Organic molecular self-assembly at metal surfaces:
From ordered metastable phases to covalently bonded 2D networks

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Molecular self-assembly of organic species on metal surfaces is observed for an assortment of monolayer preparation approaches including electrochemical deposition, Langmuir-Blodgett film formation, solution sensitization and molecular sublimation. Exploiting van der Waals interactions on single crystal surfaces is a particularly interesting path towards controlled “bottom up” formation of extended, highly ordered 2D systems with potential tunability through the choice of molecular units and substrate surfaces. Such assemblies could give rise to novel low-dimensional organic electronic systems if one could achieve controlled covalent bonding between molecular units that preserves the order of the self-assembled array.

While there have been many studies characterizing self-assembly of organic molecules at metal surfaces, how the competition between substrate-molecule interactions and intermolecular forces impact molecular arrangement during overlayer growth is poorly understood. Moreover, the nature of surface-mediated chemical reactions that can proceed for these self-assembled systems remains elusive. To address these questions we have investigated the adsorption of zinc(II) tetraphenylporphyrins (ZnTPP) on metal surfaces (Au(111), Ag(111) or Ag(100)) in ultra-high vacuum, and their subsequent reorganization and chemical transformations upon annealing, using scanning tunnel microscopy, direct and inverse photoemission spectroscopies, ab-initio computational techniques and kinetic Monte Carlo simulations.

We show that molecule/molecule and molecule/surface interactions, as well as accumulated surface stress, all play important roles in determining the nature of the self-assembly. In particular, highly-ordered, inhomogeneous, kinetically-trapped self-assembled systems are observed, indicating that far-from-equilibrium processes can play an important role in building these 2D systems. Furthermore, when self-assembled ZnTPP arrays are exposed to appropriate conditions, it is possible to induce surface-mediated chemical reactions that leads to site-selective dehydrogenation and intramolecular covalent bond formation. Intermolecular dehydrogenation also is observed which, if directed properly, could lead to tunable highly ordered 2D covalent structures.

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