Synthesis and Characterization of Functionalized Dendrimer and Dendrimer Thin Films Exhibiting Catalytic and Sensing Properties Based Upon Cooperative Effects

A Proposal

by

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I. Introduction

Nature abounds with examples of elegant and efficient chemistry. From genetic expression to photosynthesis to enzymatic processes, the chemistry of life demonstrates the potential inherent in well-designed (or evolved) biochemical systems. Making use of fundamental techniques or mimicking techniques displayed in biochemical systems is one manner in which chemists and materials scientists can use to control and design chemistries at the molecular level. One method of control and regulation commonly exhibited in biochemical systems is allosterism. Allosterism is the interaction of a specific ligand-receptor system that results in a chemical change. An example of such a system is the induced-fit lock and key model for ligand-protein binding. In this model, the interaction of a ligand with a protein results in a conformational change in the protein that alters the proteins chemical reactivity. Cooperative effects are one type of allosterism. Cooperative effects can be positive, causing a chemical event, or negative, prohibiting a chemical event. A cooperative effect is deemed homologous, if the chemical units interacting are the same, or heterologous, if the chemical units interacting are different. Thus, a positive homologous cooperative effect arises when multiple identical sites promote or cause a chemical event that would not be promoted in the absence of interaction between the sites.

My research is focused on molecules and organic thin films that have been tailored to exhibit cooperative effects. Specifically, I plan to use dendrimers and dendrimer modified thin films to arrange other molecules in a manner such that they cooperate to effect a chemical event. This event can be catalytic or sensory in nature, as determined by the molecule. My preliminary results have indicated that the preparation of such molecules and thin films is indeed possible and that they exhibit properties that warrant further investigation.

II. Background

Dendrimers

Dendrimers are a class of polymers that are unique because they are discrete molecules and because they exhibit a highly symmetric geometry. Typical size ranges of dendrimers are on the order of 1 to 10 nm, placing them in the perfect size regime to be utilized in nanostructured materials. Dendrimers are composed of three parts: the core, branches, and endgroups (Figure z.). As the dendrimers grow outward from the core, each successive set of branches is deemed a “generation”.

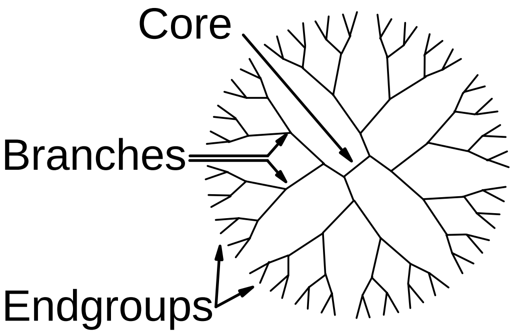


Figure z. Schematic diagram of dendrimer

While the concept and general description of a dendrimer is consistent, the actual structure and chemistry of dendrimers is far ranging and diverse.

Dendrimers have been synthesized that link the core, branches, and endgroups through purely covalent linkages, organometallic linkages, co-ordinative linkages, electrostatic linkages, and combinations thereof. Dendrimers based on organic chemistries are commonly terminated in an endgroup, such as an amine, that can be modified with specific functional groups at a later time. Functionalities that exhibit interesting optical, electrochemical, catalytic, and biological properties have been incorporated at the periphery of dendrimers by various research groups using this general strategy.

A key feature of dendrimers is that the chemical properties they exhibit are generation dependent. As the generation increases, so does the size and mass, resulting in changes in properties such as viscosity and the glass transition temperature. The shape of the dendrimer also changes, going from oblate, open molecules at low generations, to roughly spherical molecules at higher generations. Another generation-dependent property is the degree of steric interactions between branches and endgroups, especially those near the dendrimer exterior. In general, the distance between endgroups on a dendrimer depedns on dendrimer generation, with the endgroups of lower generation dendrimers relatively loosely packed, while endgroups of higher generation dendrimers are sterically crowded and in very close proximity.

Of primary interest in my research are two families of organic dendrimers, Astramol and PAMAM. Astramol (diaminobutane propyl amine) dendrimers are comprised of a diaminobutane core, with propyl amine branches. They range in size from 0.8(generation 1) to 2.8(generation 4) nm in diameter, with 4 and 64 terminal groups, respectively. They are available from commercial sources terminated in either cyano or amine moieties and are generally soluble in organic solvents. PAMAM (polyamido amine) dendrimers are comprised of an ethylene diamine core, with amide containing branches. They range in size from 1.5(generation 0) to 13.5(generation 10) nm, with 4 and 4096 terminal groups, respectively. They can are available terminated in a variety of moieties, including amine, hydroxy, and aliphatic.

Cooperative Units

To the endgroups of the dendrimers, I propose to attach modifiers which will act cooperatively with neighboring modifiers to enhance or effect a chemical event. By selectively varying the generation or species of dendrimer, I hope to gain further control over these cooperative interactions.

Porphyrins Interest in organized and nanostructured porphyrin materials is immense. This is due to the unique optical and electrochemical

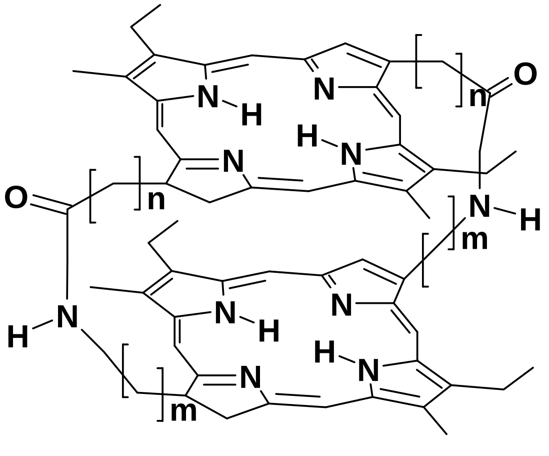


Figure r. Collman's Free base Face to Face (FTF) Porphyrin properties of porphyrins and multi-porphyrin systems. Catalysis, energy transfer, and pharmacological applications have all been demonstrated with porphyrins. In my research I plan to attach porphyrins to the exterior of a dendrimer, effectively holding them within a critical distance to serve as electocatalysts for specific substrates, similar to the famous face to face (FTF) porphyrins (figure r) prepared and characterized by Collman and Anson. In their work, Collman and Anson demonstrated that two metallated porphyrins held at a fixed distance resulted in catalytic molecules which could effectively reduce O_2 to H_2O by a four electron route (see proposed research). The catalytic properties of these FTF porphyrins are highly dependent upon the metal complexed at the center of the macrocyclic ring. Collman's work has shown that Co centers and mixed metal centers demonstrate the greatest catalytic activity.

Host-Guest Modifiers Host-guest chemistry has received much attention in recent years. Molecules such as cyclodextrins, calixarenes, cryptands and cyclophanes (figure t.) all exhibit interesting binding properties due to a regular, controlled structure. The dimensions and linkages in such molecules are of critical importance towards their chemical properties as hosts. In my research, I plan to attach specific modifiers to the surface of a dendrimer which cooperatively serve to mimic previously developed host-guest chemistries, allowing the modified dendrimer to serve as a host and effect the binding of guest molecules. These host-guest systems are useful as chemical sensors and can be used in molecular recognition strategies. To date only three examples of host-guest interactions at the surface of dendrimers has been successfully demonstrated.

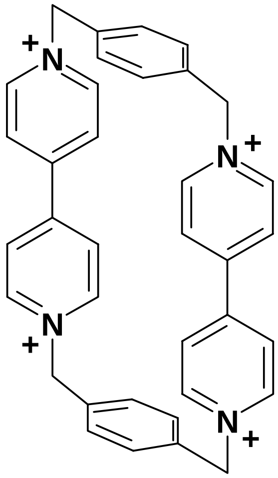


Figure t.
Cyclophane Host
Molecule

III. Materials and Techniques

Substrates

I will use three substrates in my studies. The first substrate is 2000 angstroms of gold deposited via electron beam onto a Si(100) wafer using a 100 angstrom layer of titanium for adhesion. This substrate is general purpose, but of primary importance in infrared external reflectance spectroscopic measurements. The second substrate I will employ is a "gold ball". By melting and carefully zone refining a gold wire in an H_2/O_2 flame, single crystal facets on the order of microns may be prepared. These facets provide smooth surfaces that can be imaged utilizing atomic force microscope techniques. The third substrate I will utilize is a thin (ca. 50-75 angstrom) gold film deposited on a quartz substrate with a mercaptosilane adhesion layer. These substrates are useful in UV-vis spectroscopic measurements, allowing for monolayer spectra of strongly absorbing species to be recorded in transmission mode.

Techniques

Electrochemistry is the key technique which I plan to use. It affords the ability to determine many qualitative and quantitative aspects of the chemistries employed. Simple cyclic voltammetry can determine redox potentials, surface coverages, and onset potentials for catalytically active materials. The degree of complexation or interaction between a substrate and an electroactive analyte can also be determined with cyclic voltammetry by observing the measured shift in oxidation-reduction potentials.

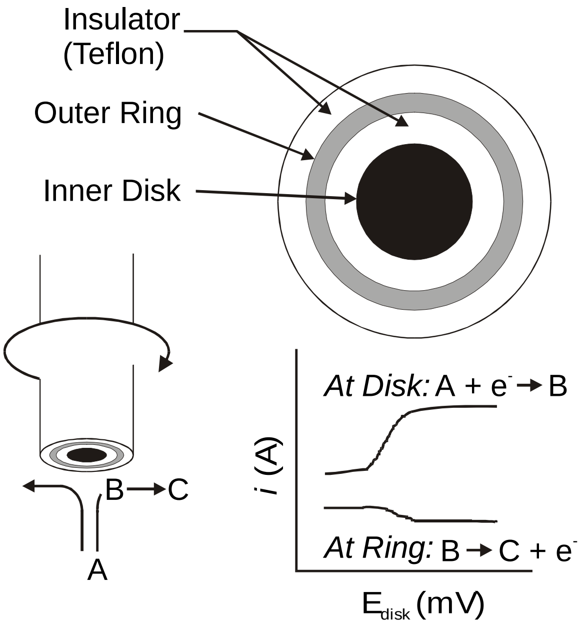


Figure X. Schematic of Rotating Ring Disk Voltammetry

Perhaps the most powerful tool for elucidating the actual mechanisms of catalytic activity is rotating ring disk (RRDE) voltammetry. In RRDE (figure x.) an electrode is rotated at fast rates, laminar flow of solution past a central disk electrode and an outer ring electrode that encircles the central electrode. By coating the central disk electrode with a catalytic material, and controlling the potentials each electrode (central disk and ring) are held at, the compounds produced during a catalytic reaction can be monitored.

Fourier Transform Infrared External Reflection Spectroscopy (FTIR-ERS) is a second method I will use to study prepared films. In this technique, polarized light is reflected of a surface at a grazing angle, giving spectroscopic information about both the functional groups present on the surface (and thereby the molecules) and the orientation of such molecules.

X-ray Photoelectron Spectroscopy (XPS) is another method I will use in my investigations. XPS irradiates samples, ejection of core electrons at discrete energies. This allows for the presence and ratios of elements to be determined. Additional information about the structural details of a film can also be gleaned by using variable angle XPS.

Ultraviolet-visible spectroscopy (UV-vis) can provide information about many aspects of metal ion complexes both in solution and on surfaces. In many cases, absorptions indicative of both the metal ion, and the organic ligand can be observed. By transmitting UV-vis radiation through the sample and measuring the amount and wavelengths that are absorbed, quantitative information such as concentration, redox state, and surface coverage may be achieved. Additionally, by observing shifts in peak wavelength, some information as to the molecular environment, such as complexation, coordination, or pi-stacking can be inferred.

Atomic Force Microscopy (AFM) will be used to assess the surface morphology of films. There are two basic modes of AFM, contact mode, and tapping mode. In contact mode, and silicon cantilever tip is rastered across a surface. The deflection of the tip is measured by a laser that is bounced of the back of the tip and detected at a photodiode. The voltages recorded at the photodiode produce a “picture” of the surface with very accurate height information. Tapping mode is very similar to contact mode, but is less destructive towards the surface, as the cantilever is vibrated in a fashion such that only momentary contact with the surface is made.

Nuclear Magnetic Resonance Spectroscopy (NMR) applies a pulsed magnetic field to molecules in solution which causes their spins to align. By observing the relaxation of these aligned spins, very detailed information about the molecular structure can be determined. This tool is fundamental in the verification of prepared precursors and intermediates.

IV. Preliminary Experiments

In the systems I plan to investigate, electron transfer among the peripheral groups of the dendrimer is of the utmost importance. In systems designed for heterogeneous catalysis, it is of further importance to demonstrate that a) modified dendrimers can, in fact, be sequestered at the surface of an electrode and b) functional groups on the dendrimer can electrochemically communicate with the surface. Model catalysts have been generated by attaching the facile redox couple ferrocene to the periphery of an Astramol dendrimer. To date, there are 2 methods for the immobilization of such ferrocene terminated dendrimers. The first method is coadsorption with thiols of functionalized dendrimers. By coadsorbing hexadecane thiol with the dendrimer of choice, a electrochemically stable surface comprised of thiol, and dendrimer is generated. The second method relies upon covalent linkage to the surface of a mercaptoundecanoic acid (MUA) monolayer. By reacting the terminal amines of a dendrimer with the carboxylic acid end groups of MUA, stable surfaces are generated. The dendrimer can be partially modified prior to attachment to the surface, or modified after attachment. Cyclic voltammetry both at the surface (figure y.) and in solution is evident with excellent reversibility and electrochemical behavior.

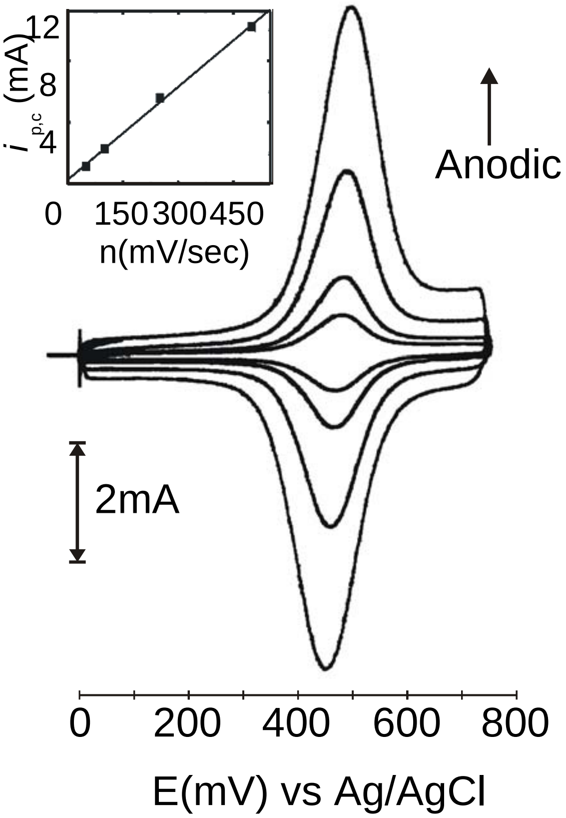


Figure y. Cyclic Voltammetry of Ferrocene Modified Dendrimers Covalently Attached to Mercaptoundecanoic Acid Monolayer.

Additionally I have prepared PAMAM dendrimers modified with viologen functional groups. Dendrimers modified with viologen molecules also showed reversible electron transfer (a 2 electron process in viologens) (figure q.) and effectively demonstrate that functionalities responsible for host-guest chemistry can be linked to the surface of a dendrimer and are electrochemically accessible.

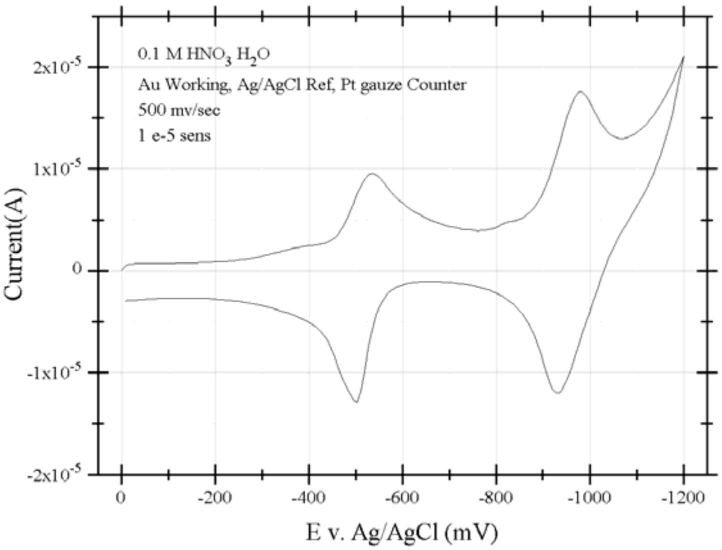


Figure q. Cyclic Voltammetry of Viologen Modified Generation 4 PAMAM

V. Proposed Research

I propose that dendrimer polymers may be used to orchestrate modifiers in a manner which promotes coopertivity between the modifiers. I specifically wish to investigate the catalytic properties of multiple porphyrin units attached to the periphery of a dendrimer. I, also, specifically wish to investigate host-guest chemistry arising from cooperative interactions of surface modified dendrimers.

In order to investigate the catalytic properties of multiple porphyrin units on attached to the exterior of the dendrimer, I first must synthesize the starting material, a porphyrin modified dendrimer. Commercially available Mesoporphyrin IX Dihydrochloride contains two carboxylic acid units at the periphery. By making use of amine-carboxylic acid coupling reactions, I will functionalize the dendrimer and characterize it by NMR, transmission IR, and UV-vis spectroscopies. NMR can give estimated ratios of dendrimer/porphyrin, and hence an estimated degree of functionalization. UV-vis spectroscopy is useful in this characterization, because the UV-vis spectrum of a modified porphyrin will blue shift relative to the monomer depending upon the orientation and degree of interaction with neighboring porphyrins. Once I have verified the porphyrin modified dendrimer, I will attach it to planar gold surfaces, as described in the preliminary results, and further characterize it by FTIR-ERS and XPS, verifying the attachment of the modified dendrimer and the presence of metal centers. I will also prepare gold balls and characterize the surface with AFM. I will then proceed to attach the porphyrin modified dendrimers to the surface of a RRDE (gold disc, platinum

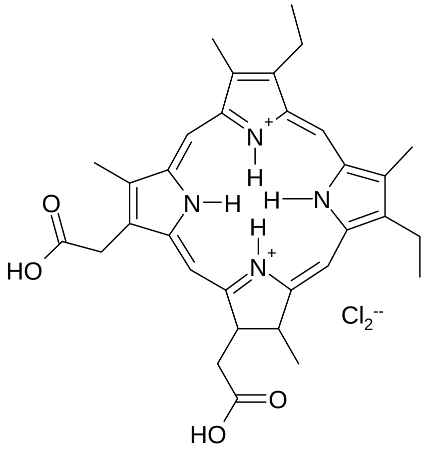
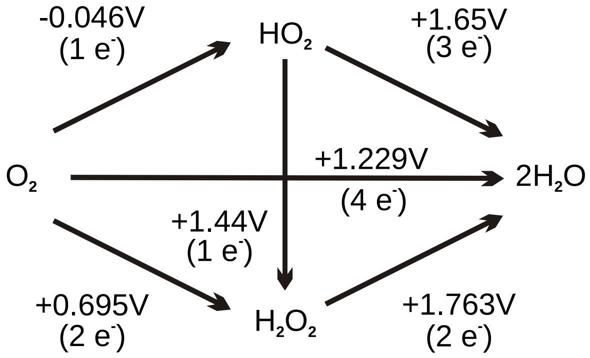


Figure v. Mesoporphyrin IX Dihydrochloride ring) electrode and perform a detailed analysis of the catalytic behaviour of these films.



Scheme w. O_2/H_2O Redox Couple

In order to understand the RRDE experiments, it is first necessary to examine the redox couple of O_2/H_2O. Efficient four electron reduction of oxygen directly to water is considered an interesting problem practically and fundamentally. The process is summarized in scheme w. Fundamentally, we would like to know how to deliver four electrons directly to one point. Practically, we would like to be able to utilize the O_2/H_2O couple for cheap and clean fuel cells. In Scheme w. the possible routes from O_2 to H_2O are shown. The favored thermodynamic route is O_2 to H_2O. Kinetically, however, it is very difficult to deliver 4 electrons simultaneously to one place. This is why a catalyst is necessary to facilitate this reduction. Platinum is the most common fuel-cell cathode, operating at an overpotential of 600mV. In Collman (and subsequently others) work, it was shown that face to face porphyrins were capable of ligating O_2 between the metal centers in a fashion that allows for a four electron transfer. (The exact nature of this ligation is still of considerable debate, but most likely involves a u-superoxo complex.) It was shown that biscobalt face to face porphyrins, biscobalt pacman porphyrins, and cobalts/iron pacman porphyrins were capable of four electron catalysis.

Voltammetry at a rotating ring disk electrode is a very powerful technique, and is the fundamental means of characterizing O_2 catalytic materials. The general equation for the limiting cathodic current (**i**) at a rotating disk electrode as a function of electrode area (**A**), the diffusion coefficient (**D**), rotation rate (ω), and concentration (**C**) is given in equation 1, the Levich equation.

$$i_{l,c} = 0.620nFAD_0^{2/3}\omega^{1/2}\nu^{-1/6}C_o^*$$

Equation 1. The Levich Equation

In order to consider a RRDE we only need to include the collection efficiency (the amount of material oxidized or reduced at the disk that actually makes it to the ring) at the ring to complete the equation, and obtain **$i_{l,a}$** at the ring. By scanning the potential as a function of time at the disk and holding the ring potential constant at +1.4V, the onset of oxygen reduction can be monitored (current at disk), while simultaneously monitoring the production of peroxide via a 2 electron process (current at ring). Further, by changing the rotation rate of the electrode, and hence the rate at which material reaches the ring from the disk, an understanding of the nature of H_2O_2 produced may be obtained. If peroxide is a short lived intermediate, it is possible that it will not be seen at low rotation rates, while at high rotation rates, it will show up as evidence by the current produced from its oxidation back to O_2. Reductions of dinitrogen and dihydrogen with face to face porphyrins is also an area of fundamental and practical interest which can be studied with this described system.

Another factor that was also shown in these studies was that the critical distance between porphyrins is in the range of 3.5 angstroms. I will rely upon the change in generation allowing for control over the spacing between the porphyrin rings. That is, with increasing generation, the surface becomes increasingly crowded and the endgroups become closer and closer. This will allow to attach the porphyrin at successively smaller separations also.

In order to investigate the cooperative host-guest properties of surface modified dendrimers, a slightly different strategy than that used with the porphyrins will be used, but the fundamental idea is the same. I propose that host-guest systems can be created by functionalizing the surface of the dendrimer with aromatic moieties, based on either bipyridyl or biphenyl species, to create a structure that in essence mimics the structure shown in figure t. This mimicry can be extended beyond cyclophanes to crown ethers, cyclodextrins and calixarenes. It is my proposal that the added flexibility present in dendrimer host-guest systems will allow for greater interaction and affinity between the host and guest. Simple coupling chemistries between the exterior amines of the dendrimer and pendant acid groups on modifiers will facilitate functionalization. These molecules will then be characterized as previously described by NMR, IR, FT-IR, and UV-vis spectroscopies.

$$\begin{tikzcd}
R + G \arrow[r, shift left, "K_L"] \arrow[d, shift left] & RG \arrow[l, shift left] \arrow[d, shift left] \\
R^- + G \arrow[u, shift left, "e^-"] \arrow[r, shift left, "K_H"] & R^-G \arrow[l, shift left] \arrow[u, shift left, "e^-"']
\end{tikzcd}$$

Scheme 2. Redox Switching Square

The guest-host interaction can be quantified in two ways, the first is UV-vis spectroscopy. Upon complexation, molecules that absorb strongly in the UV or visible region will exhibit a significant shift in peak position. A second method used to gain insight into host-guest chemistries is to exploit an electroactive guest molecule. Electroactive guests which are relevant to these studies are plentiful. Aromatic molecules, such as bipyridyls, quinones, are well suited to play the part of guest molecules, as is ferrocene. Subtle modifications such as the introduction of sulfonate or acid groups onto the ring can also be used to influence both solubilities and guest-host relationship. The concept of redox switching has also been demonstrated in such systems. Redox switching occurs when a change in oxidation state of the guest molecule results in a change in the complexation between the host and guest. (Scheme 2.) Quantitative information about the interaction can be obtained simply measuring the difference in redox potentials of the free and complexed species. The extent of interaction is

$$K_H = K_L \exp\left[-F(E_f^{o'} - E_c^{o'})/RT\right]$$

Equation 2.

measured as the binding enhancement $\mathbf{K_H/K_L}$ as shown in equation 2. To assess the host-guest and molecular recognition properties of prepared molecules with electroactive species, I will use two approaches, heterogeneous and homogenous. In a heterogeneous system, I will attach the modified dendrimer (host) to the surface of an electrode, as described in the preliminary results. I will then cycle the electrode in a solution of electroactive guest. Simple measurements of changes in the half-wave potential will then be used to provide information about the binding event as described above. This same approach can be used in solution state, with the added caveat that the host molecule can be effectively titrated with guest gain further quantitative information.

Again, as in the porphyrin modified dendrimers, it is my hypothesis that by simply changing the generation or species of dendrimer I can effectively change the spacing, thereby changing the cooperation of modifying units, and in turn the guest-host properties of these systems.

VI. Summary and Conclusions

I have proposed that certain moieties can be attached to the exterior of a dendrimer in such a manner that cooperative effects arise between these moieties. I have further proposed that these cooperative effects can be utilized in areas of catalysis, guest-host chemistry, and molecular recognition. I have finally proposed that the nature and degree of cooperativity can also be affected by systematically changing the spacing of the cooperating groups by changing the generation or species of dendrimer.