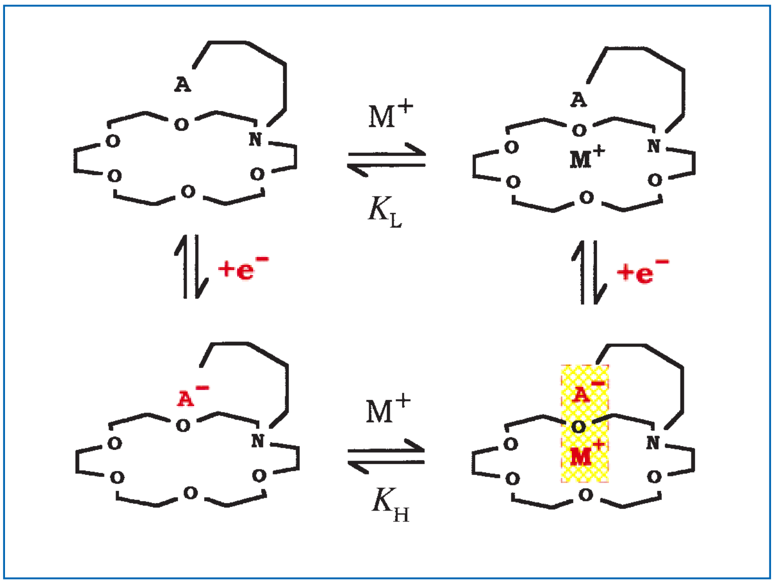
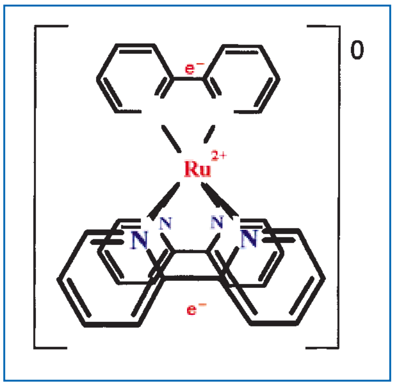
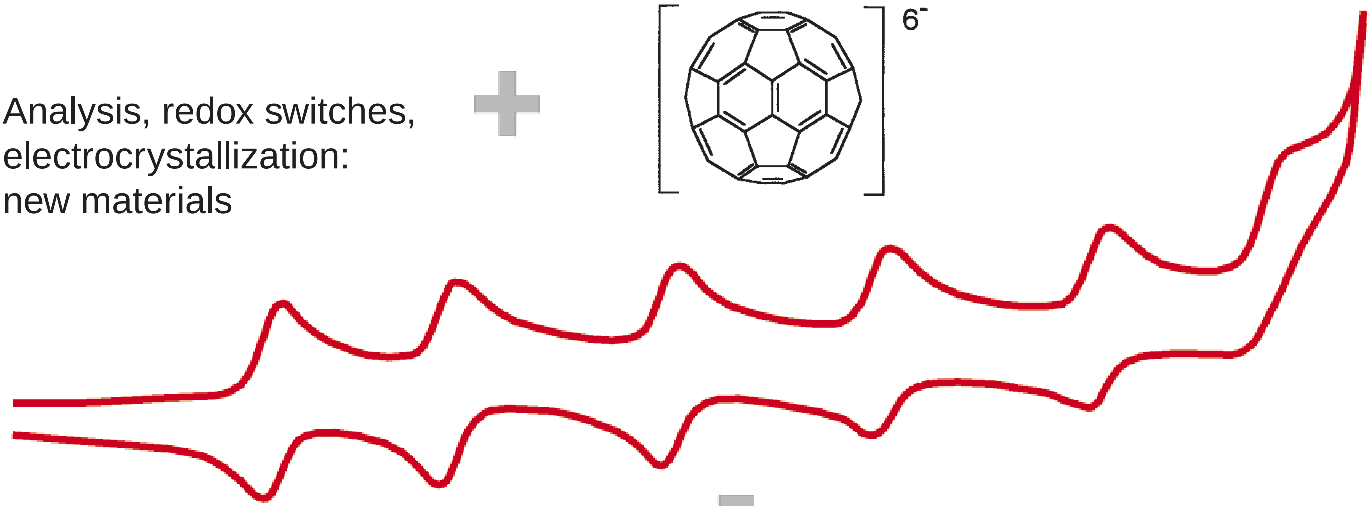
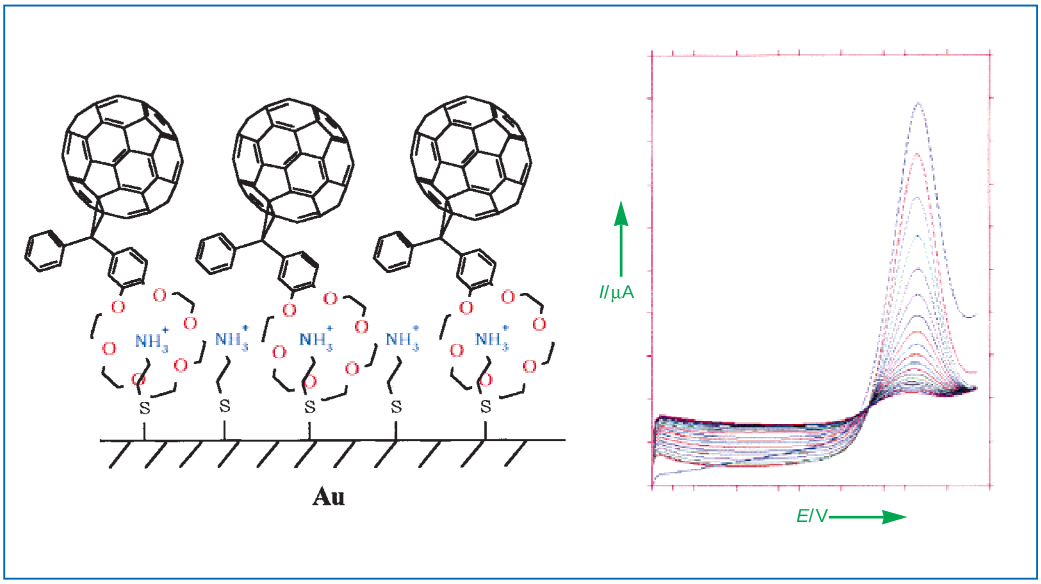




Analysis, redox switches,
electrocrystallization:
new materials





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Electrochemistry of Supramolecular Systems

Pierre L. Boulas, Marielle Gómez-Kaifer, and Luis Echegoyen*

Thirty years after the inception of the field of supramolecular chemistry, the volume of work in the area continues to expand at an ever-increasing rate. Biologists, chemists, and physicists continue to take strides in this well-established discipline and are beginning to make systems with serious potential applications. As the sizes of the molecular aggregates (prepared frequently by self-assembly) continue to increase, an unusual burden is being placed on existing analytical and physical characterization tools. The classical nuclear magnetic resonance (NMR) and mass spectral (MS) techniques sometimes fall short and thus are frequently unable to provide the necessary confirmation of structure and/or function of these aggregates. Although advances in these analytical areas have been remarkable (for example, matrix-assisted laser desorption ionization (MALDI) and electrospray mass spectroscopy (ES-MS), which allow the analysis of very large molecules and aggregates), other techniques are essential for complete structural and functional characterization of supramolecular ensembles. Additionally, as the aggregates are called upon to perform specific functions, as they are in the fields of biology and materials science, measurement of their electronic properties is of fundamental importance. Electrochemical techniques can fulfill many of these specific needs in the characterization and even in the preparation of some supramolecular aggregates. Developments in the field of electrochemistry, such as the implementation of potential pulsing techniques, have increased the sensitivity of the methods and offer relatively easy detection of dilute analyte solutions. Electrochemical techniques are particularly useful and informative for species confined to the surfaces of electrode materials. In addition to serving as sophisticated analytical tools, electrochemical techniques are also useful to produce electronic changes in host and guest molecules that induce (or inhibit) supramolecular aggregation. As such, they are switching controls that offer much promise in the field of supramolecular chemistry, since they offer the possibility to turn on or off a particular intermolecular interaction and thus to read/write information at the molecular level. These switching processes can also be used to effect directed translocation of molecular or ionic species, for example, across membranes. Be they as analytical tools or as powerful effectors to change the properties and binding of supramolecular aggregates, electrochemical techniques are of fundamental and practical importance in the rapidly growing field of supramolecular science. Here we provide examples of how these techniques have been applied to analyze and to influence the properties of guest–host complexes, aggregates, and other related structures.

Keywords: aggregation • cyclic voltammetry • electrochemistry • redox chemistry • supramolecular chemistry

1. Introduction: Electrochemistry and Supramolecular Chemistry

It seems appropriate to begin this review by asking: why should the supramolecular chemist be interested in electrochemistry?

While the usual goal of an electrochemical experiment is to determine redox potentials and to correlate these with intrinsic molecular properties, the method can offer much more to the supramolecular chemist.[1] Electrochemistry, a very powerful tool for monitoring supramolecular events such as self-aggregation on solid electrode materials, can also be used to "effect" structural and electronic changes, thus offering *control* over supramolecular processes. These latter applications are less known and thus often unappreciated by many who are not familiar with the field.

Redox changes can be used to enhance (or diminish) the binding affinity of ligands for guest molecules or ions. Such ligands can thus be viewed as redox switches (Section 2). Examples include the redox-active lariat ethers,[2a–c] and flavin cyclophanes or flavinophanes.[2d] Redox-switching has also been employed in molecular shuttles as described in Section 5.[3] Similarly, electrochemistry can also lead to pronounced structural changes in supramolecular systems. Work with the helicates, a topic of recent studies by Lehn,[4]

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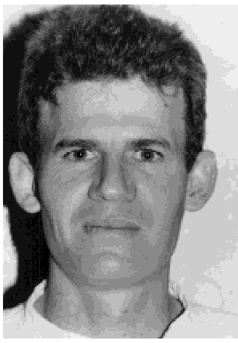
Abruña,[5] and Constable,[6] has demonstrated that as the chelating ligands in these systems are lengthened (a septipyridine system has been studied[5d]), the nuclearity of the complexes depends upon the redox state of the chelated ions. By controlling the redox state of these ions the electrochemist can switch between di-, tri- and tetranuclear complexes.

In addition to these examples in which redox chemistry can be used to control the different binding states and the structures of some aggregates, electrochemistry can also play an important role in redox-controlled self-assembly and in the generation of new materials by electrocrystallization. We have employed the latter to prepare single crystals of reduced complexes of ruthenium with pyridine-type ligands, which have interesting physical properties.[7] Electrocrystallization has also been used in the field of metalloporphyrins to generate molecular conductors with a stacked metal-over-metal structural motif.[8]

Thus, the dual utility of electrochemistry as an "effector" to direct and control supramolecular interactions, as well as a "detector" to monitor and measure the changes makes it uniquely powerful and useful in supramolecular studies. It is certainly one of the most important techniques in the field and one of the easiest to implement.

2. Switching and External Binding Control

The topic of redox switching has been of considerable interest in supramolecular chemistry for well over two decades and is one of the most important applications of electrochemistry in this field. A thorough discussion of the topic is beyond the scope of the present work, and thus the reader is referred to a number of excellent reviews for a more detailed discussion.[2c, 9]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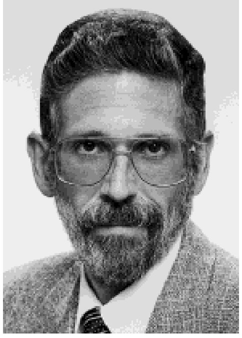

L. Echegoyen

Pierre L. Boulas was born in Villefranche/Saone, France, and educated in Libreville, Gabon. He received a diploma from the Ecole Nationale Superieure de Chimie et Physique de Bordeaux, France in 1992. He joined Professor Kadish's group at the University of Houston, Texas, in 1992 and received his PhD in Analytical Chemistry in 1995. His graduate research work dealt with the electrochemistry and spectroelectrochemistry of fullerenes, fullerene derivatives, and novel metalloporphyrinoids. In August 1995 he joined Professor Echegoyen's research group at the University of Miami, Florida, as a PRF/NSF postdoctoral fellow. His research focuses on the electrochemical and spectroelectrochemical characterization of fullerene derivatives and supramolecular complexes, and on the electrosynthesis of novel fullerene-derived materials.

Marielle Gómez-Kaifer was born and educated in Miami, Florida. The daughter of a physician/biochemist and an artist, she obtained a Bachelor of Fine Arts degree in 1981 and then turned toward science, gaining a double Bachelor of Science degree in Chemistry and Microbiolgy/Immunology in 1991. After earning a National Science Foundation Graduate Fellowship in 1992 she spent one year at the University of Texas at Austin and then returned to the University of Miami, where she completed her Ph.D. thesis on redox-active calixarenes, employing electrochemical, ESR, and NMR techniques. She is presently pursuing post-doctoral studies on encapsulated redox centers.

Luis Echegoyen was born in Habana, Cuba, and educated in Puerto Rico. He obtained both his B.S. and Ph.D. degrees from the University of Puerto Rico in Río Piedras in 1971 and 1974, respectively. After a one-year postdoctoral stay at the University of Wisconsin-Madison, he worked with Union Carbide Corporation for two years. He then returned to the University of Puerto Rico as assistant professor in 1977, where he was promoted to associate professor in 1980. In 1982 he took a leave of absence to work as a Program Officer in charge of Chemical Dynamics in the National Science Foundation in Washington, DC, while simultaneously holding an adjunct professorship at the University of Maryland-College Park. He then moved to the University of Miami-Coral Gables as associate professor and was promoted to professor in 1987. During calendar year 1990 he spent his sabbatical working with Prof. Jean-Marie Lehn at the Université Louis Pasteur in Strasbourg, France. He received the Florida-American Chemical Society Award for 1996. Professor Echegoyen has published about 120 communications, papers, reviews, and monographs and his research interests have centered around supramolecular chemistry since the early eighties. His current work involves electrochemical and magnetic resonance spectroscopic studies of supramolecular systems, with a particular emphasis on their potential applications in materials science.

During the mid-1980s much interest centered on redox-switchable cation-binding systems as potential mimics of biological transport systems.[9c] At present redox switchable host–guest systems are frequently proposed as the chief components of potential molecular devices and sensor systems.[10] Regardless of the specific structures and their intended function, the basic principles behind electrochemical switching are the same.

2.1. The Concept of Redox Switching

The concept of an electrochemically switchable system is a simple one. The oxidized and reduced states of a switchable molecule must display differing degrees of affinity for a second species. Thus, the oxidation state determines the thermodynamic stability of the complex between the receptor and a guest species. The basis of the differential interaction in such a system is typically purely electrostatic. Either the receptor or the guest, or both, need to be redox active. The requirements of an electrochemically switchable receptor or guest are essentially the same. The redox-active component of such a system must exhibit reversible heterogeneous electron transfer kinetics and interact strongly with the binding component. When the binding interaction is strong, the complexed and the free forms will typically exhibit separate redox waves. This situation is ideal for analytical work, because the intensity of each wave is proportional to the concentration of the corresponding complexed or free molecule. In such a system there are two clearly defined binding states that are readily discerned by voltammetric techniques. These states are defined as "on–off" or more accurately, "high–low" states. Both of these forms of the switchable compound must have sufficiently high binding affinity if separate redox waves for the two states are to be observed by voltammetry.[11] This is an important consideration when trying to extract binding constant information from voltammetric data, especially if digital simulations are not performed.

An electrochemically switchable system is usually described by a simple square scheme (Scheme 1) in which the redox equilibrium is coupled with the reversible binding reaction. In this situation we assume that the receptor R is electroactive.

$$\begin{tikzcd} R + G \arrow[rr, shift left, "K_L"] \arrow[d, shift right, "e^-"'] & & R\cdot G \arrow[ll, shift left] \arrow[d, shift right, "e^-"'] \\ R^- + G \arrow[rr, shift left, "K_H"] \arrow[u, shift right] & & R^-\cdot G \arrow[ll, shift left] \arrow[u, shift right] \end{tikzcd}$$

Scheme 1. Square scheme for a redox-switchable system.

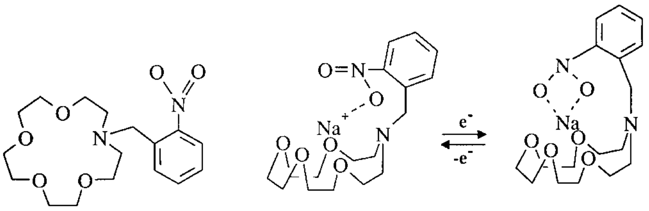
In Scheme 1, receptor R forms more stable complexes with guest G when it is reduced (R^-) than when it is oxidized (R). Therefore K_H is much larger than K_L. The magnitude K_H/K_L is defined as the binding enhancement.

The value of K_L determines whether R or $R\cdot G$ is reduced at the electrode surface. When K_L is large, the already formed complex $R\cdot G$ is electrochemically reduced to a higher affinity state, $R^-\cdot G$. In this situation the diffusion of the guest species is not a relevant factor. In contrast, if K_L is not large, the species undergoing reduction will be R, which will subsequently bind the guest to yield $R^-\cdot G$. In this instance, after reduction of the free receptor to the "high" binding state (R^-), the complexation process is essentially diffusion controlled, that is, determined by the diffusion of available guest to the reduced receptor. Generally, two separate voltammetric waves corresponding to the redox processes of the free (R) and complexed ($R\cdot G$) species will *not* be observed for systems with a low K_L value ($\leq 10^{3}$‰M^{-1}) unless the rate constants for complexation and decomplexation are very fast. The typical electrochemical response of a system with a low K_L value is a shift of the half-wave potential for the free host species as guest is added to the solution.[12] If efficient transport of a guest species is of interest, K_L should not be so high as to prevent the eventual release of the bound guest. For a discussion of these points, see ref. [13].

2.2. Early Examples of Redox Switches

2.2.1. Lariat Ethers and Other Macrocyclic Hosts

The foregoing principles can be readily applied to lariat ether **1** (Scheme 2),[11b, 14] which represents a typical example of a redox-active guest whose affinity for a host can be greatly enhanced upon reduction. In **1** the optimal placement of the nitro substituent (ortho to the pivot attachment) allows for strong interaction with a macrocycle-bound cation. When Na^+ is bound by the macrocyclic crown ring, it can simultaneously interact strongly with the nitroaromatic group. At substoichiometric amounts of Na^+, two reduction waves are seen, one for the free and one for the Na^+-bound species of **1** (Figure 1).[11b]



1 [Na(**1**)]$^+$ [Na(**1**)]^0

Scheme 2. The free and Na^+-bound lariat ether **1**.

The reduction potential of $[Na(\mathbf{1})]^+$ is anodically shifted by 260 mV relative to that of **1**, because the nitroaromatic anion radical is stabilized by Na^+. The cyclic voltammetric behavior of $[Na(\mathbf{1})]^+$ can be readily simulated, and this allows the determination of the binding enhancement (K_H/K_L) from Equation (1).[11a] In this equation $E^{0'}_F$ and $E^{0'}_C$ represent the formal potentials, often estimated from the half-wave potentials, of the free and complexed species, respectively. The

$$K_H = K_L \exp[-F(E^{0'}_F - E^{0'}_C)/RT] \qquad (1)$$

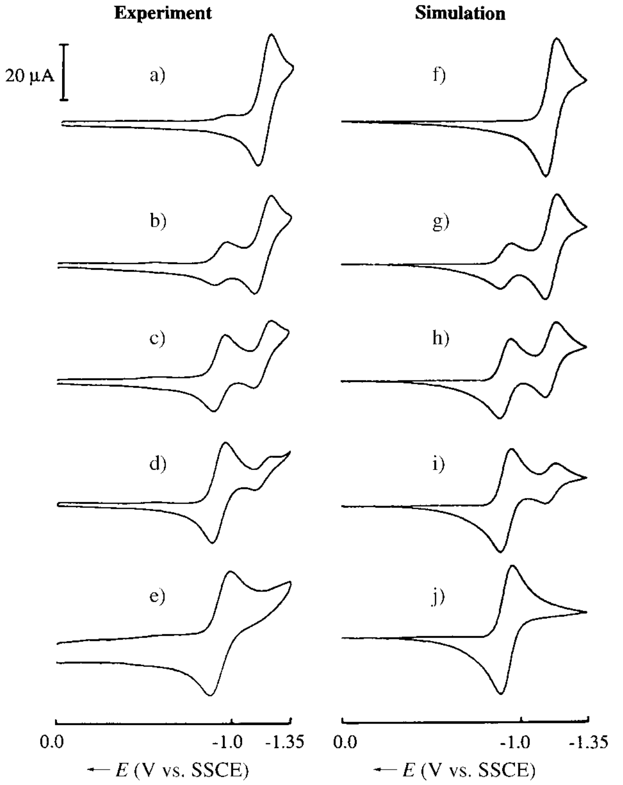
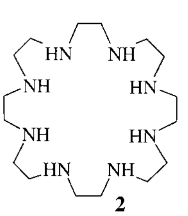


Figure 1. Cyclic voltammetry of a 1 mM solution of lariat ether **1** in the presence of increasing amounts of $NaClO_4$. a)–e): Voltammograms acquired by experiment: scan rate of 100 mVs^{-1} in CH_3CN, 0.10 M NBu_4PF_6, 25°C, potentials vs. SSCE. f)–j) Simulated voltammograms. a) and f) 0.0 equiv $NaClO_4$, b) and g) 0.25 equiv $NaClO_4$, c) and h) 0.50 equiv $NaClO_4$, d) and i) 0.75 equiv $NaClO_4$, e) and j) 1.0 equiv $NaClO_4$ (reprinted with permission from ref. [11b]).

estimated binding enhancement for $[Na(\mathbf{1})]^+$ is 2.5×10^4. In many instances the potential for the wave corresponding to the reduction of the complex may shift as the cation concentration is increased. Since a change of only 10 or 20 mV results in an order of magnitude difference in the calculated binding enhancement, digital simulations of the voltammetric behavior across the full range of cation concentrations provide the best estimate of this factor. Additionally it should be noted that when $K_\mathrm{L} \leq 10^4‰\mathrm{M}^{-1}$, values of K_H may be significantly underestimated by Equation (1).[11b]

Occasionally lower peak currents are observed for the complexed species than for the free species. This effect is typically noted when a small guest, rather than the larger host (which is more common), is the redox active species. For a truly reversible process, the lower currents observed for the complexed species are really attributable to the smaller diffusion coefficient of the complex, rather than to electrochemical irreversibility or interfering chemical reactions. One such system was reported by Lehn and co-workers, who examined a polyamine macrocycle (**2**) that binds the comparatively small ferrocyanide ion.[15]



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In this system the oxidation of ferrocyanide to ferricyanide is shifted to more positive potentials upon binding to **2**. At less than stoichiometric amounts of the polyamine ligand, two redox waves are seen. After addition of 1.2 equivalents of the macrocycle, a single wave is observed, which shows noticeably lower current intensity than the wave corresponding to the uncomplexed ferrocyanide (Figure 2).[15]

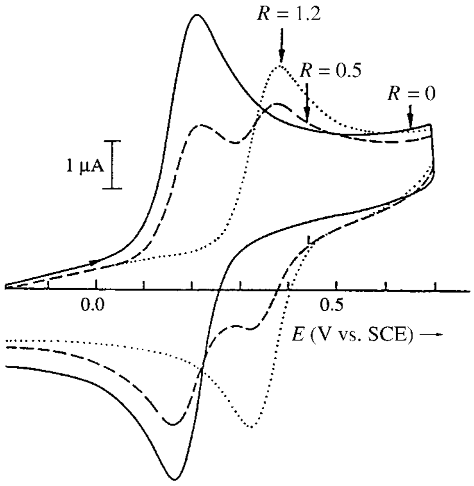
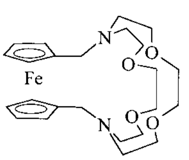


Figure 2. Cyclic voltammetry of ferrocyanide (0.9 mM in 0.1 M KCL, pH = 5.5) in the presence of increasing amounts of **2**. Platinum disk electrode, scan rate = 50 mVs^{-1}, potentials vs. SCE, $R = c(\mathbf{2})/c([Fe(CN)_6]^{4-})$ (reprinted with permission from ref. [15]).

The lower current intensity is simply due to the difference in the diffusion coefficients between the free and the bound ferrocyanide species and not to a change in the overall reversibility of the system. Differences between the diffusion coefficients of the complexed and free species have been observed in the electrochemistry of other supramolecular systems such as cyclodextrin inclusion complexes.[16] For example, a decrease in the diffusion coefficient of ferrocyanide was detected upon complexation by an amino-substituted β-cyclodextrin.[16a] In these cases, simulations of the voltammetric behavior must take into account the difference in diffusion coefficients in order to accurately reproduce the observed behavior, which can include shifts in the observed redox potentials. Simulation may also be employed to extract binding constant information based on changes in the diffusion coefficient.[16a]

2.2.2. *Ferrocenyl Macrocycles and Cryptand Switches*

The development of more complex redox-switchable cation binding receptors continued at a rapid pace throughout the 1980s and early 1990s. Ferrocene-based systems were very prevalent in the literature, perhaps due to their ease of preparation and their well-behaved electrochemistry. Ferrocene undergoes a monoelectronic quasi-reversible oxidation to ferrocenium at easily attainable potentials and has the advantage of being rather insensitive to protic solvents and to the presence of molecular oxygen. Additionally, the ferrocene ligand acts as a redox antenna in that its oxidation potential is sensitive to binding with other molecules. For example, Gokel and co-workers designed structure **3**, a redox-switched system in which the ferrocene acts as the cap of a diazacryptand.[17]



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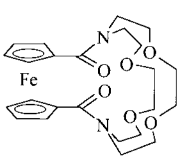

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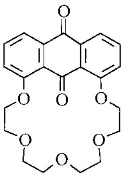
Complexation with alkali, alkaline earth, or silver ions was shown to shift the oxidation potential of the ferrocene moiety by as much as 290 mV, to more positive potentials. This is essentially a *negative* enhancement by a factor of 10^4 in favor of the neutral ferrocene ligand. (By negative enhancement we imply that oxidizing the ligand *disfavors* binding of the guest.) In this system, the binding of various cations resulted in characteristic half-wave potentials, a property with potential analytical applications.[10f] A related ferrocenyl macrocycle **4** also exhibited a "high–low" behavior with distinct oxidation waves (large K_L and $K_{H)}$ for both the free and bound forms of **4** in the presence of Be^{2+}.[18] However, differences in the cathodic and anodic current intensities suggested decomposition of the $\mathbf{4} \cdot Be^{2+}$ complex on the voltammetric time scale. In the presence of Mg^{2+}, Ca^{2+}, Sr^{2+} or Ba^{2+}, **4** exhibited voltammetric behavior typical of lower K_L systems: a single oxidation wave was observed for the free and bound ligand, at an $E_{1/2}$ shifted from that of the free ligand.[18]

Other significant results involving ferrocenyl macrocycles include the transport of cations by an electrochemically switchable ferrocenyl crown ether ligand across a bulk liquid membrane, which was achieved in 1986 by Saji and Kinoshita.[19] Transport across a CH_2Cl_2 liquid membrane was found to be enhanced upon oxidation of the ferrocene, since the Na^+ complex is destabilized in the oxidized state, favoring release of the Na^+ ion to the receiving phase.

Interestingly, Fabrizzi et al. have prepared a novel ferrocene receptor that has an *increased* affinity for cations upon oxidation.[20] Beer and co-workers have synthesized and characterized a large number of ferrocenyl receptors, as well as a series of cobaltocene- and ruthenocene-based receptor systems.[21]

2.2.3. Quinone-Based Switches

Other compounds have relied on the presence of *p*-benzoquinone and anthraquinone redox-active moieties as the switching antennae for enhanced cation binding. The quinone moiety undergoes two successive monoelectronic reductions to the anion radical and then the dianion.[22] Echegoyen et al. developed anthraquinone-based crown ethers and cryptands such as **5** and **6**.[23, 24]



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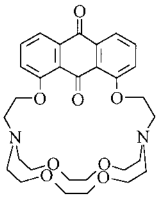


6

Compound **5** exhibits two reversible monoelectronic reduction waves in the absence of Na^+.[23] In the presence of 0.5 equivalents of Na^+ each of these waves is split into two waves, reflecting the redox processes of the free and the complexed ligand. Cryptand **6** displays even more dramatic behavior, exhibiting a 400 mV anodic shift for the reduction of the anthraquinone moiety upon binding with two Li^+ ions. Such a shift corresponds to a binding enhancement of 8×10^5.[24] Further reduction to the dianion leads to a total binding enhancement of 10^{11} relative to the neutral cryptand, a most impressive switching effect. Cryptand **6** has also shown the potential for lithium isotope discrimination.[25]

Cryptand **6** also binds Na^+ and K^+.[24] In its reduced state, **6** binds K^+ so strongly that it cannot be removed competitively by cryptand [2.2.2]. Use of anthraquinones as the redox-switchable component of cation binding compounds has continued with the work of Echegoyen and Torres, who have studied a series of anthraquinones bearing pendant diazacrown ethers, and bis(anthraquinone) systems with diazacrown ether spacers.[26] Na^+ binding enhancements obtained upon one-electron reduction in several of these systems have exceeded 10^5.

2.2.4. Other Switchable Systems

Various other cryptands such as azobenzene cryptands have also been studied.[27] These exhibited a greater degree of selectivity for K^+ than that of the cryptands mentioned above, which typically were selective for Na^+ or Li^+. True binding selectivity coupled with redox switching enhancement is an issue that has yet to be widely addressed and remains a challenge for future work.

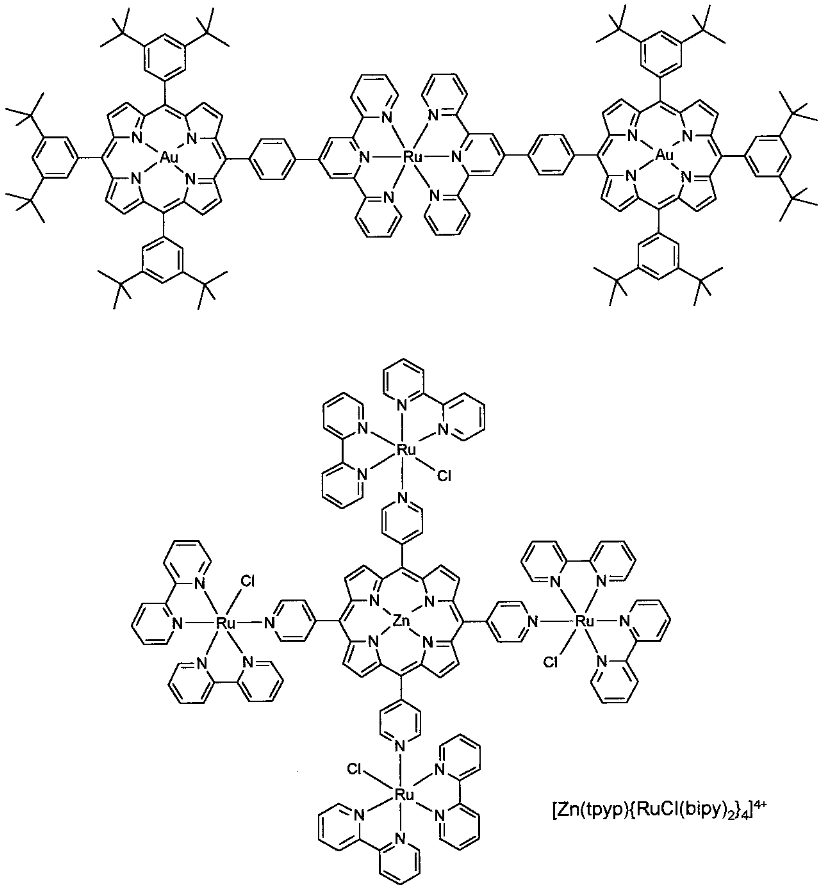
The area of anion binding enhancement by switching mechanisms has been less explored than that of cation binding. Most of the work in this area has been that of Beer and co-workers.[28] Their strategy has been to employ multiple positively charged redox moieties, which are then switched electrochemically to higher charge states. An excess of the anion guest must be added in order to see measurable changes. The effects of binding are rather modest, on the order of 50 mV or less, indicating very low binding enhancements. The reader is referred to reference [29] for further discussion of this work.

More recent work in the field of redox switching of ion binding involves the use of more complicated support frameworks. Related work will be discussed in the following sections.

3. Porphyrinoids

3.1. Porphyrins and Supramolecular Chemistry

The synthesis of porphyrinoids[28b, 30–37] is a very active field of research, and a great variety of porphyrin-like compounds with cavities of different sizes and shapes have been reported. Porphyrin-like compounds have been employed as the building blocks to form a number of supramolecular assemblies. Selected recent structural examples are shown in Scheme 3.[36]



[Zn(tpyp){RuCl(bipy)$_2$}$_4$]$^{4+}$

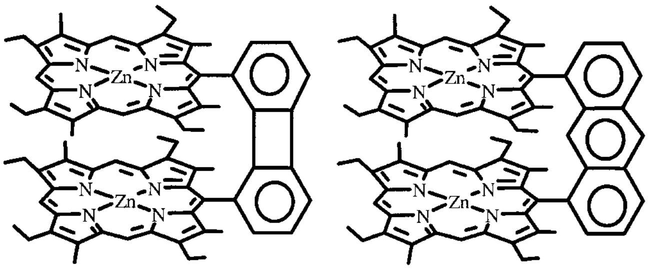
Scheme 3. Porphyrins as building blocks for supramolecular assemblies.

Considerable work has been reported in the field of the self-assembly of porphyrin oligomers and of the binding properties of these supramolecular receptors.[35] In addition to variation of the size and shape of the cavity, substitution of the porphyrinoid macrocycle is readily achieved. This allows for fine-tuning the physical and chemical properties of any given porphyrinoid ligand.[37] Some of these derivatized porphyrinoids have already revealed their potential as hosts for a variety of guest molecules.[28b, 37a–b] Thus, porphyrinoids are good precursors to supramolecular assemblies.

3.2. Cofacial Bis(metallo)porphyrinoids as Electrocatalysts

Cofacial bis(metallo)porphyrinoids (Scheme 4) were initially prepared to study the interaction between closely lying electroactive centers such as in the case of cytochromes,[38] to obtain multi-electron transfer,[39] or to find new catalysts for the reduction or oxidation of small substrate molecules such as O_2, H_2, or N_2.[40]

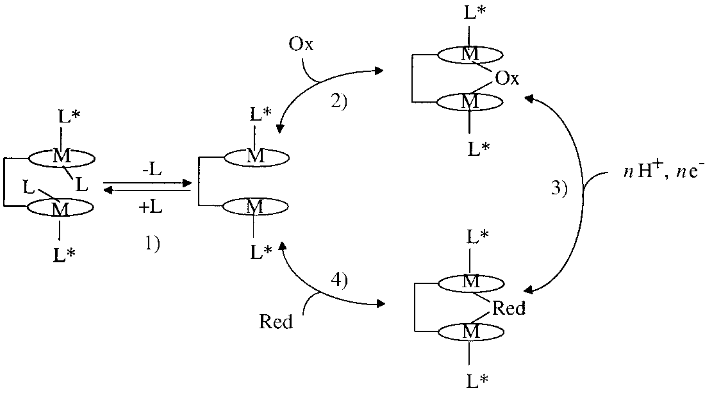
Catalytic activity in these systems can be easily detected with cyclic voltammetry (CV) or rotating disk electrode voltammetry (RDE).[41, 42] In the case of CV, a comparison of the current–voltage curves obtained for the substrate with a bare electrode and with an electrode modified with the cofacial bis(metallo)porphyrin will suffice to demonstrate catalytic activity. Higher current density and a decrease in the substrate overpotential when using the modified electrode are reliable indicators that the cofacial complex catalyzes the reduction or the oxidation of the substrate.[40] RDE is also very useful in that it provides more information about the kinetics of the catalytic process. In addition, rotating ring-disk electrode (RRDE) voltammetric experiments[42c] help to gain insight into the electrochemical nature of the intermediary and final products of the catalytic reaction.



[Zn$_2$(dpb)] [Zn$_2$(dpa)]

Scheme 4. Examples of cofacial bis(metallo)porphyrins.

Electrochemical studies of these porphyrins led to the conclusion that the rigidity and length of the spacer or linker between the two porphyrin units play a major role in how good a catalyst the cofacial complex is. If the spacer is too flexible, the two porphyrins do not adopt a face-to-face configuration.[43] Indeed, X-ray data revealed that the two units are laterally shifted with respect to each other to maximize $\pi-\pi$ overlap. If the two porphyrin units are too tightly linked to each other, the geometry of the cavity where the binding of the substrate occurs is not flexible enough to accommodate the structural changes that will take place during the catalytic process. If the linker is too long, communication between the two chromophores is absent. Anthracene and biphenylene linkers optimize this length/rigidity compromise.[44] A proposed overall catalytic process is schematically represented in Scheme 5.



Scheme 5. Cofacial bis(metallo)porphyrins as electrocatalysts.[40] 1) Formation of the active site; 2) and 4) substrate binding or product release; 3) multielectron transfer. L* = bulky ligand blocking the outer coordination sites (solvent molecule or imidazole, for example); L = smaller ligand that can be displaced by the substrate.

The latter case exemplifies the use of electrochemistry as an effector of supramolecular events and as a detection technique. The substrate binding, which allows for the catalytic activity is controlled by the redox state of the substrate. The release of the product, on the other hand, from the cofacial bis(metallo)porphyrin is also redox-controlled.

3.3. Dendritic Porphyrins

Research on dendrimers has been expanding for the last decade.[45–50] Dendritic porphyrins are a rather important class of dendrimers that present interesting properties with potential industrial applications. They were initially synthesized with the aim of mimicking the environment that surrounds a heme center such as that of cytochrome c.[46] The first one was prepared by Inoue et al.[47] The electrochemistry of dendritic porphyrins has been studied by Diederich et al.[49, 50] In this case, electrochemistry has been used solely to measure redox potentials and correlate them with electronic properties. Some examples of dendrimers studied are shown in Scheme 6.

The redox behavior of dendritic porphyrins is markedly different from that of "simple" metalloporphyrins because of the influence of the dendrimeric branching around the porphyrin core (Figure 3).[49]

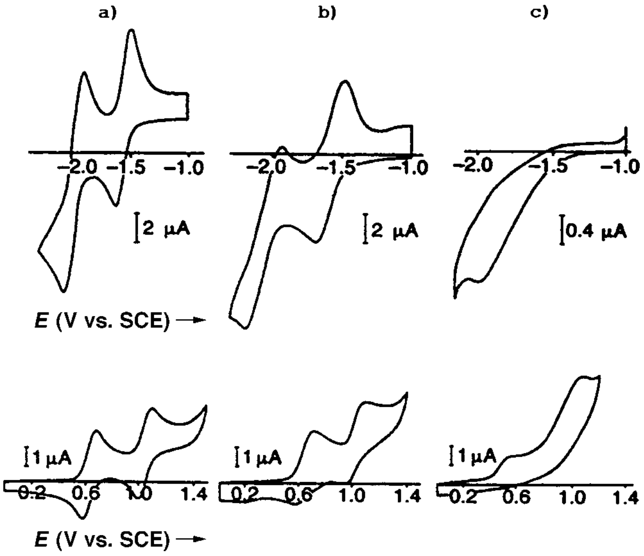
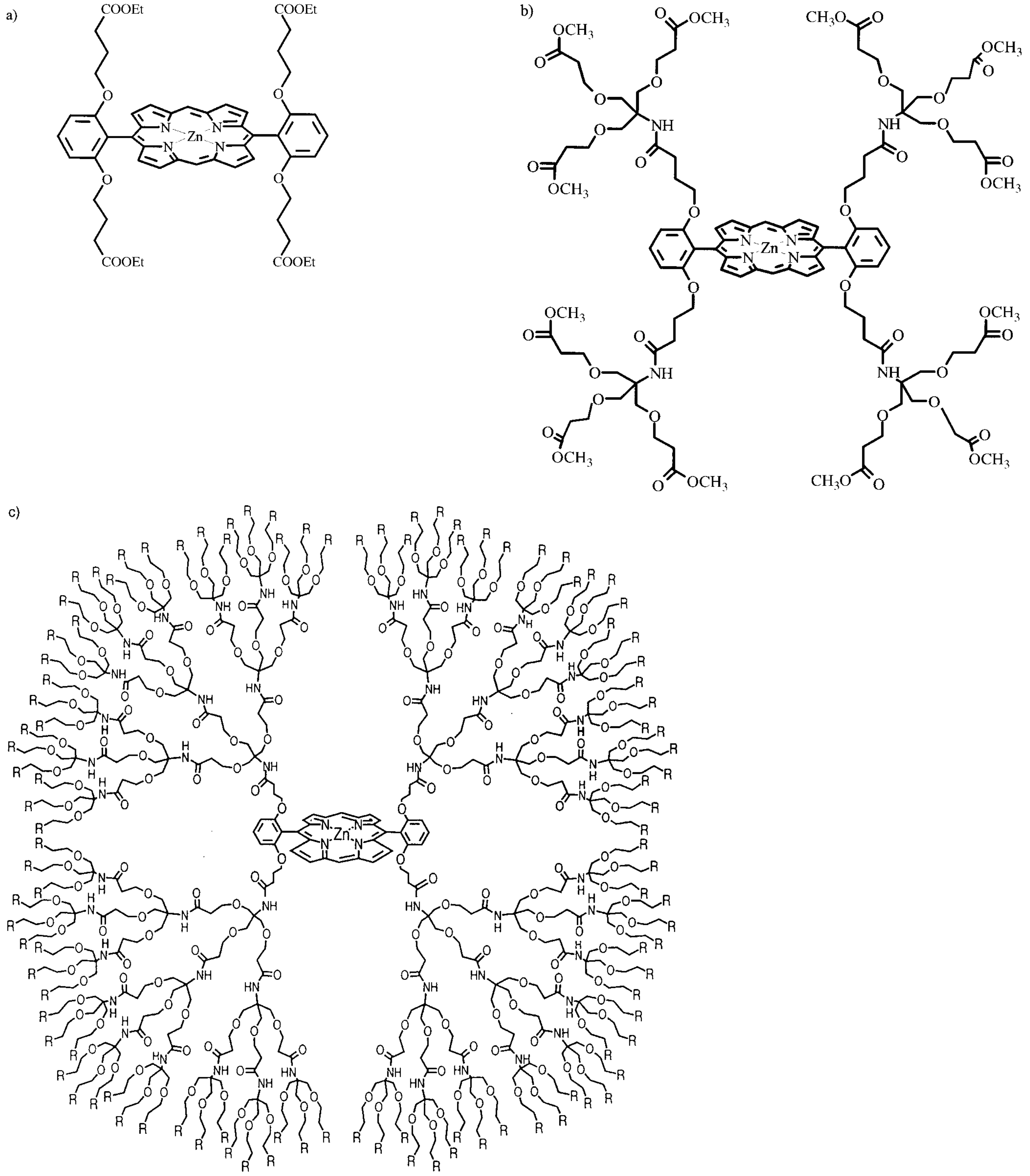


Figure 3. Cyclic voltammograms showing the reduction (top) and the oxidation (bottom) of dendritic porphyrins whose structures are represented in Scheme 6.[49] Dendrimers of a) the first, b) the second, and c) third generation. Conditions: top: THF, 0.1 M Bu_4NPF_6, Hg dropping electrode as working electrode, scan rate = 8 V s^{-1}, 25°C; bottom: CH_2Cl_2, 0.1 M Bu_4NPF_6, platinum working electrode, scan rate = 0.1 V s^{-1}, 25°C (reprinted with permission from ref. [49]).

As the dendrimer shell grows (Figure 3a to 3c), the porphyrin electrophore is more shielded by electron-rich dendritic branches, rendering the reductions more difficult and the oxidations easier. By the third generation, the zinc porphyrin dendrimer shows only ill-defined and mainly irreversible CV processes. The poor definition is due in part to the very small diffusion coefficient of the species, while the irreversibility results from the superimposition of redox processes involving the porphyrin core and the functional groups on the branches of the dendrimer. The dendrimeric branching not only affects the porphyrin ring-centered reactions but also the metal-centered ones. As reported by Diederich et al.[50] in the case of iron porphyrin dendrimers, the half-wave potentials for the metal-centered reductions ($Fe^{III} \rightarrow Fe^{II}$ and $Fe^{II} \rightarrow Fe^{I}$) were found to depend greatly on the size of the dendrimer surrounding the metalloporphyrin. The dendrimer was also found to shield the metal center from the external medium and particularly the solvent.[50]

3.4. Ruthenated Metalloporphyrins

Examples of such complexes are shown in Scheme 3.[36] Although several architectures have been designed and built that make use of the ability of pyridyl-type ligands to complex ruthenium(II), only one of them, to our knowledge, has been thoroughly characterized electrochemically (Scheme 3, bot-



Scheme 6. Examples of electrochemically characterized dendritic porphyrins (reprinted with permission from ref. [49]): first (a), second (b), and third generations (c).

tom structure).[36b] The CV recorded for the tetraruthenated zinc porphyrin $[Zn(tpyp)\{Ru(bpy)_2Cl\}_4]^{4+}$ shows a multitude of redox processes (Figure 4) in agreement with the fact that four sites of electron transfer can be envisaged: the metal center, the porphyrin ring, ruthenium(II), and the pyridyl ligands.

Two reversible oxidations can be discerned in the CV. The first one at 0.92 V has the intensity of a four-electron oxidation and corresponds to a $Ru^{II} \rightarrow Ru^{III}$ reaction for each $Ru(bpy)_2$ ligand. The fact that the four Ru^{II} centers are oxidized simultaneously indicates that only very weak coupling exists between the ruthenium centers. The second

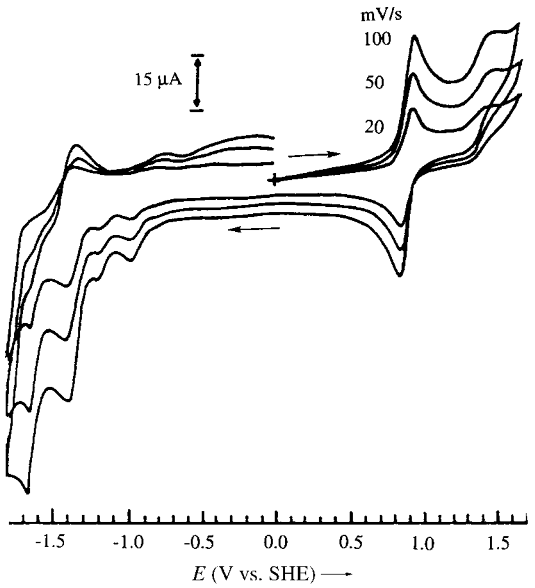
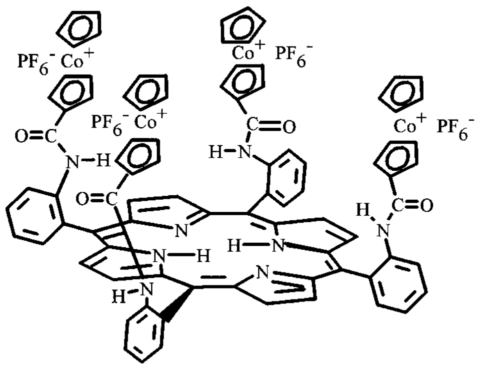


Figure 4. Cyclic voltammogram (DMF, 0.1M $TEAClO_4$, platinum disk working electrode) for the reduction and the oxidation of the $[Zn(tpyp)\{RuCl(bpy)_2\}_4]^{4+}$ (0.99mM) (reprinted with permission from ref. [36b]).

oxidation located at 1.5 V corresponds to the one-electron oxidation of the porphyrin ring. Interestingly, the first one-electron reversible reduction observed for the tetraruthenated porphyrin corresponds, as confirmed by spectroelectrochemistry, to a $Zn^{II} \rightarrow Zn^{I}$ reduction. This contrasts drastically with the electrochemistry of Zn(tpyp) for which the first reduction is ring-centered.[51] The second reduction (reversible when only the first two waves are scanned) at −1.2 V is a one-electron transfer and involves the porphyrin ring. The multi-electron process at −1.35 V is a superposition of the second porphyrin ring-centered reduction and the reduction of four bpy units, one on each $Ru(bpy)_2$ ligand. Finally, the reduction at −1.67 V is irreversible and involves the remaining four bpy ligands. The complexity of the electrochemistry of the ruthenated zinc porphyrin described above exemplifies the typical expectation when dealing with supramolecular assemblies that possess several available sites for electron transfer.

3.5. Sensing of Anions by a Porphyrin Receptor

As mentioned earlier, the porphyrin ring is amenable to chemical derivatization. A judicious choice of ligand led to the synthesis of a porphyrin (Scheme 7) with interesting anion recognition properties.[28b] This novel anion sensor presents a pronounced affinity for halides, $H_2PO_4^-$, and HSO_4^- over NO_3^-. The anion binding properties of the porphyrin sensor were monitored by NMR, UV/Vis spectroscopy, and electrochemistry. Interestingly, upon addition of anion guests to solutions containing the porphyrin host, only shifts in the oxidation potentials of the porphyrin ring and reduction potentials of the cobaltocenium ligand were detected. No influence due to anion binding was detected on the reduction potentials of the porphyrin ring.[28b]



Scheme 7. Example of a porphyrin-based anion sensor.

In two other examples a porphyrin-based system has been used for molecular recognition. The first one is the preparation of a porphyrin host for a guest analogous to ubiquinone,[52] while the second one is the synthesis of a sapphyrin–cytosine conjugate for selective through-membrane transport of guanosine 5′-monophosphate.[37a] Unfortunately none of these systems has been electrochemically characterized.

3.6. Electrochemically Induced Self-Assembling of Porphyrinoids

The porphyrin-like compounds are not only of interest because of their biological relevance but also because of their potential uses as materials, such as "molecular metals"[53] or catalysts.[40] Thus a great deal of effort has been devoted to designing and creating new conducting materials that incorporate porphyrin and its derivatives as molecular building blocks.[8, 54–56] Electrochemical[8, 55] or chemical[54, 56] oxidation of a series of metalloporphyrinoids [M(P)], where P is a phthalocyanine, a porphyrin, or a porphycene, leads to molecular conductors, which usually have the same stacked structural motif.[57] This motif is best characterized as an ABAB arrangement in which A and B are staggered by an angle that depends upon the nature of the macrocycle. Whereas the undoped materials crystallize with a stacking pattern in which the units are slipped with respect to each other, the doped materials most often crystallize in a metal-over-metal arrangement (Figure 5).[57]

The conductivity of these systems increases by several orders of magnitude from the undoped to the doped material.[54, 55] Examples of dopants include I^-, BF_4^-, PF_6^- and ReO_4^-. As mentioned earlier, these conducting materials can be prepared by chemical or electrochemical oxidation, but the latter pathway offers more alternatives than the former. Electrochemistry permits facile variation of the dopant and the ability to reach doping levels that are not accessible through chemical oxidation. Both of these factors, nature of the dopant and extent of oxidation of the metalloporphyrinoid, play a major role in the physical properties, such as conductivity, of the final product.[8, 54–57] The list of materials that have been prepared by partial oxidation of metalloporphyrinoids is vast and beyond the scope of this review. Thus we chose to describe one of the most recent examples, the

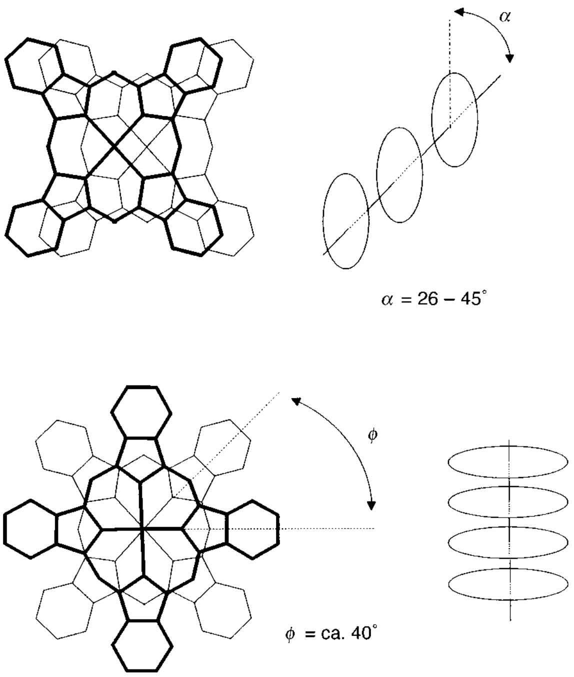


Figure 5. Schematic drawing of the strucutres of the undoped and doped crystallized metalloporphyrinoids (adapted from ref. [57]).

electrocrystallization of a new porphycene-based material, $[Ni(ompc)]_{2.5}(BF_4)_2 \cdot C_{10}H_7Cl$, where ompc stands for 2,3,6,7,12,13,16,17-octamethylporphycene.[8] Single crystals of $[Ni(ompc)]_{2.5}(BF_4)_2$ were harvested at the anode of a two-electrode system by using controlled current (5 μA) electrolysis. The unit cell consists of 10 macrocycles (Figure 6).

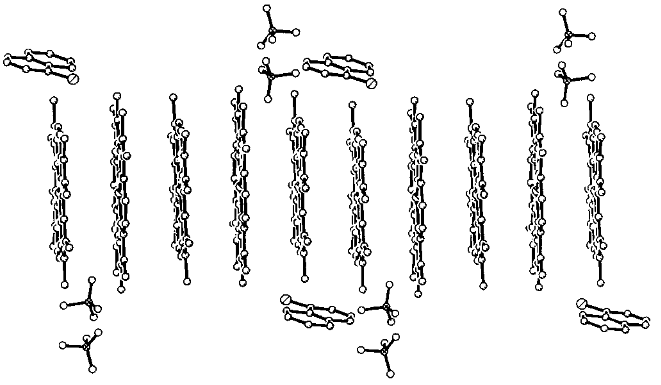


Figure 6. Stacking in the crystal of electrooxidized $[(OMPc)Ni]^+BF_4^-$ (reprinted with permission from ref. [8]).

The structural motif, as expected, consists of stacked macrocycles that are staggered by 90° (Figure 5). The stacks of metallomacrocycles are surrounded by channels, which are occupied by counter anions (BF_4^-) and solvent molecules (1-chloronaphtalene). Within the crystal unit, the 10 macrocycles are arranged as pentamers. The presence of four BF_4^- anions for each pentamer suggests four oxidation sites per pentamer. Within a pentamer, the distance between the elements is 3.33 – 3.38 Å, whereas the distance between two neighboring pentamers is 3.40 Å. The 90° staggering angle between successive units is postulated to minimize the steric hindrance between the Ni porphycenes. The conductivity of this electrocrystallized porphycene at room temperature is 0.06 Ω^{-1} cm^{-1} and was found to be thermally activated.[8]

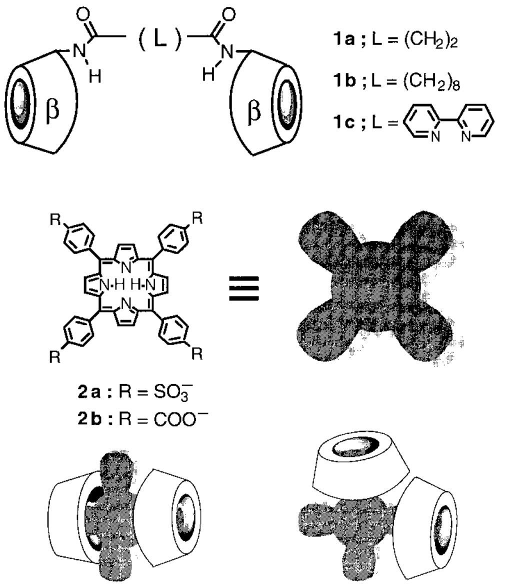
An important question for all of the conducting materials made out of metalloporphyrinoids like the one just described concerns the conduction pathway. Electrochemical studies of nickel porphycenes showed that the first reduction of these compounds is a reversible one-electron, ring-centered process.[58] Thus, it was expected that the conduction pathway in $[Ni(ompc)]_{2.5}(BF_4)_2$ was induced by intermolecular electon transfer from ring to ring. This was actually confirmed by ESR spectroscopy.[8] Modifying the central metal ion in this system, for example by replacing nickel(II) with cobalt(II), might induce another type of conductivity supported by the metal pathway of the material. Indeed, an example that displays metal-pathway conductivity, (phthalocyano)cobalt iodide, has been reported.[54d]

3.7. Outlook

Not a month goes by without a major scientific journal reporting the synthesis of a new porphyrin-based system. Thus it is an almost impossible task to follow the porphyrin literature. This last part of this section will be used to describe recently reported porphyrin-based systems that will probably play important roles in the future of supramolecular chemistry. The electrochemistry of these systems has yet to be explored and is, in our opinion, an area warranting immediate study.

First, electrochemical characterization of porphyrin oligomers is of obvious importance. Of special interest in this field are the iron and gallium porphyrin trimers recently reported by Wojaczynski et al.[59] The electrochemistry of the first binuclear $[Mn^{II}(bipy) - Fe^{III}(porphyrin)]$ could be crucial. Its potential as a biomimetic system for manganese peroxidase has already been suggested.[60] Recently porphyrin[2]catenanes, in which conformational control is exerted by simple acid – base chemistry, have been reported.[61] These systems might represent new types of supramolecular assemblies in which conformational control can be effected electrochemically or by acid–base chemistry. Finally, the self-assembly of cyclodextrins and porphyrins has already been investigated by several groups.[62, 63] Several types of porphyrin – cyclodextrin complexes have been synthesized (Scheme 8) with the aim of mimicking the hydrophobic environment around the heme center in heme proteins.[62a, b]

In addition, studies of porphyrin – cyclodextrin inclusion complexes have been justified by the search for new supramolecular catalytic systems,[62c] the inhibition of porphyrin aggregation[62d] or dimerization,[62e–g] as well as the enhancement of the spin-lattice relaxation of water protons by manganese porphyrin – cyclodextrin complexes.[62h] In spite of the interest in this area, the electrochemistry of the porphyrin – cyclodextrin inclusion compounds remains a relatively unexplored area.

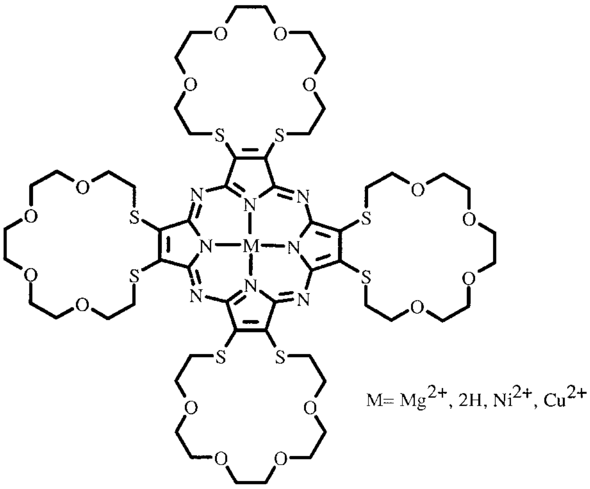


Scheme 8. Example of porphyrin–cyclodextrin inclusion complex (reproduced with permission from ref. [62].)

Since 1985 crown ethers and porphyrins have been intimately combined to generate species with multiple metal binding sites.[64] One recent example is the octathioporphyrazine crown ether,[65] the structure of which is shown in Scheme 9. Beautiful and sophisticated molecular architectures have been built from porphyrinoids and their metal complexes. As the fields of porphyrin and supramolecular chemistry merge, the tools and concepts used in both fields will surely help to create a very rich research area. Electrochemistry will, of course, play an important role in this exciting field because of the uniqueness of the information that it can provide about these systems.

4. Pyridine-Based Systems

Pyridines (py), including bipyridine (bpy), terpyridine (tpy), other extended pyridines, and biquinoline, have been among the most utilized ligands for the preparation of supramolecular structures. In this section we will consider coordination-based complexes of pyridine systems. The electrochemistry of the well-known bpy-based cyclophane systems is described in Section 5. The large number of reports in this area precludes an exhaustive review of the field. Our focus will be on the py-based cryptates, helicates, molecular wires, and the stacked and gridlike arrays that have recently dominated the supramolecular literature. We will also briefly describe the electrochemistry of dendrimer systems based on bipyridine complexes.



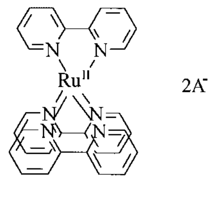
Scheme 9. Framework of the octathioporphyrazine crown ether.

The majority of the complexes described here readily self-assemble, relying on the template effect provided by the transition metal ions. Since many of the metal ions are themselves electroactive, the electrochemistry of these systems is as rich and complex as that of the porphyrinoids described in Section 3. In a number of instances, changing the valence state of the transition metal ion has profound effects on the type of coordination observed in a complex. This is especially true in the case of copper complexes, some of which are described below. Changes in the oxidation state of the metal ion can also result in changes of the nuclearity of the complexes (e.g. monometallic to di- or even trimetallic structures).

4.1. Pyridine-Based Complexes and Cryptates

Among the pyridine and polypyridine metal complexes, by far the most extensively studied ligand is bipyridine.[66] A large number of 2,2′-bipyridine (bpy) complexes with metal ions such as the tris(bipyridine) complexes are known, and most have been characterized electrochemically.[67, 68] The prototypical example of this class of complexes is $[Ru^{II}(bpy)_3]^{2+}$, which has been studied by a number of authors.[69]

Some of the most detailed work in this area was reported by DeArmond and co-workers, who studied the electrochemical and ESR behavior of $[Ru^{II}(bpy)_3]^{2+}$. This complex exhibits some characteristics that are important to describe since they are typical for this class of compound.



$[Ru^{II}(bpy)_3]A_2$ $A^- = Cl^-, PF_6^-$ etc.

In $[Ru^{II}(bpy)_3]^{2+}$ both metal- and ligand-based electron transfer processes can occur. Oxidation of $Ru^{II} \rightarrow Ru^{III}$ in the tris(bpy) complex occurs at 0.82 V vs. Fc^+/Fc in CH_3CN/TEAP (tetraethylammonium perchlorate).[70] For comparison, the Ru^{II}/Ru^{III} oxidation occurs at −0.46 V vs. Fc^+/Fc in the hexaaquo species.[71] Thus, Ru^{II} is stabilized by the chelating ligand. The free bpy ligand can accept two electrons.[72] The first electron transfers onto the bpy ligands in the $[Ru^{II}(bpy)_3]^{2+}$ complex occur (as monoelectronic reductions) at three successive potentials (Figure 7): −1.76, −1.92, and −2.14 V vs. Fc/Fc^+ in DMF/$TEAPF_6$ (tetraethylammonium hexafluorophosphate).[73a]

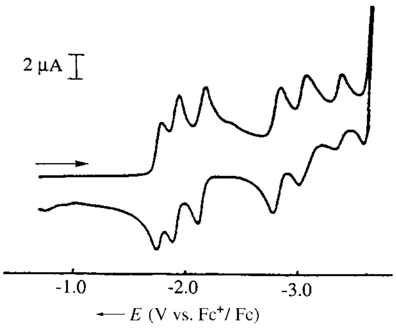
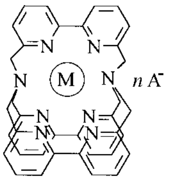


Figure 7. Cyclic voltammograms of $[Ru(bpy)_3]^{2+}$ (0.5 mM) in DMF, 0.1 M $TEAPF_6$; scan rate = 0.1 V s^{-1}, −54°C (reprinted with permission from ref. [73b]).

These reductions are more facile than those of the *free* 2,2′-bpy ligand indicating that the binding to the metal ion lowers the energy of the ligand's π* orbital. The fact that these reductions occur at three different potentials, rather than at a single potential, indicates that there is electronic coupling between the bpy units in the $[Ru^{II}(bpy)_3]$ complex.[73b]

The ESR spectrum of the single-electron reduction product, $[Ru^{II}(bpy^-)(bpy)_2]^+$, shows a single broad line, the line width of which is temperature-dependent, suggesting a thermally activated delocalization (electron hopping).[74] In fact, a number of researchers have shown that the π orbitals of the bpy ligands in $[Ru^{II}(bpy)_3]^{2+}$ are isolated but that thermally activated electrons can hop from ligand to ligand.[74] Similar ESR behavior is noted for the doubly reduced (overall neutral) species.[74] After the third monoelectronic reduction step, which results in the formation of the $[Ru^{II}(bpy)_3]^-$ complex anion, some hyperfine structure emerges, indicating that the electrons are somewhat localized on the individual bpy ligands. The fourth to sixth electron reductions for this complex were observed at low temperature,[73b] and the potentials reported, −2.78, −3.00, and −3.30 V vs. Fc/Fc⁺ in DMF/$TEAPF_6$, again indicate that electronic coupling exists between the ligands. The observation of six separate waves for the complex has been offered as confirmation of the so-called spatially isolated redox orbital model, in which the reduced species exhibit properties of the ligand alone.[75] Thus the presence of the metal ion simply provides a way to tune the potential at which the ligand reduction occurs. The electrochemical behavior of $[Ru^{II}(bpy)_3]^{2+}$ will be used as the standard for comparison with the other pyridine-based systems discussed below.

Tris(bipyrimidine)[70] and tris(biquinoline),[70b] tris(phenanthroline),[70b, 76] and terpyridine[77] complexes of transition metal ions have been characterized by a number of authors. A number of these complexes are of current interest in materials chemistry. We have successfully electrocrystallized several pyridine-based Ru^{2+} complexes.[7] These ligands have also been used as the framework for a series of cryptands and cryptates. Bpy cryptands can undergo electrochemical reduction, as can, in some instances, the cation bound in the corresponding cryptates (for example, a lanthanide such as Eu^{3+}). In these complexes the ligand surrounds and traps the metal in a cagelike coordination sphere (see Section 8). The electrochemistry of the cryptates $[M(\mathbf{7})]^+$ was studied by Echegoyen and co-workers.[78] For $[M(\mathbf{7})]^+$, where M = Na^+, Ca^{2+}, or La^{3+}, although six electrons may be transferred to the three bpy ligands overall, typically only the first three reductions are observed (Figure 8).



$[M(\mathbf{7})]$

M = Na^+, Ca^{2+}, La^{3+}, Eu^{3+}
A^- = Cl^-, Br^-

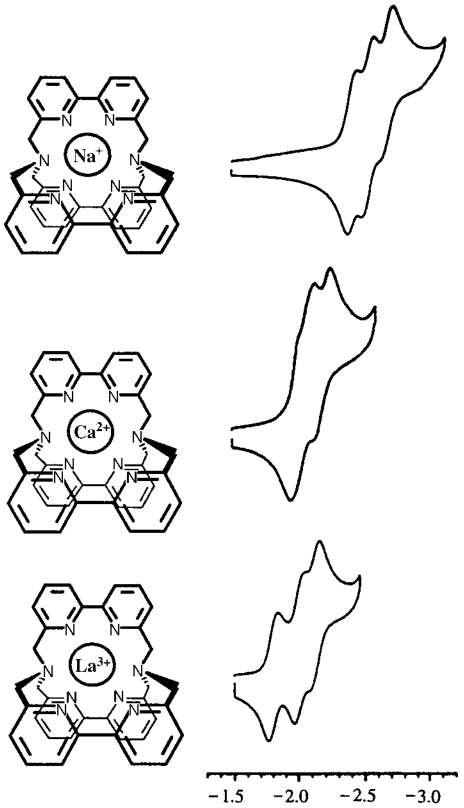


Figure 8. Cyclic voltammograms for $[Na(\mathbf{7})]^+$, $[Ca(\mathbf{7})]^{2+}$ and $[La(\mathbf{7})]^{3+}$, in DMF, 0.1 M $TBAPF_6$; Scan rate = 0.1 V s^{-1} (reprinted with permission from ref. [78b]).

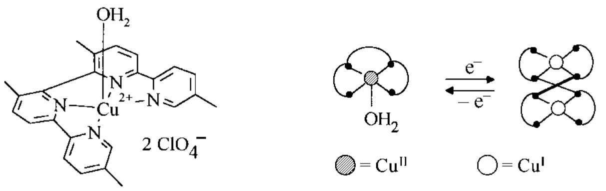
The potentials of these ligand-centered redox processes are strongly influenced by the nature of the metal ion. For example, the first reductions of $[Na(\mathbf{7})]^+$, $[Ca(\mathbf{7})]^{2+}$, and $[La(\mathbf{7})]^{3+}$ occur at −2.40, −1.98, and −1.76 V vs. Fc⁺/Fc. The positive potential shift in the series Na^+, Ca^{2+}, and La^{3+} can be easily understood in terms of simple electrostatic considerations. Interestingly, $[La(\mathbf{7})]^{3+}$ showed a total of six one-electron reductions. The first three reductions correspond to the addition of one electron on each bpy unit. A noticeable gap between the third and fourth reductions reflects the electron–electron repulsion that needs to be overcome to generate the first dianionic bpy unit. Interest in the generation of new materials led to the successful electrocrystallization of $[Na(\mathbf{7})]^+$.[78a] This work is discussed in Section 8.

The electrochemistry of the $[Eu(\mathbf{7})]^{3+}$ complex has also been examined,[79] but it deviates considerably from the behavior of the systems described above. In this complex Eu^{III} undergoes reduction to Eu^{II} at −0.245 V vs. Fc/Fc^+ in DMF/$TBAPF_6$ (tetrabutylammonium hexafluorophosphate), and two pairs of poorly resolved, quasi-reversible reduction waves follow this redox couple. A number of other pyridine-based cryptates have been studied.[78b] However, for the sake of brevity they will not be described here.

4.2. Helicates

Another type of bpy-based architecture that has received considerable attention over the past decade are the helicates, which are complexes based on oligopyridine ligands that self-assemble in the presence of metal ions, to form helical structures.[80] This work was pioneered by Constable[6] and Lehn.[4] These complexes are prime examples of how redox switching can be used to control the molecular architecture.

The first reported example of a Cu^{II} system of this type was the Cu^{II}-tetramethylquaterpyridine complex $[Cu^{II}(\mathbf{8})(H_2O)]^{2+}$ [4a] (Scheme 10), prepared and characterized electrochemically by Lehn and co-workers. This complex can undergo monomer–dimer interconversion as a consequence of switching the oxidation state of the Cu ion. The cyclic voltammetry of $[Cu^{II}(\mathbf{8})(H_2O)]^{2+}$ shows one irreversible reduction at 0.1 V vs. SCE (Figure 9). When the potential scan is reversed after this reduction, two reversible oxidations are observed ($E_{1/2} = 0.53$ and 0.73 V vs. SCE). The reduction at 0.1 V generates $[Cu^{I}(\mathbf{8})(H_2O)]^{1+}$, which is unstable and dimerizes into $[\{Cu^{I}(\mathbf{8})\}_2]^{2+}$, a primitive helicate. The dimeric complex then undergoes two reversible oxidations (labeled $(Cu^I)_2 \longrightarrow Cu^{II}-Cu^{I}$ and $Cu^{II}-Cu^{I} \longrightarrow (Cu^{II})_2$ in Figure 9), which lead to the mixed valence dimer $[Cu^{II}Cu^{I}(\mathbf{8})_2]^{3+}$ and the $[\{Cu^{II}(\mathbf{8})\}_2]^{4+}$ dimer, respectively. The latter eventually decomposes to regenerate the monomeric $[Cu^{II}(\mathbf{8})(H_2O)]^{2+}$ complex, albeit on a longer time scale. The monomeric Cu^{II} complex exists as a tetragonal pyramid with an apical water molecule, whereas the dimeric Cu^{I} complex exists as a dinuclear species with helical structure in which each metal center has a distorted tetrahedral environment. The difference in the half-wave potentials for the oxidation of the Cu^I ions in the $[\{Cu^{I}(\mathbf{8})\}_2]$ dimer indicates that the metallic centers are not electronically independent of one another. For a detailed discussion of this fascinating system the reader is referred to reference [4a].



$[Cu^{II}(\mathbf{8})(H_2O)]^{2+}$

Scheme 10. Dimerization of $[Cu^{II}(\mathbf{8})(H_2O)]^{2+}$ after reduction to form a helicate.

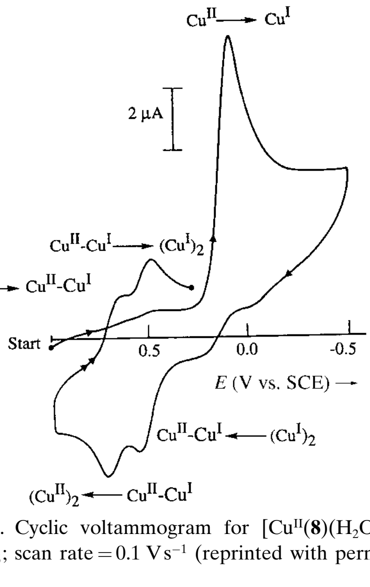
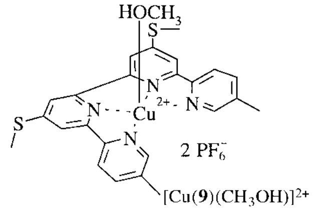


Figure 9. Cyclic voltammogram for $[Cu^{II}(\mathbf{8})(H_2O)]^{2+}$ in CH_3CN, 0.1 M NEt_4PF_6; scan rate = 0.1 Vs^{-1} (reprinted with permission from ref. [4a]).

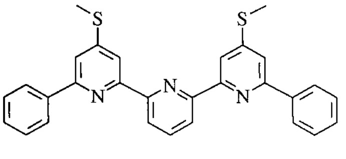
Lehn and co-workers have extended their work on the design of oligobipyridine ligands to include from two to five bipyridine ligands bridged by 2-oxapropylene linkages.[4b–d] They have also prepared Cu^{II} complexes based on oligoterpyridine structures.[4e] Constable et al. have also examined a number of oligopyridine systems,[6] complexed with a variety of transition metal ions, including a quinquepyridine ligand bearing pendant "redox spectator" ferrocene moieties.[6b] Many of these systems have been characterized electrochemically. Additionally, the electrochemical behavior of an entire series of alkylthio-substituted 2,6-oligopyridines has been reported in detail by Abruña, Potts, and co-workers.[5a–d] These authors first reported the electrochemical behavior of Cu^{II} complexes of ligand **9**, a methylthio-quaterpyridine.



$[Cu(\mathbf{9})(CH_3OH)]^{2+}$

The voltammetric results obtained for $[Cu^{II}(\mathbf{9})(CH_3OH)]^{2+}$ differ somewhat from those reported for the analogous $[Cu^{II}(\mathbf{8})(H_2O)]^{2+}$. While both the Cu^{II} complexes of ligands **8** and **9** clearly dimerize upon reduction to the corresponding Cu^I complex, only a single wave for the oxidation to the Cu^{II} state is observed (in DMSO or DMF/TBAP) in the case of **9**; that is, no mixed valent state is apparent.[5a] Furthermore, the time scale for the regeneration of monomeric $[Cu^{II}(\mathbf{9})(CH_3OH)]^{2+}$ appears to be much shorter for the thio-substituted complex. Additionally, there is a notable difference in the $Cu^{II} \rightarrow Cu^{I}$ reduction potentials (+0.13 V vs. SSCE for $[Cu^{II}(\mathbf{8})(H_2O)]^{2+}$ and −0.07 V vs. the sodium-saturated calomel electrode (SSCE) for $[Cu^{II}(\mathbf{9})(CH_3OH)]^{2+}$) that cannot be accounted for by the negligible difference between the reference electrodes. It was proposed[5a] that such a difference might be due to the different solvents used in these studies: interaction of CH_3CN with the metal center might affect the reduction of $[Cu^{II}(\mathbf{8})(H_2O)]^{2+}$. $[\{Cu^{I}(\mathbf{9})\}_2]$ undergoes four reversible or quasi-reversible ligand-centered reductions at −1.38, −1.58, −1.83, and −2.02 V vs. SSCE. Spectroelectrochemistry of this system was also reported.[5a]

The electrochemical behavior of helical complexes based on oligopyridines from quater-, quinque-, sexi-, and septipyridine have been reported.[5a–c, 6] The structural variations observed for these helicates become more complicated as the length of the ligand increases. Cu^{II} complexes as well as Ni^{II}, Ag^{I}, Fe^{II}, Co^{II}, Zn^{II}, and Pd^{II} oligopyridine complexes have been electrochemically characterized.[5, 6] The potential difference between the redox processes that involve the metal centers of the helicates reflects the degree of interaction between the metal ions. For example, a 860 mV difference between the two successive Cu^{II}/Cu^{I} redox processes was observed for $[\{Cu^{I}(\mathbf{10})\}_2]$, where **10** is a methylthiodiphenyl-substituted terpyridine.[5c]



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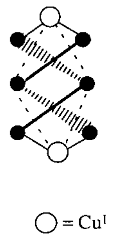
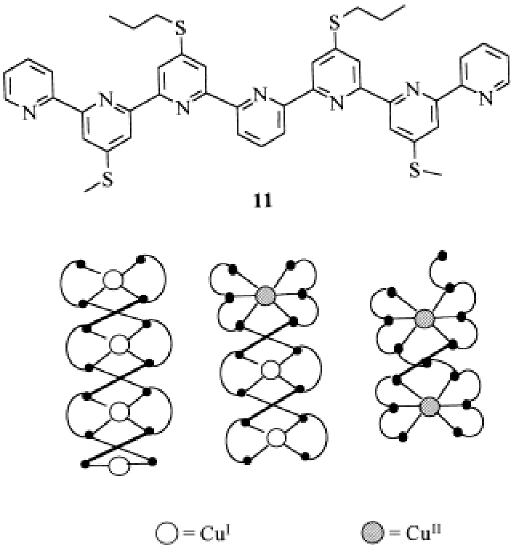


The large potential difference for the reductions indicates a strong interaction between the two copper centers in the dimeric species. This agrees well with the solid-state structural data obtained on the dimeric complex which gives a $Cu^{I}-Cu^{I}$ distance of 2.6 Å.

The ultimate example of how electrochemistry can influence the structure of helicates is that of ligand **11** (Scheme 11).[5d] This ligand was used to generate bi-, tri-, and tetrametallic species containing two Cu^{II} ions, two Cu^{I} and one Cu^{II}, or four Cu^{I} ions. In each complex, the Cu^{II} ions are expected to have an octahedral geometry and the Cu^{I} ions a tetrahedral geometry. However, whereas the dimetallic species was confirmed to have octahedral symmetry, the tetrametallic species shows evidence of a D_2-diamondlike symmetry.[5d] The Cu^{II}/Cu^{I} redox waves for $[\{Cu^{II}(\mathbf{11})\}_2]$ are quasi-reversible and located at 0.05 and 0.24 V vs. SSCE. For the trimetallic complex $[Cu^{I}(Cu^{II})_2(\mathbf{11})_2]$, the Cu-centered oxidations appear at 0.01, 0.43, and 0.82 V vs. SSCE and, as in the case of the bimetallic species, are quasi-reversible. The tetrametallic complex $[Cu^{I}_4(\mathbf{11})_2]$ undergoes four reversible one-electron oxidations involving the Cu centers at $E_{1/2} = 0.02$, 0.44, 0.84, and 1.08 V vs. SSCE. Thus, the bi-, tri-, and tetrametallic complexes all show interaction between the Cu centers. The reported ligand reductions in the tetra- and trimetallic complexes appear to differ markedly, a finding not noted in the smaller oligopyridine helicates. Reduction of the ligands were noted at −1.11, −1.27, and −1.49 V (the latter irreversible) vs. SSCE in the tetrametallic complex, while the same processes occur at −1.42, −1.62, and −1.83 V (the latter irreversible) vs. SSCE in the trimetallic complex. The transformation from the tetrametallic to the dimetallic complex was relatively slow, and spectroelectrochemical results suggested that multiple species are present and that a simple equilibrium does not exist.

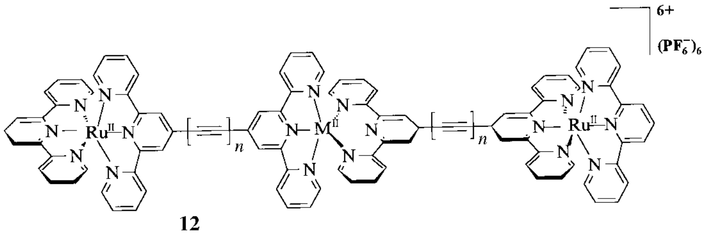


Scheme 11. Bi-, tri-, and tetranuclear complexes with ligand **11**.

One final report deserves to be mentioned in this section. Shanzer and co-workers recently prepared a triple helical system bearing bipyridine moieties.[81] This helical structure provides a coordination site for an Fe^{II} ion (bipyridine) or an Fe^{III} ion (hydroxamate). By switching the redox state of the Fe center, the ion reversibly translocates from one end of the helix to the other. Although the redox switching was accomplished chemically rather than electrochemically, this system provides a fine example of a self-assembled redox-switchable helical complex. The authors are pursuing anchoring these complexes onto conducting surfaces.

4.3. Pyridine-Based Molecular Wires

Molecular wires have been a topic of interest over the past several years.[82] We mention here a recently prepared alkyne-bridged, terpyridine-based system prepared by Harriman and Ziessel, who reported a mixed metallic wire structure **12**, containing two Ru^{II} ions and a different central ion (Zn^{II}, Fe^{II}, or Co^{II}).[83] The half-wave potentials for the oxidation of the Ru^{II} center in these complexes are similar to those of the parent terpy complexes, and the number of bridging alkyne units ($n = 1$ or 2) have only a small effect on the oxidation or reduction potentials of the Ru^{2+} metal centers.



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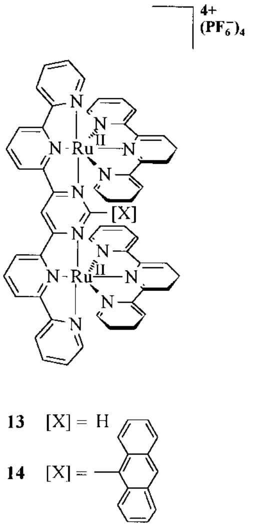
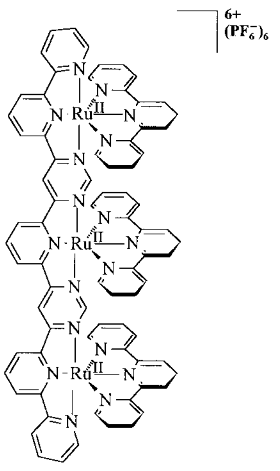
4.4. Racks, Stacks, and Grids

Another very current topic is the preparation of rack molecules that self-assemble in the presence of transition metal ions.[84] Several examples of these complexes have recently been published.[85] The electrochemistry of some of these[85b] (structures **13**–**15**) is described here.



13 [X] = H

14 [X] =



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The crystal structure of **14** displays octahedral coordination geometry about the Ru^{II} centers. The CV of **13** reveals two Ru-centered reversible oxidations at 1.41 and 1.57 V vs. SCE, while the bipyrimidine units are reversibly reduced at -0.43 and -1.03 V vs. SCE, and the terpyridine units are irreversibly reduced at $E_{pc} = -1.50$ and -1.59 V vs. SCE. A stripping peak at -1.40 V indicates absorption of the neutral species. The electrochemical behavior of **14** is similar, indicating that the anthryl spacer does not perturb the electrochemical properties of the complex. The Ru–Ru distance in **14** is 6.40 Å, which suggests a rather weak interaction between the two metal centers. The voltammetry of the trimetallic rack **15** is different, since the oxidations of the Ru^{II} ions occur in two steps, a two-electron wave at $+1.47$ V and a single-electron wave at $+1.88$ V vs. SCE. The latter process is assigned to the central Ru^{II} ion, which is likely to be more difficult to oxidize when placed between the two centers of higher charge. The ligand-based reductions in this system occur at -0.33 and -1.28 V for the bipyrimidine centers, and at -1.62 V (vs. SCE) a single irreversible adsorption wave is noted for the terpyridine units.

Lehn and co-workers are presently working on more complex systems involving ladders and grids that self-assemble in the presence of various transition metal ions.[86] Based on the results obtained for the helicates and rack complexes, the electrochemistry of these new molecular structures should be quite interesting.

4.5. Pyridine Dendrimers

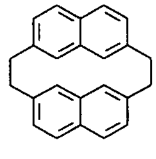
A final topic of current interest in the field of pyridine-based systems is the preparation of pyridine-bearing dendrimers.[45] The high molecular weight of these compounds and the limited availability of material renders their electrochemical characterization challenging. Balzani et al. were among the first to report a decanuclear structure complexed to Ru^{II} and/or Os^{II}, based on a bridging bis(pyridyl)pyrazine ligand and bipyridine or biquinoline ligands.[87] These authors reported the differential pulse voltammetry of these complexes. Puddephatt and co-workers reported a bipyridine-based ligand coordinated to Pt^{II} ions,[88] while Constable et al. reported a simple terpyridine-based ligand that can be used to construct Ru^{II}(terpy) arborols.[89] A common finding for these compounds is that the redox active sites are reduced at the same potential, that is, they are not coupled. Recent work of Echegoyen and Newkome confirm these results.[90] A terpyridine dendrimer that was expanded over several generations showed waves corresponding only to the two reductions of the terpy unit. As with the porphyrin dendrimers mentioned in Section 3, the reversibility of the redox processes suffers as the dendrimer becomes more sterically hindered over successive generations.

5. Cyclophane-Based Systems

This class of compounds has been extensively studied over the last three decades, although electrochemical studies of redox-active cyclophane systems have been comparatively few. Much of the early work in this field was centered on metal complexes of simple cyclophane systems, while more recent work pursues redox-switchable binding with various guests. The electrochemical studies of cyclophane systems can be divided into three general areas: 1) electroactive cyclophanes, 2) systems involving metal coordination to cyclophanes (metallocyclophanes), and 3) cyclophanes as components of catenanes, rotaxanes, and shuttles. Calixarenes, which are a special class of cyclophane, are discussed in Section 6.

5.1. Early Studies with Cyclophanes

The early work on electroactive cyclophanes, such as the studies of Wasielewski and co-workers[91] or Sato et al.,[92, 93] aimed at investigating the electrochemistry of closely positioned redox-active centers. For example, in the naphthalene-based cyclophane **16** and its model compound 2,7-dimethylnaphthalene **17**, conformational isomerism was found to be an important determinant of the redox chemistry:[92] The oxidation of the model compound **17** occurs in one step, as does that of the *cis* isomer of **16**, whereas the *trans* isomer of **16** is oxidized in two distinct steps.[92] This latter finding indicates electronic coupling between the two naphtalene units of *trans*-**16**. Some of the cyclophanes studied by these authors were



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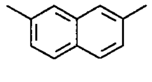

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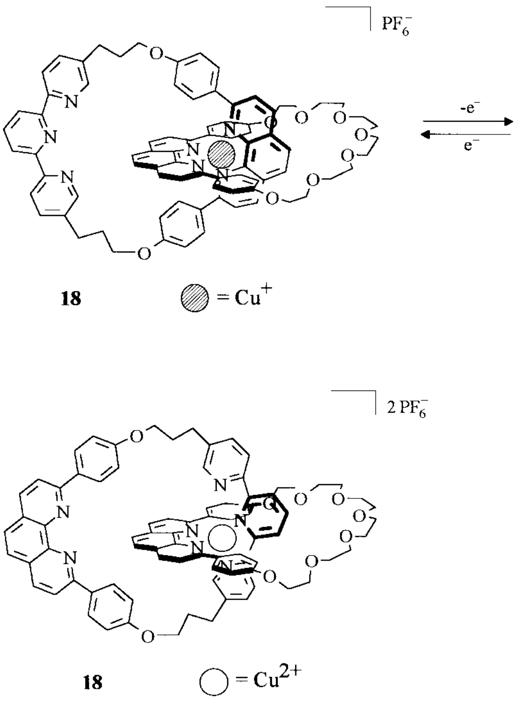
easier to oxidize than their model compounds by as much as 1 V. This is evidence for charge delocalization. A series of simple metacyclophanes with various substituents,[93] and of larger [2*n*]paracyclophane systems[94] were also characterized electrochemically in these early studies.

5.2. Metallocyclophanes

Interest in the iron and ruthenium complexes of [2*n*]cyclophanes and their electrochemistry began with the work of Boekelheide et al.,[95] but complexes with other transition metals have also been studied.[96] More recently, iron–sulfur clusters in a cyclophane cage[97] and a diamagnetic diiron–[2.2]paracyclophane complex[98] have been studied. Metal complexes of porhyrin-based cyclophanes are currently a topic of interest, studied by Staab, and co-workers[99] and Diederich et al.[100]

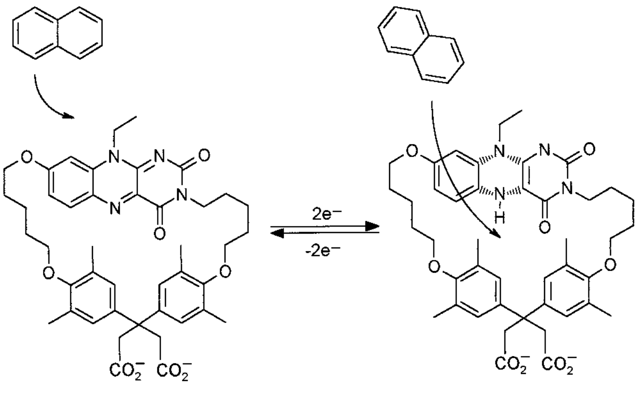
In the area of metal complexes of cyclophanes, an elegant example studied by electrochemistry was recently provided by Sauvage and co-workers: linkage isomerism in a catenane system **18** that contains an interlocking diphenylphenanthroline (dpp) and terpyridine (terpy) cyclophane and a dpp crown ether as metal binding ligands (Scheme 12).[101] As in the case of the helicates, changes in the redox state of the coordinated copper ion provides redox-switchable binding to components of the catenane system. The cyclophane component of the "swinging catenate" structure **18** is capable of binding copper(I) or copper(II). Reduction of copper(II) to copper(I) results in a rearrangement from a five-coordinate (terpy/dpp, CN = 5) structure favored by copper(II) to a four-coordinate (dpp/dpp, CN = 4) copper(I) structure. The electrochemical processes are reversible in both the four-coordinate and five-coordinate species, with half-wave potentials of 0.63 V and −0.07 V vs. the saturated calomel electrode (SCE), respectively, in CH_3CN. The more negative reduction potential of the five-coordinate species reflects the greater stabilization of copper(II) in this complex. The time scale for the coordination processes was noted to be very different for the forward and reverse steps. While the oxidation $Cu^I \rightarrow Cu^{II}$ results in a slow (on the order of days) sliding of the cyclophane into the five-coordinate structure, the reverse process, reduction back to Cu^I, restores the four-coordinate geometry in a matter of seconds. The slower kinetics of the overall forward process has been attributed to other concomitant conformational changes.



Scheme 12. The "swinging catenate" **18**: tetracoordination (top) and pentacoordination of the copper ion.

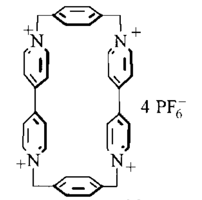
5.3. Switchable Cyclophanes, Catenanes, Rotaxanes, and Shuttles

Within the past decade, attention has centered on the molecular binding capabilities of redox-switchable cyclophanes. In 1990 Diederich and co-workers were the first to report a redox-switchable cyclophane system.[2d] A flavin cyclophane, or flavinophane (**19**, Scheme 13) as termed by the authors, displayed switchable binding ability due to a change in the geometry of the isoalloxazine unit from a planar to a "butterfly," or bent state, after a 2 e− reduction. The reduced form of compound **19** formed inclusion complexes with naphthalene derivatives, while the oxidized form displayed external association. The association constants for these complexes are similar. The 2 e− reduction of **19** is quasi-reversible and occurs at −0.581 V vs. Ag/AgCl in an aqueous borate buffer at pH 10.



19 **19**

Scheme 13. Different binding modes of flavinophane **19**: the oxidized form (left) favors the binding of naphthalene at an external site, whereas the reduced form (right) forms inclusion complexes.



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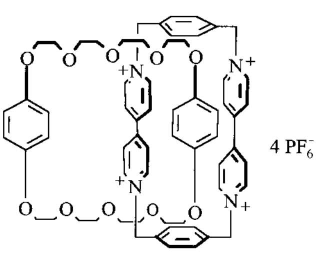
The electrochemistry of **20** has been the subject of considerable attention.[102] This cyclophane has been elec-



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trochemically characterized as a component of catenanes (**21**),[102c, 102e, 102f] rotaxanes (**22**),[103] and molecular shuttles (**23**).[3a] Thus, **20** can be used to exemplify effects on the redox properties of a cyclophane when it is embedded in more complicated architectures. In addition, **20** can also be used to demonstrate how electrochemistry can control the structure of a supramolecular assembly. The reversible redox processes are characteristic of the parent methylviologen unit;[102f] that is, each viologen unit can undergo two monoelectronic redox processes.

Figure 10 shows the cyclic voltammetric behavior of cyclophane **20** and that of the same cyclophane as a component of catenane **21**.[102e] The first wave in Figure 10a, a two-electron process, corresponds to the reduction of the two viologen moieties (one electron each) of **20** to their corresponding cation radicals at −0.279 V vs. SSCE in CH_3CN/$TBAPF_6$, while the second wave (two electrons) corresponds to their subsequent reduction to the neutral viologens, which occurs at −0.703 V. Clearly no electronic coupling is evidenced by the voltammetry.[104] In contrast, catenane **21** exhibits three waves, the first two of which correspond to the separate monoelectronic reductions of the two viologen moieties (Figure 10b).

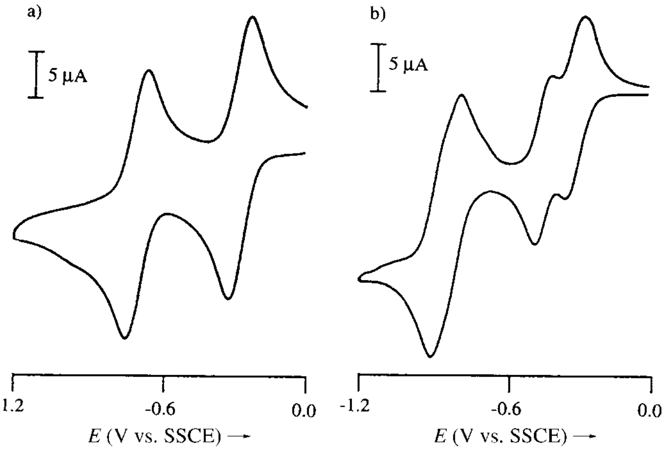
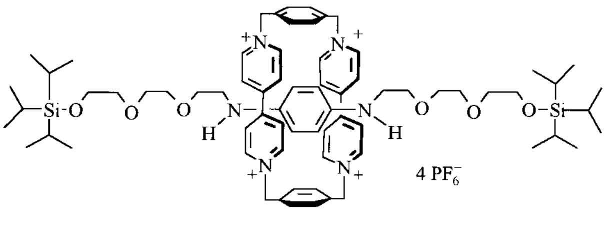


Figure 10. Cyclic voltammograms of 0.50 mM solutions of cyclophane **20** (a) and catenane **21** (b) in CH_3N, 0.1 M $TBAPF_6$; scan rate = 50 mV s^{-1}, 25°C (reprinted with permission from ref. [102e].).

The reduction of the first viologen unit occurs at −0.307 V and the second at −0.438 V. The final two-electron reduction occurs as a single redox wave (reduction of both viologens to their neutral state) at −0.841 V. The fact that two separate reductions are observed for the first redox processes is attributed to the topological differences between the "inside" and "outside" viologen units in the catenane. The inner viologen is stabilized to a greater extent by the two-electron-rich hydroquinone units, while the "outside" viologen interacts with only one of these units. Interestingly, subsequent work on a related surface-attached catenane comprising **20** and a bis(thiol)-terminated poly(ether) hydroquinone thread does *not* show a splitting of the first reduction processes, but rather exhibits behavior similar to that of free **20** in which the first reduction of the two viologen moieties occurs as a single two-electron wave.[105]

Catenanes containing cyclic crown ethers with napthyl spacers in combination with **20** or cyclophanes with π-extended viologens have recently been examined by Stoddart and Balzani.[106] The electrochemistry of **20** in these naphthyl-bearing catenanes exhibits split waves for both the first and the second viologen reduction waves. Cyclophane **20** has also been used as a component of a series of novel [3]pseudocatenanes containing TTF-based macrocycles (TTF = tetrathiafulvalene).[107] The orientation of the cyclophane bead about the TTF moiety affected the electrochemical reversibility of the oxidation of the TTF moiety.

Cyclophane **20** has recently been used as the bead component in a rotaxane.[103] In structure **22**, both the cyclophane bead and the thread are electroactive and exhibit reversible electrochemistry (Figure 11). Rotaxane **22** shows two redox waves for the first reduction of the viologen moieties at −0.272 V and −0.362 V vs. Ag/AgCl in CH_3CN/$TBAPF_6$. The second electron transfer to the viologen moieties occurs in a single step at a half-wave potential of −0.780 V vs. Ag/AgCl. While the free thread exhibits two oxidation waves at 0.203 V and 0.732 V, the thread in the



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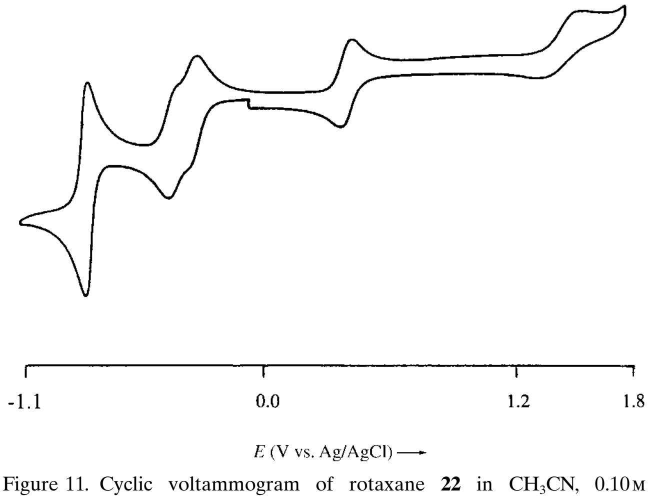
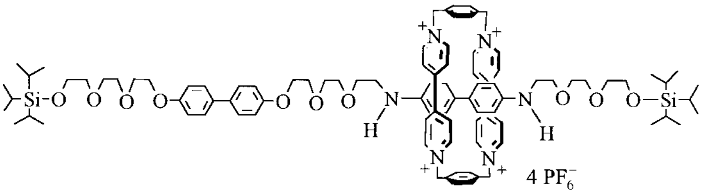


Figure 11. Cyclic voltammogram of rotaxane **22** in CH_3CN, 0.10 M $TBAPF_6$; scan rate = 200 mV s^{-1}; 25°C (reprinted with permission from ref. [103]).

rotaxane undergoes oxidation at 0.463 V and 1.505 V (all potentials vs. Ag/AgCl). Electron transfer is thus slower, reflecting the unfavorable electrostatics.

In the molecular shuttle **23**, which contains cyclophane **20** and a thread with benzidine and biphenyl stations,[3a] the electrochemistry of **20** is similar to that of the *free* cyclophane, with two-electron reductions in single waves at −0.235 V and −0.755 V vs. Ag/AgCl in CH_3CN. Relative to that of the free benzidine thread, the first oxidation of the benzidine station in **23** occurs at a more positive potential (0.570 V vs. Ag/AgCl), whereas the second oxidation occurs at a comparable potential value (0.720 V). The difficulty of the first oxidation of the benzidine station is attributable to the stabilizing presence of the cyclophane **20** bead, while the ease of the second oxidation (comparable to that of the free elongated benzidine thread) indicates that **20** has shuttled off the benzidine station to the other portions of the thread, presumably to the second (weaker) donor biphenyl station.



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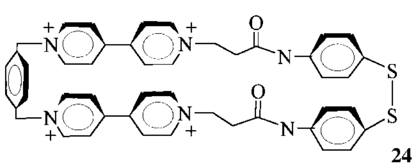
Analytical applications for **20** have also been explored: this redox-switchable receptor binds both aromatic amino acids and neurotransmitters.[108, 10d] While the solubility of **20** in organic solvents is high even in its fully reduced neutral state, its solubility in aqueous solution in the reduced state is quite poor and results in precipitation on the electrode surface. Kaifer et al. conducted binding studies with Nafion-modified electrodes.[10d] Differential pulse voltammetry of **20** was useful in the detection of binding to catechol and indole and their related neurotransmitters in the micromolar concentration range. The half-wave potential shifts exhibited by the host–guest complex were modest (10–70 mV).[10d] This work was recently extended with the self-assembly of a surface-attached cyclophane capable of molecular recognition.[109] Compound **24** self-assembles through thiol bonds with the gold electrode surface. Binding of catechol and indole at an even lower concentration range has been achieved.



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6. Calixarene Systems

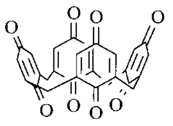
The calixarenes are a special class of cyclophanes capable of binding both neutral and charged guests. Electrochemical analyses of these systems may be divided into two broad areas: 1) electroactive calixarenes, in which the redox unit is an integral part of the σ-bonded framework, and 2) complexes of electroinactive calixarenes with electroactive guest species. The electroactive calixarenes may be further subdivided into two groups, those with the redox-active unit in the main cyclophane framework (e.g., where the phenolic groups are transformed into nitroaromatic or quinone units) and those containing electroactive pendant groups covalently attached as tethers.

6.1. Electroactive Calixarenes

The interest in electroactive calixarenes revolves around the type, number, and location of the electroactive groups in the macrocycle. If the redox units are within the cyclophane framework, the overall size of the calixarene (as represented by the common nomenclature calix[4], calix[6], etc.) is important in understanding its redox behavior. In smaller calixarene systems, such as the calix[4]arenes, the constraints of distance and rotational flexibility are expected to influence the electrochemical behavior of the redox-active units in the basic framework dramatically. The close proximity of neighboring redox units in smaller calixarenes should have strong effects on the redox behavior. Identical neighboring redox units should reduce sequentially as opposed to simultaneously if electronic communication exists between proximal units.[104] On the other hand, the electrochemistry of pendant electroactive groups should be affected less by the size of the calixarene ring, although this may not always be the case.

6.1.1. Calixquinones

The calixquinone series **25**–**28** provides a prototypical example of electroactive calixarenes. The first compound of the series the calix[4]quinone (**25**) was synthesized and its electrochemistry reported in 1989.[110–112] Interest in the other calixquinones quickly followed.[113–117]



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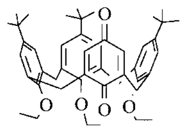

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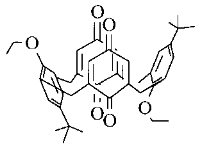

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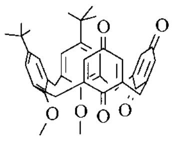

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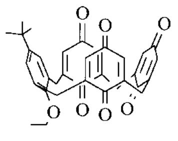

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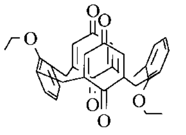
In general, compounds functionalized with quinones are capable of undergoing two-electron reductions for each quinone, the first of which is generally reversible, while the second is typically quasi-reversible.[22] The presence of protons complicates the electrochemical behavior of quinones.[22]

The redox potentials of quinones in the calix[4]quinone series **25**–**28** were found to be dependent upon the number of quinone units present as well as their respective locations[115] and orientations.[114a] Successive quinone substitutions resulted in a greater ease of reduction, that is, a shift of the half-wave potentials to more positive values, due to electron withdrawing effects. For example, the first reduction potential of triethoxycalix[4]monoquinone (**26**) in $CH_3CN/TBAPF_6$ occurred at −0.823 V vs. Ag/AgCl, whereas for the related 1,3-diquinone **27a** the first electron reduction is −0.699 V.[115] The placement of the quinones is important for the contrasting electrochemical behavior in the isomeric diquinone compounds **27a** and **27b**,. The 1,2-substituted system **27b** is reduced more readily (by about 70 mV) than the related 1,3-substituted system **27a**. This behavior indicates that the adjacent quinone units in **27b** have a stronger electronic communication than those in the 1,3-isomer **27a**. The potential gap between successive reductions reflects the extent of this electronic communication between the neighboring redox sites. In **27a**, where the quinone moieties are opposite each other, the potential gap between the first reductions of the first quinone and second quinone units is 140 mV. In **27b** this gap increases to 300 mV. Conformations of the calix[4]quinones have been found to influence the potentials of the first and second electron reductions in the diquinones by as much as 45 mV.[114a]

The voltammetry in $CH_2Cl_2/TBAPF_6$ of chromatographically separated **29** and pure **30** revealed that the reduction of the first quinone was only slightly more positive (5 mV) in **29** (−0.760 V vs. SCE) than reduction of the corresponding quinone unit in **30**.[114a] The effect on the *second* reduction is more pronounced, however: as the potential difference between the first and second reductions of the quinone units in **29** and **30** is 145 and 95 mV, respectively. Thus, it appears that electronic coupling between the quinone sites is stronger in the partial cone conformer **29** than in **30**.



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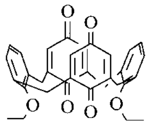

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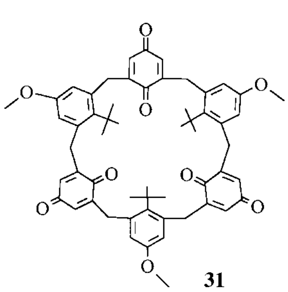
As the calixquinone ring is enlarged on going from the calix[4] to the calix[6] and calix[8] series, the more conformational mobility leads to the electrochemical behavior typically observed for systems bearing multiple, noninteracting, identical redox units.[104] For instance, in a 1,3,5-triquinone calix[6]arene (**31**)[118] all three quinone units are reduced simultaneously at −0.587 V vs. Ag/AgCl. This contrasts with the behavior of calix[4]di- or triquinone systems, in which each quinone unit is reduced at a different potential (Figure 12).[115, 118]



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Conceptually, the calix[6]triquinone **31** is a simple extension of the calix[4]diquinone **27**, with alternating quinone and arene units. Though the simultaneous quinone reduction observed in **31** would appear to be a consequence of the greater conformational mobility afforded by the larger framework, results with a series of calix[6]diquinones[119] suggest that this may not always be the case, vide infra.

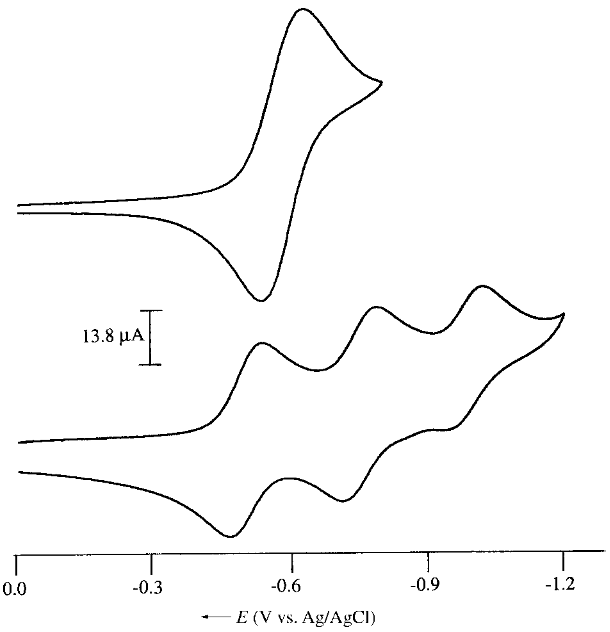


Figure 12. Cyclic voltammograms for the reduction of 1 mM solutions of calix[4]arenetriquinone (**28**)[115] (bottom) and calix[6]arenetriquinone (**31**)[118] (top) obtained on a glassy carbon electrode in CH_3CN, 0.10 M $TBAPF_6$; scan rate = 100 mV s^{-1}, 22°C.

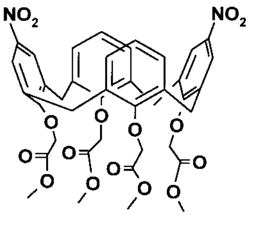
6.1.2. Cation Binding by Calixquinones

As expected, binding of calixarenes with alkali, alkaline earth, or transition metal ions, or with ammonium ions, has an effect on their electrochemistry.[115–117] The first electron reduction potentials of these compounds with binding constant on the order of those exhibited by the crown ethers shift anodically between 90–600 mV in the presence of a bound ion, corresponding to sizable binding enhancements.[115–117] Recent work has also suggested that binding to ions can affect the conformations of calixarenes.[120, 121] This point has not been directly noted as a significant factor when interpreting the electrochemistry of the free and bound calixarenes, but the finding that different conformations[114a] may well have (albeit slightly) different reduction potentials does make conformational change an important consideration when determining binding constants by electrochemical methods. Care must be exercised to assure that any potential shift used to estimate binding or binding enhancements does not include a component due to a concomitant change in the conformation of the calixarene.

6.1.3. Nitroaromatic Calixarenes

Calixarenes with nitro groups in the *para* position of the phenol rings (nitroaromatic calixarenes) have been prepared,[122] and these exhibit slightly different electrochemical behavior. In contrast to results obtained for **26**, a symmetrically 1,3-

substituted calix[4]nitroarene tetramethylester **32** undergoes a quasi-reversible single-electron reduction at each nitroaromatic unit at −1.22 V vs. Ag/AgCl in CH_2Cl_2/$TBAPF_6$.[119]



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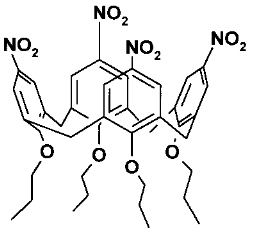

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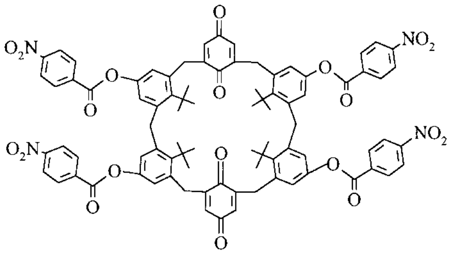
The cyclic voltammetry of a calixarene bearing four nitroaromatic groups (**33**) shows two two-electron reduction waves.[119] Each wave corresponds to the simultaneous reduction of diagonally opposite pairs of nitroaromatic units. A calix[6]diquinone bearing four pendant nitroaromatic esters (**34**) has also been examined.[119] In CH_2Cl_2/$TBAPF_6$ the reversible first electron reduction for each of the quinones occurs at different potentials (−0.472 and −0.785 V vs. Ag/AgCl), reminiscent of the observations with **27a** and **27b**. The bulky lower rim substituents may introduce greater conformational rigidity than would normally be anticipated for the larger calix[6] system and permit greater electronic communication between the quinones than would be expected for this larger system. The second electron transfers, to the quinone radicals, occur simultaneously at −1.15 V vs. Ag/AgCl and are quasi-reversible. The four pendant nitroaromatic units are then reduced simultaneously at −1.50 V vs. Ag/AgCl in a quasi-reversible electron transfer process.



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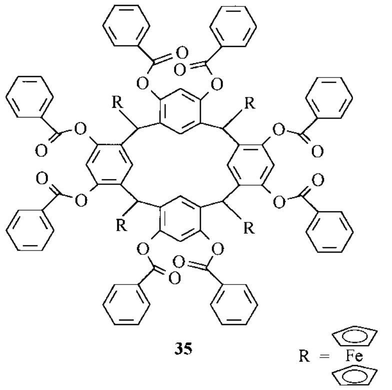
6.1.4. *Calixarenes with Pendant Electroactive Groups*

Attachment of pendant electroactive groups to the upper, lower, or methylene side-arm positions has been explored by several groups. Recently, Beer and co-workers utilized pendant lower rim pyrrole moieties to electropolymerize calix[4]arenes onto the surface of a glassy carbon electrode.[123] Other compounds that have been reported include calix[4]arenes and resorcinarenes with pendant metallocene units,[124] with a pendant $\{Ru(bpy)_3\}^{2+}$ group,[125] and a calix[8]arene with a pendant C_{60}.[126] The ferrocenyl resorcinarenes[124b] provide an interesting comparison between the electrochemical behavior of ferrocenyl substitution at the methylene bridge sites and that observed when the units are appended to the upper rim.

Compound **35**, a resorcinarene substituted at the methylene bridge positions, shows two separate cyclic voltammetric peaks (+0.60, +0.69 V vs. SCE) corresponding to two monoelectronic processes.[124b] The two reversible waves have been ascribed to the two differing ferrocenyl environments detected in ^1H and ^{13}C NMR studies. In contrast, an upper rim substituted ferrocenyl resorcinarene analogue (**36**) demonstrated a single reversible oxidation wave in which the eight ferrocenyl units are independently oxidized at roughly the same potential (0.89 V vs. SCE).[124b] This result agrees with the fact that, in the latter case, the ferrocene units are farther apart from one another than they are in **35**.



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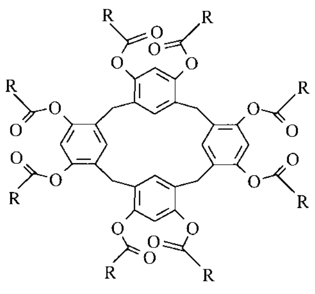

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6.2. Calixarene Complexes with Electroactive Guests

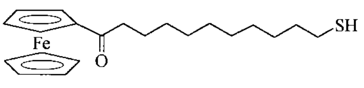
Another area where electrochemical studies have been useful is in the study of complexes of calixarenes with electroactive species. In complexes between sulfonic acid calix[6]arenes and surface-attached ferrocene units,[127] as well as dissolved viologen[128] and ferrocene,[129, 130] the presence of the calixarene has been shown to affect the electrochemistry of the included guest.[127–130]

A particularly striking example is the complex between the ferrocenethiol **37** and the sulfonated host calix[6]arene **38**.[127] Compound **37** self-assembles on the surface of smooth gold electrodes and exhibits surface-confined electrochemistry. It is oxidized at a half-wave potential of 0.51 V vs. SSCE. In the presence of submicromolar amounts of **38**, the single voltammetric wave observed for pure surface-confined **37** is split into two waves, corresponding to the oxidation of the free and bound ferrocene sites. At 2 μM, a single wave is observed for **38** at the formal potential of the bound ferrocene, which occurs 90 mV more positive than that of the unbound, surface-confined ferrocene.

7. Fullerene-Based Systems

7.1. Fullerene Inclusion Complexes: Fullerenes as Hosts and as Guests

Complexes between calixarenes and fullerenes have also been of interest to a number of authors.[126, 131–135] Two types of



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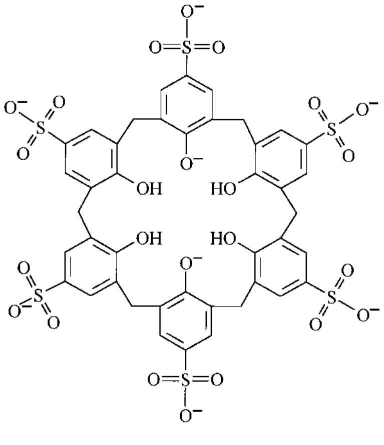

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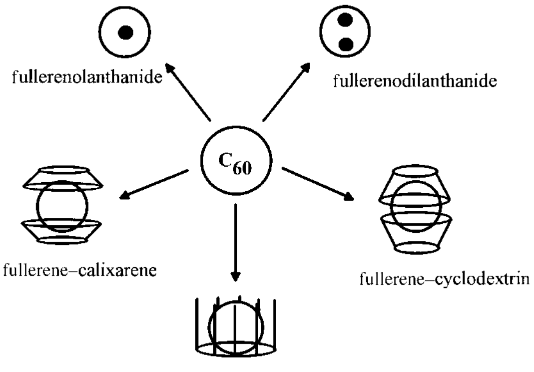
fullerene inclusion structures have been electrochemically characterized. In the first type, called endohedral fullerenes,[136] the fullerene is host to a small molecule or ion such as a lanthanide cation, while in the second type the fullerene is embedded in the cavity of a larger molecule such as a cyclodextrin,[137a–c, 137f] a calixarene,[126, 131–135, 137d] or a crown ether[137e] (Scheme 14).



Scheme 14. Supramolecular host–guest complexes with fullerenes.

7.1.1. *Fullerenes as Hosts*

Endohedral structures have been synthesized[136] with C_{82}, C_{84}, and C_{86} as hosts with lanthanide cations (La^{3+}, Y^{3+}, Sc^{3+}, Ce^{4+}...) as guests. These compounds are designated by the formula $M_m@C_{2n}$ where M is the lanthanide, C_{2n} the carbon cage, and $m = 1$, 2, or 3. These supramolecular structures are conceptually very intriguing, since they are formed from the ionic association between an anion (fulleride) of charge n^- and a cation (lanthanide) of charge n^+ which cannot escape from the anion. In the strictest sense of the word, these cannot be considered classical complexes, since the ion pairing interactions are not really the only ones holding together the complete structure. As a matter of fact, endohedral structures of C_{60} with noble gases are known,[138] and these are definitely not complexes, but more like "molecular rattles." In these, the noble gas molecule is incarcerated inside the fullerene but is not truly held by intermolecular electronic forces. In a way they are analogous to the catenanes, where two or more molecules are held together like the links of a chain.

The electrochemistry of fullerenolanthanides[139] is completely different from that of empty fullerenes, which usually displays equidistant one-electron reductions.[140, 141] Even though the fullerenolanthanides can be reduced by stepwise electrode processes, these reductions are not equally spaced on the potential scale, and they do not correspond always to one-electron processes. For example, $Y@C_{82}$ and $Gd@C_{82}$ undergo four reductions, but the second one is a two-electron process (Figure 13).

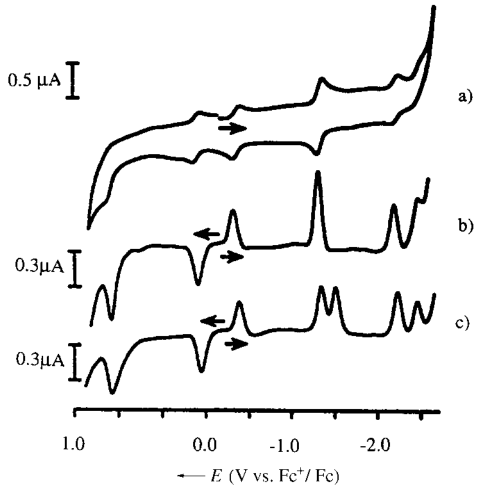
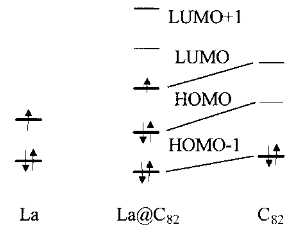


Figure 13. a) Cyclic voltammogram of $Y@C_{82}$; scan rate 20 mV s^{-1}. b) and c) Differential pulse voltammograms of $Y@C_{82}$ (b) and $La@C_{82}$ (c) in 1,2-dichlorobenzene, 0.1 M $TBAPF_6$; scan rate 20 mV s^{-1} (reprinted with permission from ref. [139b]).

On the other hand, $La@C_{82}$ and $Ce@C_{82}$ undergo five distinct one-electron reductions (Figure 13). An explanation for such a peculiar electrochemical behavior for the fullerenolanthanides is still needed. Another noticeable characteristic of the electrochemistry of fullerenolanthanides is that all undergo a relatively easy reversible one-electron oxidation (see Figure 13). This might reflect the single occupancy of the HOMO for these complexes, where the metal ion is in its +3 oxidation state (Scheme 15). In other words, the ease of the first oxidation of fullerenolanthanides may be because removal of one electron in $M^{3+}@C_{82}$ leads to a closed-shell species.[139]



Scheme 15. Schematic MO diagrams of La, $La@C_{82}$, and C_{82}.

Changing the nature of the metal inside the cage affects the electrochemistry of the endohedral fullerenes only slightly. It was proposed[139b] that the 4f orbitals of the lanthanide cations do not play a significant role in the electrochemistry of fullerenolanthanides and that the first reduction and the first oxidation occur on the Singly Occupied Molecular Orbital (SOMO). The electron density of the latter is located mainly on the part of the fullerene cage closest to the lanthanide cation. Thus, the bigger the lanthanide, the closer it is to the cage and the more stabilized the negative charge on the cage. In other words, the larger the lanthanide, the easier the reduction and the more difficult the oxidation.

Very recently[139d,e] preliminary results on the physical and chemical properties of endohedral fullerene complexes containing two metal cations have appeared. Only very preliminary electrochemical data were listed, and no discussion of these data was provided in this article.

7.1.2. Fullerenes as Guests

Mainly three types of inclusion complexes in which a fullerene is the guest have been synthesized: C_{60} – cyclodextrin complexes (C_{60}/CD),[137a–c,f] C_{60} – calixarene complexes,[126, 131–134, 137d] and a C_{60} – azacrown complex.[137e]

Interestingly, the inclusion of the fullerene derivative $C_{61}(C_6H_5)_2$ inside the cavity of an HIV protease was studied by computer modeling with the hope of altering the reactivity of the protease.[142a,b] The results obtained are surprisingly promising, and several laboratories are now participating in the study of the biological activity of C_{60} and its derivatives.[142c]

The electrochemistry of C_{60}/γ-CD in DMF is very similar to that of C_{60}.[137c] However, in the case of C_{60}/γ-CD, the third reduction wave is followed by a chemical reaction that produces a species yet to be identified. C_{60}/γ-CD is only slightly soluble in water, but enough dissolves to allow recording its electrochemistry (Figure 14).

Cyclic voltammetry of C_{60}/γ-CD in water containing 0.15 M $LiClO_4$ at scan rates higher than $200\,mV\,s^{-1}$ reveals two reversible one-electron reductions at $E_{1/2} = -0.62$ and -1.03 V vs. SCE, and one irreversible reduction at $E_{pc} = -1.34$ V vs. SCE. At slower scan rates ($< 200\,mV\,s^{-1}$), only the first reduction is reversible, and, as can be shown by differential pulse voltammetry (DPV), the second reduction is followed by a chemical reaction. The authors speculated that C_{60}^{-} is still embedded in γ-CD whereas C_{60}^{2-} is released and undergoes a chemical reaction with water.

As mentioned above, a second type of supramolecular complex where a fullerene is the guest has appeared in the literature: the C_{60}/calixarene complexes.[126, 131–135, 137d] Interestingly, the only calixarene to complex C_{60} and C_{70} efficiently is **39** (Scheme 16). The forces that induce formation of such a complex are probably of the CH – π and π – π type. To our knowledge, only one report that succinctly investigated the electrochemical behavior of C_{60} in the presence of calixarenes (the diethyl esters of *para-tert*-butylcalix[8]arene, *para-tert*-butylcalix[5]arene, and *para-tert*-butylcalix[4]arene) has been published.[134] The calixarenes, whatever their size, interact or react with C_{60} anions. The products of these reactions are more difficult to reduce than C_{60} itself. During the electrochemical experiments, addition of calixarene to a solution of C_{60} also caused adsorption on the working electrode at potentials more negative than the second reduction wave of C_{60}.

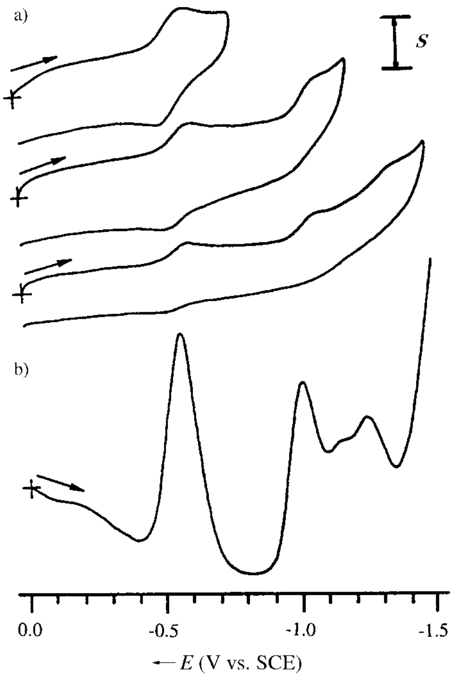
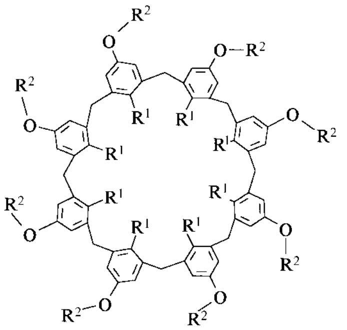


Figure 14. a) Cyclic voltammograms and b) differential pulse voltammograms of nearly saturated magenta γ-CD/C_{60} solution in water, 0.15 M $LiClO_4$; glassy carbon electrode. CV: potential scan rate $50\,mV\,s^{-1}$; DPV: potential scan rate $10\,mV\,s^{-1}$, pulse amplitude 20 mV, pulse width 50 ms. *S* is equal to 1.0, 1.5, 2.0, and 0.2 mA for the curves from top to bottom (reprinted with permission from ref. [137c]).



39 $R^1 = tBu, R^2 = H$

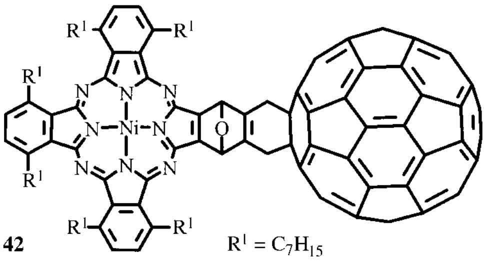
40 $R^1 = H, R^2 = H$

41 $R^1 = tBu, R^2 = CH_3$

Scheme 16. Calixarenes investigated as hosts for complexation of C_{60}.

7.2. Latest Work on Fullerenes Related to Supramolecular Chemistry

Recently C_{60} was derivatized with the aim of building a starting block to form supramolecular complexes. Initially Hirsch et al. reported the synthesis and electrochemistry of **42**, the Diels – Alder adduct of C_{60} with a phthalocyanine.[143] The CV of the complex reveals five reversible one-electron reductions, which involve either the fullerene or the Ni



42 $R^1 = C_7H_{15}$

metallophthalocyanine center. Reduction potentials for two complexes in which a porphyrin is covalently bonded to C_{60} have been reported.[144, 145] In both cases redox processes centered on C_{60} and on the porphyrin ligand can be observed. In all of these studies, the electrochemical results suggested that the coupling between the carbon cage and the ligand is not very effective when both molecules are in the ground state. A second example of a C_{60} derivative for further supramolecular binding is a C_{60}–[Ru^{II}(bpy)$_3$] complex.[146]

7.3. Electrocrystallization of Fulleride Salts

As already discussed, electrochemistry can be used as an effector to prepare novel materials mainly by electrocrystallization. The final electrogenerated products are crystalline supramolecular assemblies with unique properties. This is truly a field of research in which electrochemistry, supramolecular chemistry, and material science merge. The first electrochemical preparation of a fulleride salt was reported in 1991 by Wudl et al.[147] Attempts by these authors to prepare a bulk solution of C_{60}^{-} with tetraphenylphosphonium iodide (TPPI) as supporting electrolyte resulted in the precipitation of its salt, $C_{60}^{-}(TPP^+)_3(Cl^-)_2$. Because the sample precipitated as a powder, no structural information was obtained.

The first electrocrystallization of a fulleride salt was achieved by Moriyama et al. in 1993.[148] Needlelike single crystals of $C_{60}^{-}(PPN^+)$ ($PPN^+ = \{N[P(C_6H_5)_3]_2\}^+$) are air- and light-sensitive and showed no electrical conductivity at room temperature.[148] No detailed X-ray characterization of the crystal was provided in this article. Later the same year, Pénicaud et al. reported the X-ray characterization of electrocrystallized $[(C_6H_5)_4P]_2(C_{60})(I)_x$ ($x \ll 1$).[149] The black shiny single crystals that grew under controlled current electrocrystallization of C_{60} in a toluene/CH_2Cl_2 mixture with tetraphenylphosphonium iodide as supporting electrolyte revealed that the C_{60} monoanions were separated at least by 12.588 Å (center-to-center distance for C_{60}: $d = 10$ Å). This indicates that the C_{60} monoanions in $[(C_6H_5)_4P]_2(C_{60})(I)_x$ are isolated.[149] The tetraphenylphosphonium C_{60}^{-} salt was stable in air, and its conductivity at room temperature was $2-5 \times 10^{-5}\ \Omega^{-1}cm^{-1}$.[149] Interestingly, even though the C_{60} radical anions are well separated from each other, the magnetic susceptibility data did not follow a Curie–Weiss law.[149]

Controlled-potential electrocrystallization of $[(C_6H_5)_4P]C_{60} \cdot [(C_6H_5)_4P]Cl$ in 1,2-dichlorobenzene was reported in 1994 by Bilow et al.[150] The black, air-stable, square-pyramidal crystals were characterized by X-ray.[150] As expected, this salt is isostructural with the one electrocrystallized by Pénicaud et al. Similarly, electrocrystallization of the tetraphenylarsonium salt of C_{60}^{-} was also reported.[151] It is important to note that both X-ray structures (Pénicaud's and Bilow's) showed disorder in the arrangement of the C_{60} monoanions and this precluded a clear picture of the distortions that the carbon cage undergoes upon addition of one electron. The first example of a highly ordered salt of C_{60}^{-} was reported in 1995.[152] $[Ni\{C_5(CH_3)_5\}_2]^+[C_{60}]^-$ was prepared by chemical reduction of C_{60} with one equivalent of decamethylnickelocene.[152] The X-ray characterization of the dark red parallelepiped crystals revealed structural evidence of a Jahn–Teller distortion of the C_{60} cage upon reduction.

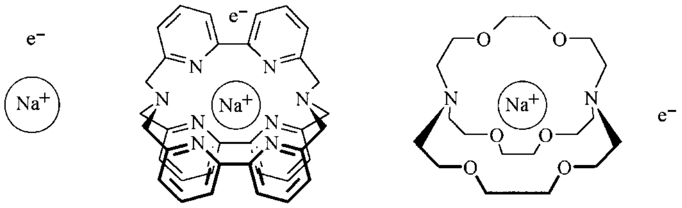
In an attempt to generate new materials with interesting electrochemical and photochemical properties, Foss et al. electrocrystallized $[Ru(bpy)_3](C_{60})_2$.[153] The conductivity of powdered samples was $0.01\ \Omega^{-1}cm^{-1}$ at room temperature.[153] No photoconductivity was observed.[153] In 1994 Kobayashi et al. reported the first electrocrystallization of an alkali metal fulleride salt, $Na_{0.39}C_{60}(THF)_{2.2}$.[154] The room temperature conductivity of the sodium salt was $50\ \Omega^{-1}cm^{-1}$ and increased to $1000\ \Omega^{-1}cm^{-1}$ at 100 K.[154] This sodium salt was found to be isostructural with respect to other chemically prepared alkali metal fulleride salts, $M_xC_{60}(THF)_y$ (M = Li, Na, K).[154] The X-ray data for the electrocrystallized sodium salt indicate that there are direct interactions between the C_{60} monoanions (shortest distance of 9.93 Å), and this might explain the metallic character of the salt.[154] Only one fulleride salt made from a higher fullerene has been electrocrystallized to date.[155] Single crystals of $[(C_6H_5)_4P]_2(C_{70})[I]$ are air-stable, and their magnetic susceptibility follows a Curie-Weiss law, which suggests isolated C_{70} monoanions. This was confirmed by X-ray data, which revealed a shortest center-to-center C_{70} distance of 12.682 Å[155] ($d \approx 10$ Å for C_{70} itself, along its equatorial belt). However, as for the corresponding C_{60} salt, disorder in the crystals prevented any clear picture of how the C_{70} molecular structure is affected by the addition of one electron.

Finally, it is important to note that only salts of C_{60}^{-} and C_{70}^{-} have been electrocrystallized. No salts with higher charges have been prepared by electrocrystallization. However, chemical reduction of C_{60} to C_{60}^{2-} with either Na or cobaltocene as reducing agent has been reported.[156] Black shiny single crystals of $[PPN^+]_2C_{60}^{2-}$ are "somewhat air sensitive", and their magnetic characteristics led the authors to the conclusion that C_{60}^{2-} is paramagnetic at room temperature.[156b] The high precision of the X-ray structure obtained for the crystals of this C_{60}^{2-} salt allowed the observation that Jahn–Teller distortion in the dianion changed the icosahedral symmetry of the neutral molecule to C_i.[156a] These results reported by Boyd et al. suggests that the electrocrystallization of salts of C_{60}^{2-} and probably C_{70}^{2-} are possible and should be attempted.

8. Electrogeneration of Expanded Atomlike Structures

A conceptual link between reduced cryptates (cryptatia) and endohedral fullerene complexes exists, even though the two types of materials seem rather unrelated. A cryptatium is obtained by reduction of a positively charged complex between cation and cryptand (cryptate)[78, 157] to its neutral form. In other words, a cryptatium can be visualized as an anionic armor surrounding a metallic heart. The analogy with endohedral fullerene structures containing metal ions[136] then becomes obvious. The endohedral fullerenes that contain metal ions inside are also made of a positively charged core surrounded by a negatively charged spherical shield. Both cryptatia and endohedral fullerene structures are neutral entities. However, if one was to approach either of these molecules on a nanometer scale, the first observation would be that of a negative electron density corresponding to the electrons located on the cryptate ligand or on the fullerene cage. Beyond this negatively charged shield, one would find the positively charged metal ion, the "nucleus" of such a "pseudo-atom." Thus both are classified as "expanded atoms."

Cryptatia and endohedral fullerene complexes thus can be considered as intermediate between a metal atom and an electride[158, 159] (Scheme 17). In the metal atom, for example sodium, the loosely bound electron is confined to the 3s orbital. Because of the very strong affinity of the cryptand [2,2,2] for metal cations such as the sodium cation, the electron of the metal in the electride is expelled from its interaction with the cationic center into the cavities present in the crystal lattice.[158] In cryptatia and endohedral fullerene structures, the electron is not confined to the corresponding s orbital of the metal cation but neither is it completely expelled from its interaction with the metal cation.



Scheme 17. The relationship between an alkali metal atom (left), a cryptatium (center), and an electride (right).

It is not a simple task to establish that in a given cryptatium, the electrons balancing the metal ion charge are located on the cryptate ligand. This was accomplished in 1991 by X-ray characterization of single crystals of the first cryptatium, $[Na\subset(bpy_3)]^0$.[78] Single crystals of this sodio-cryptatium were grown at a platinum electrode by the electrocrystallization technique, which is probably the most efficient way to grow crystals of cryptatium species. $[Na\subset(bpy_3)]^0$ (bpy_3 is a cryptand constructed from three bpy units as shown in Scheme 17) is the only cryptatium for which a crystal structure has been determined successfully to date. Its crystal structure revealed that of the three bipyridine units that are covalently linked to form the cryptand ligand, only one was planar. In addition, the Na^+-N distance for the planar bpy unit was shorter than that for the other two (2.59 vs. 2.82–2.83 Å). This suggests that the electron added to the cryptate ligand during its reduction is located on the flat bpy unit. Thus, the sodio-cryptatium is more accurately described as $[Na^+\subset(bpy^-)(bpy)_2]$.

The conceptually related endohedral fullerene systrems still have to be structurally characterized. One striking result was recently reported by Takata and co-workers, who used synchrotron X-ray diffraction spectroscopy.[160] They were able to detect the encapsulated metal ion of $Y@C_{82}$ (Figure 15).[160]

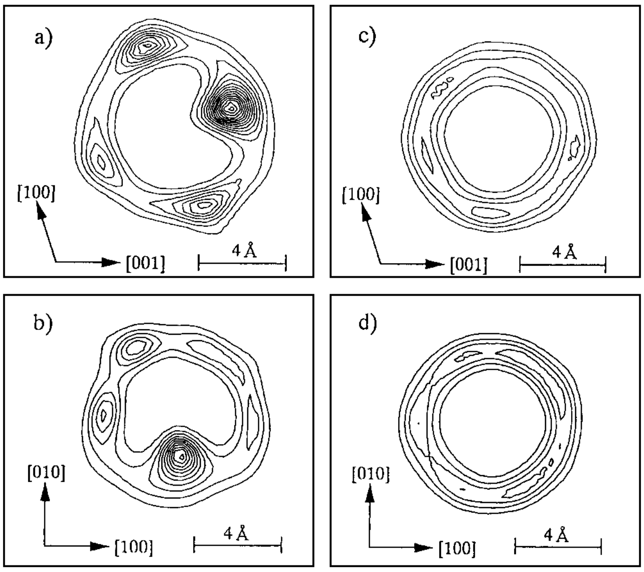
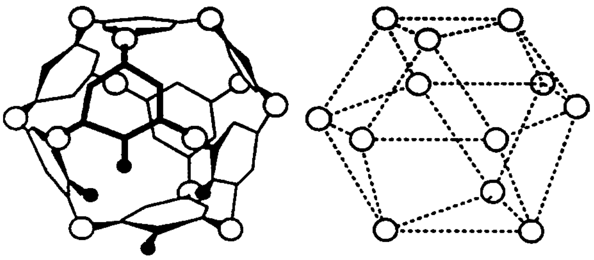


Figure 15. The maximum entropy model (MEM) electron density distribution of $Y@C_{82}$ for a) the (010) and b) the (001) sections, and of C_{82} for c) the (010) and d) the (001) sections. The contour lines are drawn from $0.0\,e\,A^{-3}$ at $0.5\,e\,A^{-3}$ intervals. The yttrium atom's seat inside C_{82} can be clearly seen in a) and b). (Reprinted with permission from ref. [160].)

The family of compounds $[M(bpy)_3]^0$ (M = Fe, Ru, or Os) is also another example of the general class of structures defined as "expanded atoms." Even though these cationic complexes have been studied for 30 years, only recently was their potential as novel "expanded atoms" revealed.[161, 162] In these complexes the three bpy units are not covalently linked to each other; nevertheless they surround the positively charged metal center in a similar fashion to the tris(bpy) cryptand ligand. The series of compounds, $[M(bpy)_3]^0$ (M = Fe, Ru, or Os) was successfully electrocrystallized at a platinum electrode from the corresponding precursor cations, $[M(bpy)_3]^{2+}$.[7, 161] The structures of these complexes have not yet been published, but they seem to retain the original octahedral symmetry of the unreduced complex. This surprising result is currently under intense investigation. Another intriguing result with the $[M(bpy)_3]^0$ single crystals is their lack of an ESR signal. This contrasts with results reported by DeArmond et al.,[74, 163] who described a 250 G wide ESR line centered at $g = 2.23$ for the same materials but studied as powders. This might indicate interesting conducting or semiconducting properties. Only the reduced ruthenium complex has been thoroughly characterized at the present time.[162]

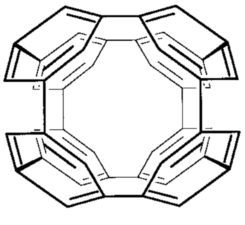
Magnetic susceptibility measurements on electrochemically prepared single crystals revealed that $[Ru(bpy)_3]^0$ is best characterized by the spatially isolated redox orbital model.[162] The reduction electrons are located on two of the three bpy units of each molecule in the ligand's π* orbitals. A comparison of the magnetic properties of $[Ru(bpy)_3]^0$ in solution and in the solid state suggests that removal of the solvent leads to a decrease in the energy gap between the metal $d\sigma^*$ and the ligand π^* orbitals. The best fit of the experimental magnetic data was obtained when $[Ru(bpy)_3]^0$ was considered as a one-dimensional chain structure in which each electron on a ligand is coupled intramolecularly to the electron on the other bpy ligand and intermolecularly to the closest bpy unit of the neighboring molecule. $[Ru(bpy)_3]^0$ is a semi-conductor, and the temperature dependence of its conductivity can be rationalized with a hopping conduction mechanism.

Four years ago Ross et al.[164] reported the theoretical calculations of the polarizabilities of a series of spherical molecules with encapsulated cations, the heterospherophanes (Scheme 18). These compounds, yet to be synthesized, are closely related to the cryptatia and the endohedral fullerene complexes. In the particular case of the thiaspherophanes, the sulfur atoms should allow the electrons that balance the charge of the embedded cation to be delocalized over the entire molecule and, in the crystalline state, should favor intermolecular electronic coupling. The cation would be shielded by the field generated by the delocalized charge, producing a true "expanded atom."

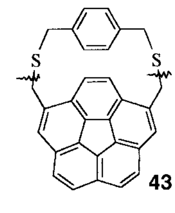


Scheme 18. Schematic representation of heterospherophanes (reprinted with permission from ref. [164]). Open spheres = heteroatoms, solid spheres = selected hydrogen atoms to show steric crowding around cavity entrance.

Two recent reports are also conceptually related to "expanded atoms". In 1995 Diederich et al.[165] reported the electrochemistry of the mono- through hexakis-adducts of C_{60}. One of their conclusions was that successive rupture of the C_{60} double bonds during six successive addition processes to the cage ultimately revealed the benzenoid "cubic" cyclophane structure enclosed in the fullerene framework (Scheme 19). Synthesis (or retrosynthesis from C_{60}) of such a "cubic" cyclophane would truly represent an important step toward the synthesis of a novel "expanded atom". Finally, Siegel and co-workers[166] recently reported the synthesis of the first corannulene cyclophane (**43**), which obviously is a well-suited candidate for the synthesis of "expanded atoms" given that the "organic skin" could allow for delocalization of the excess negative charge around a centrally located and bound cation.



Scheme 19. Benzenoid "cubic" cyclophane structure contained in C_{60}.



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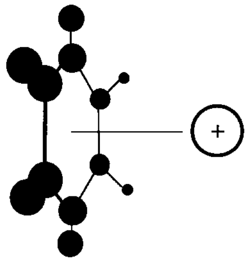
In conclusion, the concept of an "expanded atom" is more than just an idea and its exploration could easily lead to the preparation of novel materials with unique properties. The most solid experimental evidence that "expanded atoms" can be made is the successful synthesis of endohedral fullerene structures. In fact, endohedral fullerenes containing more than one metal ion have been isolated and characterized.[139d, 139e] In those cases, in addition to the attractive interaction between the cations and the negatively charged fullerene sphere, one has to take into account the electrostatic repulsion between the two metal cations within the cage. In a way, the entire situation is reminiscent of charge repulsion in nuclei and their attractive interactions with the orbiting electrons in an atom.

In all of the previously mentioned examples of "expanded atoms", the metal cation is surrounded by a structure derived from the benzene ring. One can envisage then that cation – π interactions (Scheme 20)[167] will be omnipresent in these systems. These noncovalent bonds between cations and π-rings might be used as a driving force in the tethered synthesis of novel "expanded atoms".



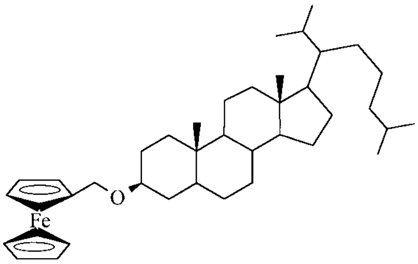
Scheme 20. The cation – π interaction.

9. Potentially Functional Aggregates and Some Future Prospects

In the previous sections examples were presented of how electrochemical techniques have been used to characterize single molecules, complexes, and aggregates composed of a relatively small number of molecules. Instead of using this last section as a prophetic platform to try to preach about the future, two additional examples of work from our laboratory have been selected to illustrate how important electrochemistry is for the formation and detection of large aggregates of supramolecular assemblies. In one example, electrochemistry was used to induce the formation of liposomal aggregates,[168] while in the other it was the technique used to detect aggregate formation on a surface, which occurred spontaneously through molecular recognition.[169]

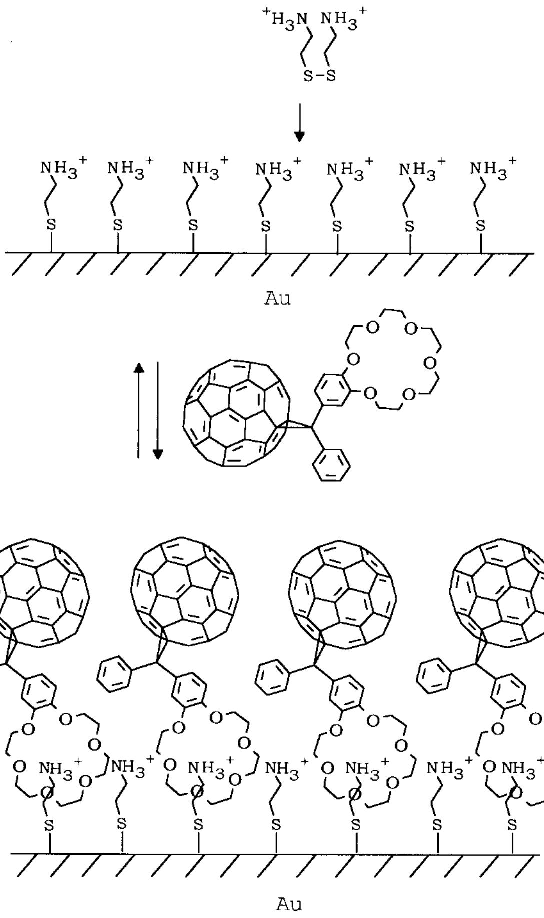
Typical natural bilayer membranes are formed from phospholipids derived from glycerol and fatty acids. The formation of these membranes primarily relies on the hydrophilic/hydrophobic balance that exists between the headgroup/tail portions of these compounds. It is this balance that confers the unusual stabilities associated with these highly organized supramolecular aggregates. Either polar or charged moieties in the headgroups interact strongly with the surrounding water medium, while the hydrophobic alkyl tails interact with each other inside the bilayer. A while back we showed that a crown ether, even uncomplexed, was sufficiently hydrophilic to induce formation of nonionic liposomes (niosomes) when attached to a cholesterol group.[170]

The concept of redox switching as applied to binding control was already discussed in Section 2. In those cases, electrochemistry was used to generate charge in part of a molecule, and this charge resulted in inter- or intramolecular electrostatic interactions with species of the opposite charge, thus leading to enhanced binding. In the present context of bilayer membrane formation, electrochemical switching was used to generate charged headgroups for enhanced hydrophilicity. The switchable headgroup that was selected originally was ferrocene, and the hydrophobic tail was either cholesterol or cholestanyl (Scheme 21).[168] Electrochemical oxidation of the ferrocene group to ferrocinium followed by sonication in water led to the formation of stable vesicles.[168] These vesicles constitute rather complex aggregates with potential applications as redox-active drug delivery systems. Reduction of the vesicles back to their neutral states, either chemically or electrochemically, resulted in their total disruption. An extension of this work was reported very recently.[171]



Scheme 21. Structure of steroidal ferrocene derivatives used to form liposomes after oxidation of the ferrocene head group to ferricinium.

A striking example of how electrochemistry is uniquely useful in characterizing the formation of architecturally complex and dimensionally large assemblies was published very recently.[169] A self-assembled monolayer (SAM) of cystamine was first allowed to form on a gold [111] electrode by following well-established procedures.[172] This monolayer, which forms spontaneously, terminates in positively charged ammonium groups, as represented in Scheme 22. If this monolayer is now exposed to a solution of a crown ether-containing compound such as the methanofullerene shown in Scheme 22, hydrogen bonding between these two functional groups should induce the formation of a secondary SAM.[173] The overall process is described in Scheme 45. Although reflectance spectroscopic techniques can be applied to characterize the formation of such monolayers at the electrode–solution interface, electrochemistry offers an easy and convenient way to establish whether such supramolecular aggregates form. Since the fullerene group is electroactive, as described in Section 7, it is very easy to detect the current for the first reduction of the fullerene moiety to its monoanionic state. The current detected for the same solution of the methanofullerene in the absence of a cystamine monolayer can be easily subtracted from that observed in the presence of the monolayer to obtain the surface concentration effect. After simulation and appropriate calibration of the electrode surface area, a surface covarage of 1.4×10^{-10} mol cm^{-2} was determined. Assuming an area per molecule of 100 Å^2 for the C_{60} group, a close-packed coverage of 1.9×10^{-10} mol cm^{-2} is calculated. This means that about 75 % of the surface is covered by this double self-assembly process driven.



Scheme 22. Formation of a cystamine monolayer on gold followed by its interaction with a benzo[18]crown-6 methanofullerene. A secondary monolayer of fullerenes is formed by self-assembly due to molecular recognition between the ammonium groups and the crown ethers.

These two examples should give the reader some concrete ideas on how electrochemistry can be used to either induce or measure the formation of rather complex supramolecular aggregates. In the field of SAMs, electrochemistry is undoubtedly one of, if not the premier, technique used to characterize the aggregates. Future uses in this field, as well as in supramolecular science, in general are certain to continue to increase in view of the power and simplicity of the techniques involved.

Addendum

Since this article was initially accepted for publication, the application of electrochemical techniques to supramolecular structures has continued apace. Here we highlight but a few of the latest articles in the field. In the area of redox switching the group of Rotello has recently reported a novel, electrochemically controlled three-component molecular switch based on hydrogen bonding.[174] Kaifer, Morán and co-workers have reported the electrochemically switchable formation of inclusion complexes of β-cyclodextrins and multisite guests, dendrimers bearing up to 16 ferrocenyl moieties.[175] Beer and co-workers have continued to make progress in the area of anion binding and have recently reported enhanced selectivity for $H_2PO_4^-$ anions employing a calix[4]arene derivative with a pendant $[Ru^{II}(bpy)_3]^{2-}$ group.[176] With respect to cyclophane chemistry, the work of Becher and co-workers on TTF-based systems has expanded rapidly and includes pseudocatenanes, catenanes, and rotaxanes, among others.[177] In the area of pyridine-based systems, the beautiful and intricate helicates reported within the past year[178] are sure to have attracted much attention among supramolecular electrochemists, though potential solubility problems and limited amounts of material appear to have curbed reports on the electrochemical behavior of these fascinating systems.

In the area of endohedral metallofullerenes, a recent report by Suzuki and co-workers reviews the electrochemistry of $La@C_{82}$, $Ce@C_{82}$, $Gd@C_{82}$, and $Y@C_{82}$.[179] Anderson and co-workers have reported very interesting results on the electrochemistry of the trinuclear endohedral complex, $Sc_3@C_{82}$.[180] These results indicate that the MOs of the trinuclear complex are very similar in energy to those of the mononuclear complexes. However, considering that more electrons are transferred to the cage by the trimetallic system, occupancy of the energy levels is different. Therefore, its second oxidation and first reduction occur at potentials close to where the first oxidation and second reduction occur for mononuclear endohedral complexes. These considerations, along with the fact that the neutral state is EPR silent, have led the authors to suggest that $Sc_3^{4+}@C_{82}^{4-}$ represents the formal charges of the complex. Further progress in the isolation and purification of endohedral complexes has been made by Dunsch and co-workers. They have successfully isolated three stable isomers of $Tm@C_{82}$, and preliminary electrochemical studies for all three isomers have been reported.[181]

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