**Abstract:** Optoelectronic and mechanical properties of a thin film device are dramatically affected by the nature of the first layers of material in contact with its support—often an electrode. Therefore, a method for the rational design of structures on conductors is highly desirable. Scanning Tunneling Microscopy (STM) was used to investigate the structure and evolution of Co(II) octaethylporpyrin (CoOEP) at the solution/gold interface.

Solvent choice was observed to affect the surface structure of CoOEP on Au(111), shown above. Compared to the pseudo-hexagonal structure of CoOEP under phenyloctane, a second rectangular phase is also seen when decane solvent is used. To understand the cause of this variation in structure, we will look at the structure of CoOEP under solvents with selected viscosities and solubilities. If this is a kinetic phenomena, then a variation in solvent viscosity would cause an observable structure difference. If this variation is thermodynamically driven, then a variation of CoOEP solubility (in a given solvent) would affect the surface structure.

Scanning Tunneling Microscopy (STM) is a high-sensitivity technique that can be used to probe the nanoscopic world and achieve molecular and submolecular resolution. Here is a schematic of a typical experimental setup. A tunneling current occurs when the scanning probe tip is within nanometers of a conductive sample. As the tip raster scans across the sample surface, an image of the electronic density is collected. Shown above is the resolved lattice structure of carbon in highly ordered pyrolytic graphite (HOPG), as well as the self-assembled monolayer (SAM) of Zn(II) didecylporpyrin (ZnD10P) at the phenyloctane/HOPG interface.

**The time evolution** of the spontaneous self-assembly of CoOEP on Au(111) can be seen in the series of images above. The island nucleation and growth of CoOEP is observed at the phenyloctane/Au(111) interface. When the molecules in the 1 μM solution come into equilibrium with the molecules on the surface, a near monolayer of pseudo-hexagonally packed CoOEP is observed. By measuring the surface coverage over time, kinetic rates constants of adsorption and desorption could be extracted; and if the equilibrium coverage is measured over a range of temperatures, energetic values of this self-assembly could be extracted.