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Abstract for an Invited Paper
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Bonding at the Metal-Organic Interface¹

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We present the results of density functional theory calculations that account for dispersion, which systematically study the perturbations of the electronic structure of various organic molecules physisorbed or weakly chemisorbed to the (111) surfaces of the coinage metal surfaces copper, silver and gold. The molecules considered include: benzene, substituted benzenes, 4-fluorostyrene, tetraphenyl porphyrin, a quinonoid zwitterion, croconic acid and rhodizonic acid. We have employed a frontier orbital perspective to analyze the bonding between the substrate and the adsorbate, studied the charge redistribution at the organic-metal interface, and analyzed how this affects the self-assembly. Our theoretical studies have helped to explain the experimental observations of STM (scanning tunneling microscopy) groups by showing that: tetraphenyl-porphyrin forms attractive networks on the Ag(111) surface and repulsive ones on Cu(111) because of the larger amount of charge transfer on Cu(111); the 10 D dipole of a quinonoid zwitterion changes substantially upon adsorption to the coinage metal surfaces Cu(111), Ag(111) and Au(111) as a result of donation of charge from the molecular HOMO to the surface and back donation to the LUMO; the charge transfer which occurs between the quinonoid zwitterion and Au(111) has been studied as a function of surface coverage; 4-fluorostyrene molecules form clusters of “magic” sizes that depend on the metal surface and can be understood in terms of a balance between attractive H-bonding and van der Waals interactions as well as Coulomb repulsion between the molecules; the topological organic ferroelectric molecule croconic acid forms chiral honeycomb networks on the Ag(111) surface. Moreover, our calculations have illustrated that classic activating groups generally increase and prototypical deactivating groups decrease the amount and direction of charge transferred from a substituted benzene derivative to the Cu(111) and Ag(111) surfaces. The effect of functionalization on the binding site preferences of benzenes substituted with various activating and deactivating functional groups has been explored.

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