Soft Materials

Traditional materials

* Colloids
* Polymers
* Emulsions
* Liquid crystals
* Surfactants
* Food / Living matter etc.

Foams

**Organic** / Inorganic **Thin Films**

Cells
Gels
Tissues etc.

Not so traditional !!
Why are Self Assembled Structures Important / why understand them at all?

• Self Assembly
• Collective Properties
• Interactions – weak!!

Self Assembly / Interactions

* Building Blocks – scale, shape and structure
* Forces – Attractive / Repulsive
* Association / Dissociation – Reversible?
* Interfaces / Templates / Solvents
* Dynamics of formation / Mass transport
* Introduction

* Why SAMs? – Applications Envisaged / Demonstrated

* Formation of Monolayers – LB method and SAM formation

* Some characterization methods
  * Electrochemistry
  * Vibrational Spectroscopy
  * Contact angle
  * STM

* Hydrophobicity / orientation dependent catalysis
Organized Monolayer Assemblies

**Thin Films**
- Organic Thin Films

- Single molecular layer on substrate
- Share a common orientation
- High degree of order and packing
- Amenable for surface modification

Thickness - 0.5 – 4 (!) nm
Applications

- Wetting Studies – Hydrophobicity
- (Bio) Sensors
- Long range electron transfer
- Corrosion Protection
- Nanotribology – Lubrication – Molecular study of wear and friction
- Molecular Electronics
- Lithographic Patterning
- Supramolecular Assemblies - Molecular Recognition
- Surfaces for Study of Biological Systems
Why Organized Monolayers

- D Allara / R Nuzzo / A. Ulman /

• Offer unique opportunities –
  • Fundamental understanding of self-organization, structure-property relationships, and interfacial phenomena.

• Excellent systems - Intermolecular, molecular - substrate and molecular - solvent interactions
  • Ordering and growth
  • Wetting
  • Adhesion
  • Lubrication
  • Corrosion

• Good model systems - Studies on physical chemistry and statistical physics in two dimensions, and the crossover to three dimensions because of the well-defined structure.

• Design flexibility
  → applicable in many areas such as microarrays, molecular electronics, and sensors
Molecular Electronics (Molecular Rectifier)

Converts Alternating current to Direct current

Solid state rectifier: Diode

p-n junction

Unidirectional flow of current

Organic molecule:

electron-rich DONOR (D: TTF)
electron-poor ACCEPTOR (A: TCNQ)

Mixed crystal

p-n junction

Rectifying molecule

Positive bias:
Electrons emitted from Au
Electrons collected by Hg

Negative bias:
Electrons emitted from Hg
Electrons collected by Au

D: (n-hexadecyl) quinolinium  
A: tricyanoquinodimethane  
π-bridge  
Metal: Pt and Mg  
Rectification ratio: 4


D: Pyrene  
A: Dinitrobenzene  
σ-bridge  
Metal: Ag and Mg  
Rectification ratio: 130

Molecular Electronics: Assembling Nanocircuits - Bottom Up Approach

Next generation electronic circuits through Chemistry

Science, 2001, 293, 782
Gold SAM as a Tool to Study Single Molecular Electronics.

Gold forms excellent electrical contacts.
(a) Structures of the long and short linked cobalt coordinated terpyridine thiols used as gate molecules. (b) A topographic AFM image of the gold electrodes with a gap. (c) A schematic representation of the assembled single atom transistor.
Scheme 1. Reconstitution of Glucose Oxidase onto a PQQ/FAD Monolayer Au-Electrode and Direct Electro catalyzed Oxidation of Glucose by the Modified Electrode

Sensitivity and turn-over number
SAMs on Au: DNA and Protein Arrays

Plasmon Imager®

Zyomyx: Protein Biochip

Thermo Hybaid: XNA on Gold™
Substrate modification for attachment of Biomolecules

-protein + 2-iminothiolane

-protein-\text{NH}_2+\text{NH}_2^+\text{Cl}^-

-protein-\text{NH}+\text{C-CH}_2\text{CH}_2\text{CH}_2\text{SH}

-protein-\text{NH}_2\text{Cl}^-

-protein-\text{NH}+\text{C-CH}_2\text{CH}_2\text{CH}_2\text{S}-

Gold-coated substrate

3-MPA \text{HO-C-CH}_2\text{CH}_2\text{SH} \rightarrow \text{Gold-coated substrate}

11-MUA \text{HO-C(}\text{CH}_2\text{)_{10}}\text{SH} \rightarrow \text{Gold-coated substrate}

N-hydroxysuccinimide, NHS

N-ethyl-N'-(dimethylaminopropyl) carbodiimide hydrochloride, EDC

H_2\text{N-}\text{C-CH}_2\text{CH}_2\text{CH}_2\text{NH}_2\text{Cl}

H_3\text{N}---\text{Protein}

protein-\text{NH}+\text{C-(CH}_2\text{)_{x}S}-
Formation of Organized Monolayers
**Organized Monolayer Assembly**

- Single molecular layer on substrate
- Share a common orientation
- High degree of order and packing
- Amenable for surface modification

---

**Langmuir-Blodgett**

- Physisorption
- Organization prior to transfer on substrate

**Self-Assembly**

- Chemisorption
- Adsorption to substrate followed by organization
Compressed monolayer
Applying pressure by a barrier at the air-water interphase
Deposition of first monolayer onto hydrophobic surface
Substrate reverses
Deposition of second layer
Langmuir-Blodgett Technique
Interactions:
- Hydrophobic-hydrophobic
- Hydrophilic-hydrophilic

No substrate specificity

Same molecule can be aligned in either direction
Self-Assembly

- Spontaneous organization of molecules on substrate
- Specific interaction between substrate and molecule
  - Covalent: Alkoxy silane on glass
  - Electrostatic: Carboxylates on Ag
  - Chemisorption: Alkanethiol on Au

Interactions involved in a self-assembled monolayer
* Stability *
- Strong interaction of head group with substrate
- Lateral interaction between the molecules on the surface: van der Waals interaction
- Head group-head group interaction
Thermodynamics of Self-Assembled Monolayers on a Substrate

The free energy of a self-assembled monolayer is minimized because of three main processes:

- Chemisorption of the surfactant onto the surface, \(\sim 40-45\) kcal/mole
- Interchain van der Waals interaction, \(< 10\) kcal/mole
- Terminal Functionality, \(\sim 0.7-1.0\) kcal/mole for CH\(_3\) termination
Bigelow, W. C.; Pickett, D. L.; Zisman, W. A.
Oleophobic monolayers. I. Films adsorbed from solution in non-polar liquids.
Journal of Colloid Science (1946), 1, 513-38.

Pt substrate – Octadecylamine in hexadecane

Sagiv, J
JACS (1980), 102, 92.

Oxide surfaces – Silane monolayers

Nuzzo, R and Allara, D
JACS (1983), 105, 4481.

Gold – Sulphur containing compounds
• Monolayers of Fatty Acids

• Monolayers of Organosilicon Derivatives

• Alkyl Monolayers on Silicon

Organosulfur Adsorbates on Metal and Semiconductor Surfaces
- Monolayers of Alkanethiolates on Au(111) Surfaces

• The most studied SAMs to date

Where is the hydrogen?
SAMs on Oxide Surfaces

- Alkylchlorosilanes or alkoxyisilanes
- Requires hydroxylated surfaces
- *in situ* formation of polysiloxane, which is connected to surface silanol groups (-SiOH) via Si-O-Si bonds
SAMs on Oxide Surfaces

- **not easy to produce**, mainly because of the need to carefully control the amount of water in solution

  - Incomplete monolayers are formed in the absence of water

  - Excess water results in facile polymerization in solution and polysiloxane deposition of the surface

- For the formation of closely packed monolayers, a moisture quantity of 0.15 mg/100 mL of solvent was suggested as the optimum condition

- Temperature: the threshold temperature below which an ordered monolayer is formed.

  - The threshold temperature is a function of the chain length [higher for octadecyl (18 °C) than for tetradecyl chain (10 °C)].
Vapor Phase Deposition
- Silane Monolayers

- Silane bubbler is used for introducing gas phase silane into quartz reaction tube
- \( N_2 \) is used as the carrier gas and the byproducts and/or non-reacted silanes are trapped in the by-product condenser
SAMs on Au(111): Mechanism

• Proposed mechanism: oxidative addition of the S-H bond to the gold surface, followed by a reductive elimination of the hydrogen

\[
R-S-H + Au^n \rightarrow R-S-Au^+\cdot Au^n + \frac{1}{2}H_2
\]

• On the basis of the bond energies of RS-H, H-H, and RS-Au (87, 104, and 40 kcal/mol, respectively), the net energy for adsorption of alkanethiolates on gold would be ca. –5 kcal/mol, which is exothermic.
Characterization Methods
How Does One Know That The Monolayer Exists On the Surface !!

Characterization Techniques

* Contact Angle Measurements
* Thickness measurements / Pinhole defects – Electrochemistry
* Surface Analysis –
  * Microscopy – STM / AFM
  * Spectroscopy - Vibrational Spectroscopy

* Others – SAXS / HREELS / XPS / Diffraction etc.
Electrochemical Measurements

• The well organized nature of the monolayers has led to their use in various long range electron transfer studies.

• Pinhole defects in monolayers can be characterized through Cyclic Voltammetry (CV) in electrolyte solutions containing aqueous redox probes (e.g. K₃Fe(CN)₆).
Cyclic voltammetry – DC measurement

K₃Fe(CN)₆ / K₄Fe(CN)₆

Surface Coverage

- Ip : Peak current for oxidation / reduction
- Percentage of the current observed for the modified surface
- Apparent coverage values only
Impedance Studies – AC Measurement

A small ac signal is impressed over a dc bias.

Resulting ac current response from the electrochemical cell is monitored as a function of frequency of the ac signal.
Coverage of cystamine SAM

1 mM $K_4(Fe(CN))_6/K_3Fe(CN)_6$ in 0.1 M KCl

R\textsubscript{CT}: Charge transfer resistance
Percent coverage: 1 - (R\textsubscript{CT\,bare} / R\textsubscript{CT\,mod}) x 100
Apparent coverage: 50%
Short chain - highly disordered - poor blocking
Equivalent circuit - Electrical elements such as resistors / capacitors etc.
Infrared Reflection Absorption Spectroscopy - IRRAS

\[ \text{CH}_2 \text{ – symmetric, } d^+ \text{ - } 2850 \text{ cm}^{-1} \]
In-plane CCC backbone plane, In-plane HCH plane

\[ \text{CH}_2 \text{ – anti symmetric, } d^- \text{ - } 2920 \text{ cm}^{-1} \]
Perpendicular (⊥) CCC backbone plane
Grazing angle Incidence IR

Metal electrons screen the components of the electric field vector parallel to the surface

Component normal to the surface can couple to molecular vibrations

Direct analysis becomes difficult

Indirect methods:

Bulk IR spectra

Excitation probabilities of a vib.mode
Relative prob. of two or more modes
Intensity proportional to transition dipole moment

\[
\left( \frac{|TDM_1|}{|TDM_2|} \right)^2 \text{ of two different bands} = \frac{I_1}{I_2} \text{ bulk}
\]

\[
\left( \frac{|TDM_{1,z}|}{|TDM_{2,z}|} \right)^2 = \frac{I_1}{I_2} \text{ SAM}
\]

\[
\tan^2 \theta = \frac{I_1 \text{ bulk}}{I_2 \text{ SAM}} \frac{I_2 \text{ bulk}}{I_1 \text{ SAM}}
\]

The frequency of CH\(_2\) vibrational modes give the order of the monolayer – all trans configuration

- CH\(_2\) symmetric: 2850 cm\(^{-1}\)
- CH\(_2\) asymmetric: 2920 cm\(^{-1}\)
SAMs on Au(111): Structure STM / AFM

- Sulphur atoms occupy 3-fold hollow sites of the Au(111) lattice

- From \textit{ab initio} calculations for the alkanethiolate-gold bonding, it has been concluded that the hollow sites, involving a second-layer Au atom located directly below the S atom from the thiol molecule, are the most stable sites for adsorption on Au(111). This type of bonding would imply a mixed $\sigma$- and $\pi$-bonding character with a dominating contribution of the latter.
Structure of SAMs on Gold: STM Study

Octanethiol on Au(111)

Gregory E. Poirier
Chemical Science and Technology Laboratory, National Institute of Standards and Technology
http://www.cstl.nist.gov/div836/836.04/SAMS/structure.htm

Chem. Rev. 1997, 97, 1117
Unit cell defined by two vectors, $b_1$ and $b_2$

Substrate: fcc (111)  
$(\sqrt{3} \times \sqrt{3})_{R30°}$

(100) and

2 X 2 adlayer +  
a central atom crystallographically equivalent  

c( 2 x 2 )

$(\sqrt{2} \times \sqrt{2})_{R45°}$ - True primitive unit cell
Contact angle

Advancing contact angle
Receding contact angle

Three phase boundary is moving!!

Hysterisis – heterogeneity / roughness / mobility

$$\gamma_{lv} \cos \theta = \gamma_{sv} - \gamma_{sl}$$

$\gamma$ - Interfacial energy
Measurement

Goniometry - liquid drop - light sources / image capture

Tensiometry – surface forces –

force of interaction / geometry of the solid and surface tension of the liquid

Wetting force = \( \gamma_{LV} \cdot P \cdot \cos \theta \)

\( \gamma_{LV} = \) liquid surface tension

\( P = \) perimeter of the probe

\( F_{\text{total}} = \) wetting force + weight of probe - buoyancy
Self-Assembled Monolayers (SAMs)

CHARACTERISTICS

- Molecularly-Defined Surfaces
- Surfaces with Specific Chemical Functionalities
- Precise Tuning of Surface Properties
- Lubrication, Corrosion Protection, Resists, and Sensing
- $7 \times 10^{-10}$ mol cm$^{-2}$ (alkanethiols on gold)

CHARACTERIZATION

- Contact Angle Measurement
- Ellipsometry
- IR Spectroscopy (Grazing Angle Reflection and Transmission)
- Atomic Force Microscopy (AFM) and Scanning Tunneling Microscopy (STM)
- X-ray Photoelectron Spectroscopy (XPS) and Auger Electron Spectroscopy (AES)
- UV-vis and Fluorescence Spectroscopy
- Surface Plasmon Resonance (SPR) Spectroscopy
- Quartz Crystal Microbalance (QCM)
- Electrochemical Characterization (CV and Impedance Spectroscopy)
HYDROPHOBIC EFFECTS

- Structure of hydrophobic SAM - aqueous interface

Driving force for many biological and physiological processes

* Protein folding
* Micellization
* Adhesion
* Wetting
* Friction
* Coagulation
* Conformation changes of bio-polymers etc.,
Figure 1. (a) Schematic view of local water structure near a small hydrophobic sphere. Dashed lines indicate hydrogen bonds. (b) Schematic view of water structure near large parallel hydrophobic plates. Shaded area indicates regions where water density is essentially that of the bulk liquid; vacant regions indicate where water density is essentially that of the bulk vapor.
Au on mica: Template stripping
Smooth surface

SAM formation: Adsorption under potential control

HEXANETHIOL (C6SH) on Au

* Thiols $> C_{12}SH$ - Well ordered, defect-free

* Thiols $< C_{12}SH$ Less ordered containing pinholes with defects
Blocking behavior for electron transfer - ordered monolayer

Impedance characteristics
$R_{\text{CT-SAM}} = 3.1 \ \text{M}\Theta \ \text{cm}^2$

Coverage $\approx 99\%$

Grazing angle - IR
$d^+ = 2849 \ \& \ d^- = 2916 \ \text{cm}^{-1}$

Well ordered structure
SAM modified Au  Aqueous electrolyte

Phase angle  = 88.1 degrees

Log (ω, Hz)  

Potential(V)

Current(μA)

Capacitance per unit area

Experimental value  = 1.2 μF

Expected  = 3.48 μF
Capacitance in various solvents – Wetting characteristics  
\((C_6SH \text{ on Au})\)

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Dielectric constant</th>
<th>Capacitance ((\mu F/cm^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dichloromethane</td>
<td>9.1</td>
<td>8.8</td>
</tr>
<tr>
<td>Ethanol</td>
<td>24.9</td>
<td>2.45</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>37.5</td>
<td>3.5</td>
</tr>
<tr>
<td>Dimethyl sulfoxide</td>
<td>46.6</td>
<td>4.15</td>
</tr>
<tr>
<td>Propylene carbonate</td>
<td>69.1</td>
<td>3.3</td>
</tr>
<tr>
<td>Water</td>
<td>78</td>
<td>1.2</td>
</tr>
</tbody>
</table>

Theoretically expected capacitance \(C(\mu F/cm^2) = \epsilon \epsilon_0 / d\)

- \(\epsilon\), Dielectric constant of the monolayer
- \(\epsilon_0\), Permittivity in air
- \(d\), thickness of the monolayer

Expected capacitance 3.48 (\(\mu F/cm^2\))
Capacitance values of short chain thiol monolayers on gold in various solvents

<table>
<thead>
<tr>
<th>Thiol</th>
<th>Expected value</th>
<th>In water</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(µF/cm²)</td>
<td>(µF/cm²)</td>
<td></td>
</tr>
<tr>
<td>C₃SH</td>
<td>6.95</td>
<td>1.82</td>
<td></td>
</tr>
<tr>
<td>C₄SH</td>
<td>5.22</td>
<td>1.51</td>
<td></td>
</tr>
<tr>
<td>C₆SH</td>
<td>3.48</td>
<td>1.20</td>
<td></td>
</tr>
<tr>
<td>C₈SH</td>
<td>2.61</td>
<td>0.95</td>
<td></td>
</tr>
<tr>
<td>C₉SH</td>
<td>2.32</td>
<td>0.77</td>
<td></td>
</tr>
</tbody>
</table>

Distance dependent hydrophobicity; Hydrophobicity at small and large length scales

*Figure 1.* (a) Schematic view of local water structure near a small hydrophobic sphere. Dashed lines indicate hydrogen bonds. (b) Schematic view of water structure near large parallel hydrophobic plates. Shaded area indicates regions where water density is essentially that of the bulk liquid; vacant regions indicate where water density is essentially that of the bulk vapor.
Large length scale regime - Extended hydrophobic units

- Energetically unfavorable to maintain H-bonds
- Depletion of water density
- $\Delta G$ of transfer proportional to surface area
- Entropic cost arises due to limited configurational space for H-bonding
- Entropy versus Enthalpy - Breaking of H-Bonds

“Thin vapour-like region at the interface!!”
Some Possible Reasons

* Vapour-like region?
* Presence of Nanobubbles – dissolved gases?
* Liquid- liquid transition (LDL / HDL – water)?
\[ \frac{1}{C} = \left( \frac{1}{C_1} \right) + \left( \frac{1}{C_2} \right) \]

\[ \frac{1}{1.2} = \left( \frac{1}{3.48} \right) + \left( \frac{1}{C_2} \right) \]

\[ C_2 = 1.83 \, \mu F \]

Bulk water

Interfacial gap - Low water density

\[ C_{SAM} = \left( \frac{1}{C_1} \right) + \left( \frac{1}{C_2} \right) \]

\[ C_{Bulk} \]

\[ C_{SAM} \]
## Interfacial capacitance of water at various thiol monolayers

<table>
<thead>
<tr>
<th>Thiol</th>
<th>$C_{SAM}$ $\mu F/cm^2$</th>
<th>$C_{SAM-OBTAINED}$ $\mu F/cm^2$</th>
<th>$C_{INTERPHASE}$ $\mu F/cm^2$</th>
<th>Thickness of the interphase $\epsilon = 1$ / nm</th>
<th>Thickness of the interphase $\epsilon = 78$ / nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>C3SH</td>
<td>6.95</td>
<td>1.82</td>
<td>2.46</td>
<td>0.36</td>
<td>28</td>
</tr>
<tr>
<td>C4SH</td>
<td>5.22</td>
<td>1.51</td>
<td>2.12</td>
<td>0.42</td>
<td>32.5</td>
</tr>
<tr>
<td>C6SH</td>
<td>3.48</td>
<td>1.2</td>
<td>1.83</td>
<td>0.48</td>
<td>37.7</td>
</tr>
<tr>
<td>C8SH</td>
<td>2.61</td>
<td>0.95</td>
<td>1.49</td>
<td>0.59</td>
<td>46.3</td>
</tr>
<tr>
<td>C9SH</td>
<td>2.32</td>
<td>0.77</td>
<td>1.15</td>
<td>0.71</td>
<td>60</td>
</tr>
</tbody>
</table>
Atomic Force Microscopy (AFM)

Adhesion force - Pull-off force to retract the tip away from the substrate
AFM - Force Curves

Au-C₆SH SAM in Water

Au-C₆SH SAM in Ethanol

Adhesion Force (nN)

No. of trials

Adhesion Force (nN)

No. of trials
Electrostatic response of hydrophobic surfaces measured by atomic force microscopy

* Arrangement of water near a hydrophobic surface

* Force acting on neutral tips as a function of distance

The force acting on the tip is modeled by the gradient of the electrostatic energy variation
Force is the gradient of the energy expression, \( F = - (\partial / \partial x) \Delta W \)

where,

\[
\Delta W = \frac{1}{2} \int_{0}^{10\lambda-d} (\varepsilon_{\text{tip}} - \varepsilon_{\text{int}}) E^2 \varepsilon_0 \pi \left[ R + (\tan \alpha) Z \right]^2 dz
\]

- \( E \) - Interfacial electric field
- \( \varepsilon_{\text{int}} \) - Coupling between interfacial charges and the polarization charges of the solvent molecules
- \( \lambda \) - Exponential decay length

\( Z, R \) and \( \alpha \) are the tip parameters with respect to the solvent

Orientation of the water molecules are described by a spatially variable dielectric permitivity given by an expression
Schematic model for probing the interfacial water structure

Electric field at the interface =
\[ E(z) = E_0 \exp \left( -\frac{z}{\lambda} \right) \]

Variable dielectric permitivity
\[ \varepsilon_{\text{int}}(z) = \varepsilon_{\text{bulk}} - [\varepsilon_{\text{bulk}} - \varepsilon(z=0)] \exp(-z/\lambda) \]

Force = \(-\frac{\delta}{\delta z} \Delta W\)

\[
\Delta W = \frac{1}{2} \int_{0}^{10\lambda-d} (\varepsilon_{\text{tip}} - \varepsilon_{\text{int}}) E^2 \varepsilon_0 \pi [R + (\tan \alpha)z]^2 dz, \quad (1)
\]
AFM studies on hexanethiol monolayer in presence of water

Force Vs Distance

Dielectric permitivity Profile
Water structure at Interfaces:

- X-Ray reflectivity
- Neutron Reflectivity
- Ellipsometry

**THEORY**
- Predicts only a thin interfacial layer where the properties of water differ

* Typically 1000 water molecules taken  
  (Self dissociated of water – not accounted for)
* Dissolved gases – not accounted for

**Electrostatics** - Known to affect water orientation up to a certain distance
Formamide √  H-bonded solvent

Acetonitrile  X
Propylene carbonate  X

- Drying transition is not unique to water alone!
ORIENTATION DEPENDENT CATALYSIS
Macromolecules
- Orienting molecules on substrates

Phthalocyanines
- Electrochromic devices
- Photovoltaics
- Optical data storage
- Sensors
- Catalysts in fuel cells etc.

Substrates: Au and Ag

Immersion of the substrate in a saturated solution of the TACoPc in n-butanol for 24h
Impedance measurements for blocking and coverage

(i) Bare Au surface
(ii) TACoPc modified Au

R_{ct} - Bare Au surface - 24.4 \, \Omega cm^2
R_{ct} - TACoPc modified Au surface - 164.0 \, \Omega cm^2

Coverage (\%) = 1 - \left( \frac{R_{ct-bare}}{R_{ct-modified}} \right) \times 100
\approx 90 \, \%
FT-Raman spectra of TACoPc self assembled monolayer

Table I. FT-Raman spectral bands (in cm\(^{-1}\)) of TACo(II)Pc films on Ag and Au. Relative intensities are given in brackets.

<table>
<thead>
<tr>
<th>Silver</th>
<th>(I/I_{\text{Ag-N}})</th>
<th>Gold</th>
<th>(I/I_{\text{Au-N}})</th>
<th>Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>1608(26)</td>
<td></td>
<td>1605(46)</td>
<td></td>
<td>(\delta\text{NH}_2)</td>
</tr>
<tr>
<td>1553(44)</td>
<td>1.83</td>
<td>1549(75)</td>
<td>4.90</td>
<td>(\gamma\text{CoN\text{(\alpha)}})</td>
</tr>
<tr>
<td>1469(56)</td>
<td>2.36</td>
<td>1484(77)</td>
<td>5.20</td>
<td>Isoindole ring stretching</td>
</tr>
<tr>
<td>1396(67)</td>
<td></td>
<td>1401(86)</td>
<td></td>
<td>(\gamma\text{CoN\text{(\beta)}}), (\gamma\text{C\text{(\beta)}}\text{C\text{(\beta)}})</td>
</tr>
<tr>
<td>1349(80)</td>
<td>3.33</td>
<td>1349(100)</td>
<td>6.70</td>
<td>(\gamma\text{C\text{(\beta)}}\text{C\text{(\beta)}}), (\gamma\text{C\text{(\alpha)}}\text{N\text{(\alpha)}})</td>
</tr>
<tr>
<td>1328(80)</td>
<td></td>
<td>1331(96)</td>
<td></td>
<td>Pyrrole stretch</td>
</tr>
<tr>
<td>1272(33)</td>
<td></td>
<td>1272(52)</td>
<td></td>
<td>(\delta\text{CH})</td>
</tr>
<tr>
<td>952(39)</td>
<td></td>
<td>951(37)</td>
<td></td>
<td>Benzene breathing</td>
</tr>
<tr>
<td>754(34)</td>
<td>1.42</td>
<td>754(46)</td>
<td>3.10</td>
<td>In-plane macrocycle stretching</td>
</tr>
<tr>
<td>736(42)</td>
<td></td>
<td>736(36)</td>
<td></td>
<td>Pyrrole ring out-of-plane bending</td>
</tr>
<tr>
<td>236(24)</td>
<td></td>
<td>235(15)</td>
<td></td>
<td>(\gamma\text{Ag—N and }\gamma\text{Au—N})</td>
</tr>
</tbody>
</table>

\(\gamma\) Stretching, \(\delta\), Bending
Orientation dependent catalysis

Possibility of controlling the kinetics and product distribution by orienting the molecules appropriately on the surface!!
Spectro-electrochemical study of BQ SAM

Reduction of quinone

Band at 1660 cm\(^{-1}\) disappears at \(-0.229\) V
Band at 1386 cm\(^{-1}\) increases in intensity till \(-0.229\) V
After \(-0.541\) V, all the quinonoid bands go down in intensity
Spectro-electrochemical study of BQ SAM (0.5 M, 3h)

Oxidation of hydroquinone

After –0.339 V, all the quinonoid bands increase in intensity
\[ P = \alpha E \]
Hexagonal coverage scheme for \( n \)-alkanethiols on \( \text{Au}(111) \). Empty circles are gold atoms; shaded circles are sulfur atoms. The space outlined by the thick solid lines is the lattice space of \((3 \times 3)R30^\circ\) and by the thick dashed lines is the superlattice space of \(c(4 \times 2)\).