Cooperativity

**Chemical Reactions Dynamics and Supramolecular Chemistry at the Solution-Solid Interface**

**Kristen Johnson**

**Ursula Mazur & KW Hipps Research Group**

**Washington State University**

**Department of Chemistry & Materials Science Program**

**Metalloporphyrin Ligation Reaction Dynamics & Cooperativity**

- **4-methoxypyridine (MeOPy)**
- **Cobalt(II)octaethylporphyrin**
- **CoOEP**
- **Substrate: HOPG**
- **Atmosphere: Argon**

**System follows a Langmuir isotherm, consistent with reversible adsorption of one ligand per porphyrin site. This allows us to determine equilibrium constants for the reaction. Further thermodynamic values can be determined by monitoring the temperature dependence of the reaction.**

\[
\theta = \frac{K_c}{1 + K_c} \]

**MeOPy binds reversibly to CoOEP. The system is in dynamic equilibrium since the average θ value remains unchanged. All systems shown are in dynamic equilibrium.**

**Acknowledgements:** This material is based on work sponsored by the National Science Foundation under grant CHE-1807225. We gratefully acknowledge their support.

**Supramolecular Chemistry: Hydrogen Bonded Organic Frameworks (HOFs)**

**Influence of Substrate**

- **ETC**
- **BPDC**
- **ETTC**

**Influence of Concentration**

- **HOPG**

We investigated the influence of intermolecular interactions (molecule-molecule & molecule-substrate) on self-assembled monolayers with scanning tunneling microscopy (STM). The molecules of interest have been used as ligands in metal-organic frameworks (MOFs) are aromatic and non-planar.

**Sample Preparation:**

A 10 μL aliquot of the molecule of interest in heptanoic acid (1 × 10⁻⁴ to 1 × 10⁻⁵ M) was added to prepared substrate and imaged using scanning tunneling microscopy in constant current mode. Typical scanning parameters were -0.5 V sample bias and 20 pA tunneling current. All images shown are 10x10 nm.

**Supramolecular Chemistry: Hydrogen Bonded Organic Frameworks (HOFs)**

**Influence of Concentration**

- **HOPG**

We investigated the influence of intermolecular interactions (molecule-molecule & molecule-substrate) on self-assembled monolayers with scanning tunneling microscopy (STM). The molecules of interest have been used as ligands in metal-organic frameworks (MOFs) are aromatic and non-planar.

**Sample Preparation:**

A 10 μL aliquot of the molecule of interest in heptanoic acid (1 × 10⁻⁴ to 1 × 10⁻⁵ M) was added to prepared substrate and imaged using scanning tunneling microscopy in constant current mode. Typical scanning parameters were -0.5 V sample bias and 20 pA tunneling current. All images shown are 10x10 nm.

**CoOEP + MeOPy:**


**HOFs:**


**Chemical changes in adsorbates produce observable changes in the STM images. Image changes are interpreted as changes to the local density of electronic states at the energy of the tunneling electron.**

**Investigations of cooperative molecular recognition behavior in metalloporphyrin can provide basic understanding of kinetics and thermodynamics of multisite catalysis where the ligand binding information is communicated to all the active sites simultaneously.**

**Thermodynamics**

**Cooperative effects can be investigated by comparing the proximity distribution of reacted molecules to a random distribution, here modeled by a binomial distribution. In preliminary results, the reaction with MOPy shows positive cooperativity as there is an increase in the observed numbers of higher reacted neighbors (2 - 4).**

**Acknowledgements:** This material is based on work sponsored by the National Science Foundation under grant CHE-1807225. We gratefully acknowledge their support.