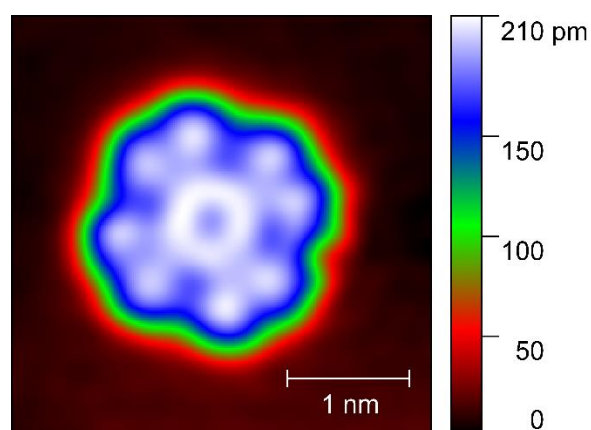


Fig. 1. STM image of AlPc resulting from crossmetalation of ZnPc on Al(100).

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