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Review

Electrochemically controlled supramolecular systems[☆]

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Contents

Abstract

Large and complex molecular structures can be assembled by supramolecular chemistry and self-organization. For practical purposes it is required that the assembly and disassembly of supramolecular complexes and materials can be directed and controlled by external stimuli in order to build, for instance, molecular machines or components for molecular electronics. In this respect, redox-responsive molecules or supramolecular complexes are a logical choice since they are directly compatible with state-of-the-art semiconductor-based microelectronics. Here, redox-switchable supramolecular assemblies, host–guest complexes and materials are reviewed. Ferrocenes, viologens, quinones, tetrathiafulvalenes, and transition metals, e.g. Ni and Cu, have two or three stable redox states and their electrochemical interconversion is completely reversible. Therefore, these redox centers are frequently used as active components in supramolecular assembly. The electrochemical action of the redox-active component can be divided into two main categories: (i) conformational changes within a molecule and/or the motion of one component with respect to another in interlocked molecules, and (ii) the assembly and/or disassembly of supramolecular complexes. The first part of this review deals with the conformational changes within molecules, and with electrochemically induced movement of one component with respect to the other in interlocked molecules. The second part describes the electrochemically controlled formation of supramolecular complexes. A wide range of non-covalent interactions, i.e. hydrophobic interactions, Van der Waals interactions, hydrogen bonds, electrostatic interactions, and π–π stacking can be electrochemically controlled to direct the association or dissociation of supramolecular complexes and materials.

Keywords: Self-assembly; Ferrocene; Redox-active complexes; Supramolecular materials; Electrochemistry

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1. Introduction

The miniaturization of electronic components, such as transistors and diodes, by conventional semiconductor based technology is increasingly difficult below 100 nm [1]. Molecules span the range of 1–10 nm and are promising candidates to be employed as building blocks to construct devices in the sub-100 nm regime. Self-assembly and supramolecular chemistry allow the construction of large scale, complicated molecular structures that can be used in electronic circuitry and sensors. Moreover, molecules consisting of components that can move relative to each other in response to an external stimulus can be used to construct molecular machines or actuators [2,3]. Nature provides sophisticated examples of molecular machines composed of multiple subunits that rotate or move along fibers unidirectionally and with high efficiency [4].

In order to build molecular machinery or devices it is a prerequisite to have precise control over the thermodynamics and kinetics of self-assembly processes and to include components that respond to external stimuli. Molecules or supramolecular complexes that are sensitive to the oxidation state of one or more components are a logical choice to incorporate in electronic circuitry due to the compatibility with silicon-based technology. Here, an overview is given of electrochemically controlled supramolecular systems. Altering the redox state of one the components in an assembly can effect profound structural changes or induce molecular motion. Redox-switchable molecules, along with rotaxanes and catenanes, which have frequently been the subject in studies for these purposes [5,6], are reviewed in Section 2. Switching between "on" and "off" states can also be achieved by controlling non-covalent interactions, which in addition gives control over assembly processes [7–9]. The electrochemical control over different types of interactions, i.e. hydrophobic interactions, Van der Waals interactions, hydrogen bonding, and electrostatic interactions, will be discussed in Section 3. Electrochemical control over these interactions can induce, for instance, the bending of self-assembled monolayers (SAMs), the orientation of liquid crystals, the immobilization of molecules on surfaces, and the formation of vesicles. Cyclodextrin and cucurbituril host molecules are of interest because a variety of small molecules can be accommodated in well-defined host–guest complexes [10–12]. The electrochemically controlled binding of the redox-active guests to these hosts is also briefly reviewed. Redox-responsive receptors are useful in sensing applications and constitute another example of how electro-active components in supramolecular chemistry can be used to induce and control molecular recognition [13].

2. Molecular motion induced by electrochemistry

The ability to trigger and control directional motion in molecular systems by external stimuli is one of the major goals in the field of so-called "molecular machines" [14–16]. Nature uses proteins that can be considered as molecular machines [4], such as F_0F_1ATP synthase, in which a rotary motion of subunits results from proton flow [14]. Other proteins such as myosin and kinesin display linear motion. Motion may proceed via intramolecular conformational change leading to rotation, bending, or flipping of one or more components of a molecule. Artificial molecular machines are still far from perfection but interlocked molecules, i.e. catenanes and rotaxanes, that change shape or conformation in response to, for instance, irradiation, change of pH, or ion exchange, are promising candidates. Here, several types of interlocked molecules (based on transition metals and π–π-stacking or hydrogen bonds) in which movement of one of the interlocked components with respect to the other one can be electrochemically controlled will be briefly reviewed.

2.1. *Conformational change*

Conformational changes within molecules in response to electrochemical conversion of the redox state have been the subject of a number of investigations to achieve mechanical output on the nanometre scale. Different types of motion, i.e. rotation, bending, flipping, or the orientation of liquid crystals, are possible and – ideally – also need to be controlled precisely. In this context, the group of Tatamoto described a macrocycle based on a two paraphenylenediamine rotors (Fig. 1) [17]. Paraphenylenediamine can undergo a highly reversible two electron oxidation resulting in a paraquinonediimine. This is the basis for the switching when the molecules are incorporated into macrocycles. Two different cyclophanes were prepared by reaction of 4,4′-dimethylenedianiline with duroquinone (DM_4) or anthraquinone (AM_4). According to cyclic voltammetry (CV), AM_4 was stable for 100 CV cycles and DM_4 for 10 cycles. In the reductive state, the cyclophanes have a planar conformation with a closed cavity, but oxidation forces the quinones into a face conformation and, thus, induces the opening of the cavity. The "flipping" of the quinones was confirmed in the

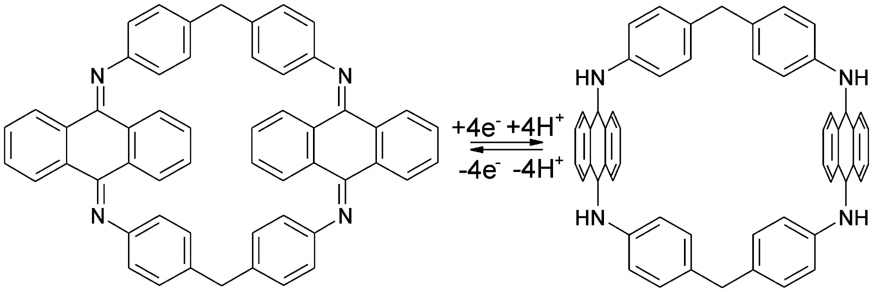

Fig. 1. A redox-active cyclophane switching from face to lateral conformation [17].

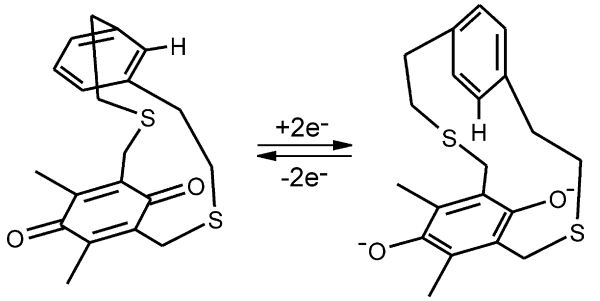

Fig. 2. Electrochemically induced flipping motion of the benzene ring with respect to the quinone moiety in a macrocycle [18].

solid state by X-ray crystallography and in solution by CV and spectroelectrochemistry.

Reduction of a quinone covalently linked to a benzene moiety resulted in a conformational change from face-to-face to face-to-edge within the macrocycle (Fig. 2) [18]. In the neutral form, the molecule adopts a face-to-face orientation that is stabilized by π–π interactions of the quinone and benzene moieties. Reduction of the quinone results in a negatively charged aromatic π-system. The face-to-edge conformer is favored due to electrostatic interactions between the positively charged H-atom of the benzene and the negatively charged quinone and by the π–H interaction between the π electrons of the quinone and the H-atom of the benzene. The face-to-edge conformer could be stabilized by conversion of the corresponding hydroquinone in the presence of H^+. The flipping motion could be followed by ^1H NMR spectroscopy and CV.

Hawthorne et al. reported a *commo*-bis-7,8-dicarbollo metallacarborane based on Ni^{3+} and Ni^{4+} of which the two ligands can rotate with respect to each other (Fig. 3) [19]. Metallocenes also show rotation of the ligands with respect to each other with an energy barrier of ca. 2 kcal/mol, but metallocarboranes have rotation barriers of ca. 6 kcal/mol. The ligand possesses two neighboring carbon atoms which normally gives a *trans* configuration in metallocarborane complexes with Ni^{3+}. On the contrary, Ni^{4+} leads to *cis* complexes, with both carbon vertices on the same side of the molecule. Electrochemical conversion of Ni^{4+} to Ni^{3+} triggers the rotation of the ligand with respect to each other and a change in conformation from *cis* to *trans*. Unidirectional motion could be achieved by introducing a methyl group to both rings in the R^2 and R^4 positions. Clockwise rotation is preferred upon electrochemical oxidation of the methylated complex, since this prevents overlap of the two methyl groups, as would be the case in counterclockwise rotation.

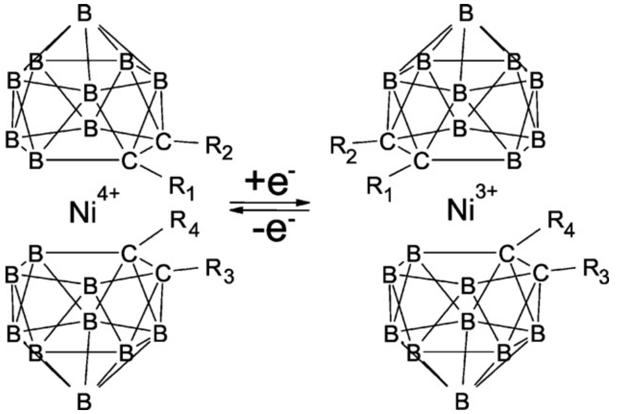

Fig. 3. Electrochemically induced twist of the upper and lower rings of a metallocarborane. R = H or Me [19].

Electrochemistry can also be used to induce collective motion of molecules in materials. For example, liquid crystals on surfaces assume orientations that are sensitive to the surface properties, which can be electrochemically controlled. Abbott et al. reported the formation of thermotropic liquid crystals of 4,4′-pentylcyanobiphenyl (5CB) or *N*-(*p*-methoxybenzylidine)-*p*-butylaniline (MBBA) on SAMs of ferrocene (Fc) terminated alkanethiols on Au [20]. When CV was applied in the case of 5CB, the reversible oxidation of Fc head groups could be measured together with color changes of the liquid crystal. When the potential was held at −0.2 V, the 5CB was green, indicating a planar alignment with no azimuthal preference for either electrode, while at 0.28 V yellow regions were observed indicating a perpendicular alignment at the working electrode. The process was reversible and this behavior could not be observed for the liquid crystal on an alkanethiol reference SAM.

Recently, the group of Willner reported redox controlled bending of bipyridinium (= viologen, V) terminated monolayers on Au surfaces [21]. The monolayers were loosely packed to allow bending of the molecules upon electrochemical conversion of the V head groups. In the V^{2+} form the head groups are electrostatically repelled from the Au electrode and face the exterior of the monolayer at positive bias. At negative bias, the head groups are attracted to the Au surface causing the molecules to bend toward the surface. If the bias was sufficiently lowered the head groups were reduced. The bending of the monolayer could be followed by contact angle measurements and electrochemical methods. A monolayer lacking the V head groups showed no bending behavior and a reference monolayer consisting of a short tether between the thiol functionality and V moiety showed only a moderate change in contact angle upon reduction of the V moiety and no significant changes at potentials that cause bending. Recently, a negatively charged carboxylate-terminated monolayer also has been used to bend a monolayer toward the surface upon changing the electrical potential [22].

2.2. Interlocked molecules based on transition metals

The group of Sauvage et al. reported Cu-based catenanes and rotaxanes that respond to an electrochemical signal causing one of the interlocked molecules to pirouette around the second one [23–26]. The rotaxane consists of an axle that contains a bipyridine (bipy) or phenantroline chelate ligand with two bulky stopper groups and a ring consisting of a bidentate and a tridendate binding site to which Cu ions can bind (Fig. 4, left). Cu^+ forms four-coordinate complexes while Cu^{2+} forms five-coordinate complexes. Electrochemical conversion of Cu^+ to Cu^{2+} results in reorganization from a four-coordinate to a five-coordinate complex which can only proceed by pirouetting the ring. The rate of pirouetting depended on the oxidation

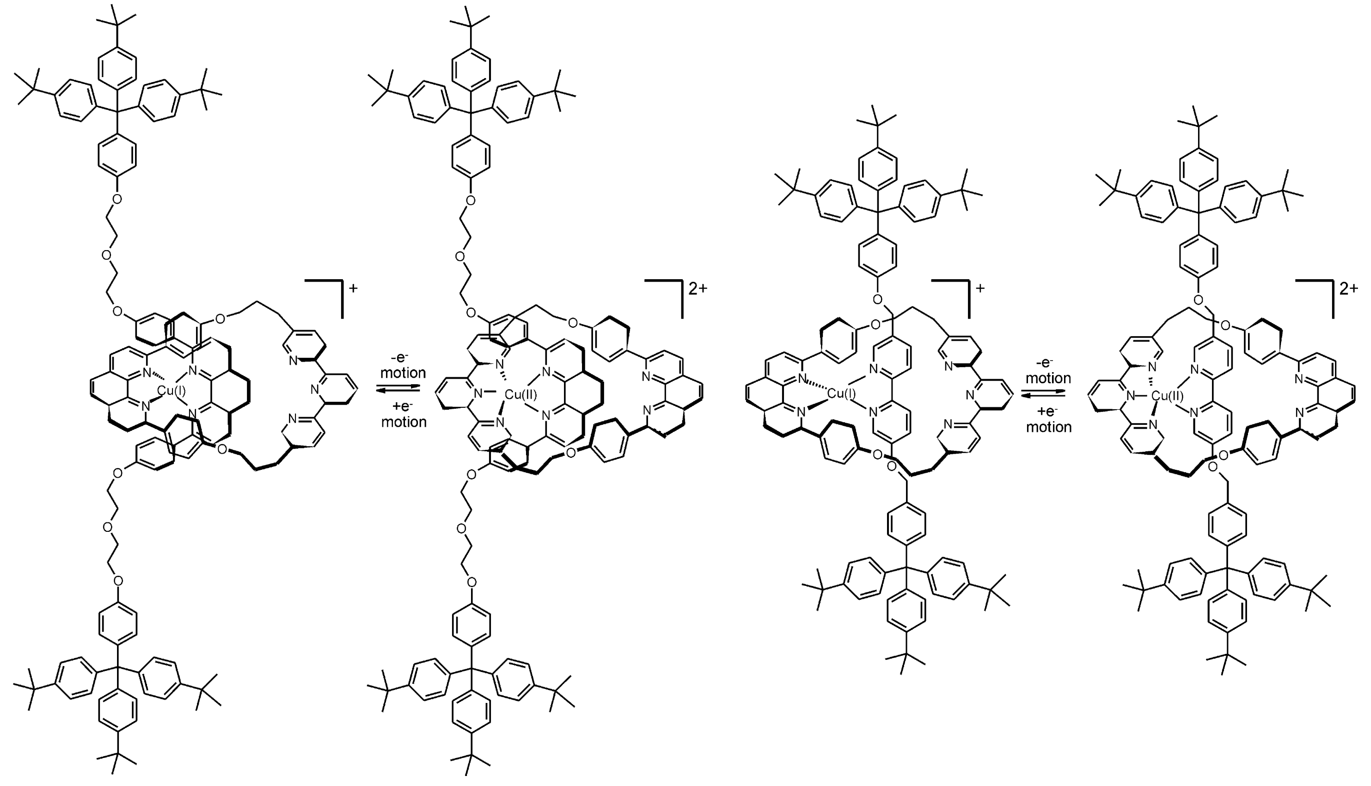

Fig. 4. Pirouetting rotaxanes based on Cu^+ and Cu^{2+}. The pirouetting rate of the rotaxane on the left is lower than that of the rotaxane on the right due to steric hindrance [27].

state of Cu. The five-coordinate Cu changed in about 50 ms, but the four-coordinate Cu changed in the order of minutes. The response time could be reduced by lowering the steric hindrance of the axle around the bipy moiety since the rate limiting step is the ligand exchange reaction of Cu (Fig. 4, right). The lower limit for the rate constant of the rearrangement for the five-coordinate-Cu^+ complex to the four-coordinate-Cu^{2+} was found to be $k > 500\ s^{-1}$, while the backward reaction proceeded much slower ($k = 5\ s^{-1}$) [27].

Woźniak et al. reported electrochemically controlled rotaxanes and catenanes based on transition metal (Ni and Cu) tetraazamacrocyclic complexes and benzo-24-crown-8 as building blocks (Fig. 5) [28–31]. The major difference with Sauvage's system is that the metal centers are used as docking stations for the ring. The macrocycle consisting of two different metal centers adopts a face-to-face geometry. The crown ether aromatic ring interacts with the metal coordinated ring in such a way that a sandwich structure is formed with one of the aromatic rings in between the two metal centers while the second ring coordinates in a parallel fashion outside the ring. The result is a rectangular structure. Electrochemical analysis revealed that the metal centers were not electrochemically communicating unless the linkers are very short [31]. The most striking feature in the electrochemical data was the observation of the splitting of the oxidation wave for the Ni-center at lower temperatures. Initially, the crown ether is located at the Ni-center, but oxidation of the Cu center initiates the translocation of the crown ether from the Ni-center to the more positively charged Cu-center. At lower temperatures or at shorter experimental time scales, the translocation of the ring is slow ($5\ s^{-1}$) and, consequently, a part of the Ni-centers still interact with the crown ether while others are not, resulting in a splitting of the wave [28]. A second oxidation of the Ni-center initiates a second translocation of the crown ether macrocycle back to its original position, i.e. the Ni-center.

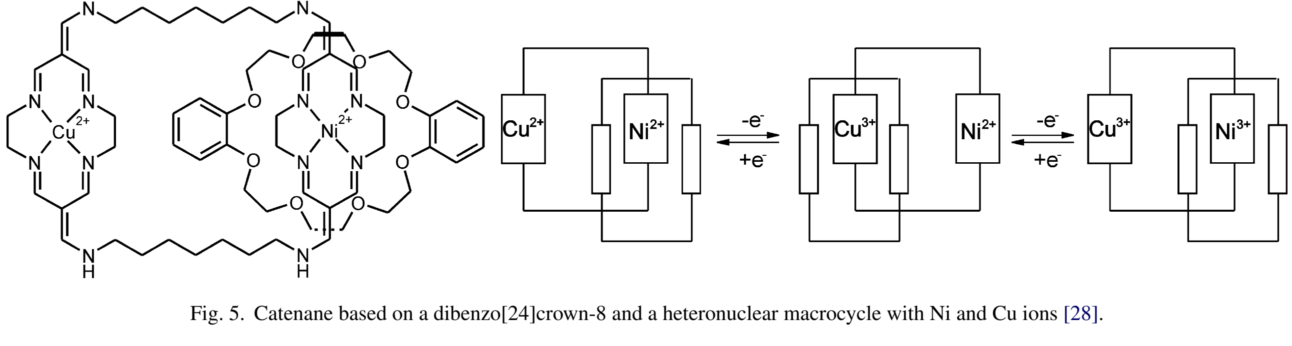

Fig. 5. Catenane based on a dibenzo[24]crown-8 and a heteronuclear macrocycle with Ni and Cu ions [28].

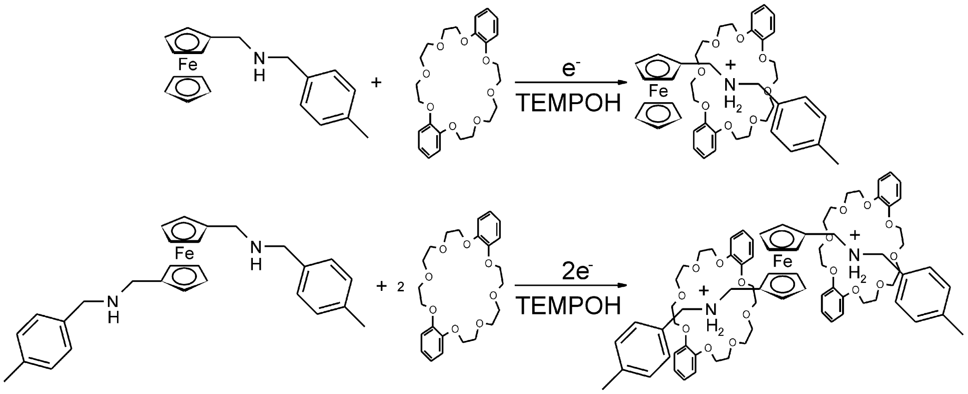

Fig. 6. The formation of ferrocene (Fc) based [2] [34] and [3]pseudorotaxane [33] is induced by electrochemical conversion of the Fc moiety in the presence of 1-hydroxy-2,2,6,6-tetramethylpiperidine (TEMPOH), followed by an electron transfer reaction from the nitrogen to the Fc^+ cation resulting in a cationic radical at the nitrogen (right). Subsequently, transfer of hydrogen from TEMPOH results in a dialkylammonium species followed by rotaxane formation.

The position of interlocked molecules with respect to each other can be electrochemically controlled. Additionally, the formation of different types of rotaxanes can also be electrochemically induced. The switch between the two oxidation states of ferrocene (Fc) has been used to control the formation of [2]rotaxanes,[32] [3]rotaxanes, [33] or pseudo rotaxanes (Fig. 6) [34]. A dibenzo[24]crown-8 ring interacts with an axle with a Fc terminus (which is bulky enough to prevent unthreading) and a *p*-phenylene group (which has CH–π interactions with the ring) [32]. Electrochemical oxidation of the Fc moiety triggers the rotaxane formation (Fig. 6) [35]. The oxidation potential of the Fc moiety is 80 mV lower due to the stabilization of the Fc^+ by the ring compared to the oxidation potential of the axle without the crown ether. The ring is translocated along the axle due to the attractive positive charge between the ring and the Fc^+. The oxidation of the Fc moiety of Fc terminated axle in the presence of dibenzo[24]crown-8 also can trigger the formation of a pseudo rotaxane [34]. Symmetrically, 1,1′-substituted Fc with two *p*-xylylaminomethyl moieties forms both [2] and [3]pseudorotaxanes [33].

2.3. Interlocked molecules based on π–π-stacking or hydrogen bonding

The immobilization of functional molecular architectures at surfaces can be achieved using two strategies: immobilization of the entire supamolecular structure or step-by-step surface-confined synthesis. The group of Willner reported a monolayer on Au of rotaxanes consisting of the cyclophane, cyclobis(paraquat-*p*-phenylene), that includes a σ-donor diiminobenzene unit stoppered by an adamantyl (Ad) unit (Fig. 7) by a step-by-step synthesis [36,37]. The cyclophane is localized on the molecular axle by generating a σ-donor-acceptor complex with the diiminobenzene units of the molecular axle. The cyclophane acts as a molecular shuttle, revealing electrochemically driven mechanical translocations along the molecular axle. The translocation occurs within 70 ms. Reduction of the cyclophane to the respective biradical-dication results in its dissociation from the σ-donor site, and the reduced cyclophane is translocated toward the electrode. Oxidation of the reduced cyclophane reorganizes the σ-donor diiminobenzene sites. The reduced cyclophane moves toward the electrode with a rate constant corresponding to $k_1 = 320\,s^{-1}$, whereas the translocation of the oxidized cyclophane from the electrode to the σ-donor binding site proceeds with a rate constant of $k_2 = 80\,s^{-1}$. *In situ* electrochemical and contact angle measurements reveal that the electrochemically driven translocation of the cyclophane on the molecular axle reversibly controls the wettability of the surface. In the latter system, the translation of the molecular motion into the macroscopic motion of a water droplet was demonstrated. Replacing the Ad stopper by glucose oxidase resulted in a system where the enzyme is “wired” to the Au electrode because the shuttling of the ring assisted in the electron transfer processes [38].

Altieri et al. reported a rotaxane in which the shuttling between two stations only took about 50 μs (Fig. 8) [39]. The rotaxane is composed of succinamide and naphthalimide hydrogen bonding stations separated by seven CH_2 units and a benzylic amide macrocycle. The formation of hydrogen bonds between the naphthalimide and the ring is sensitive to the redox

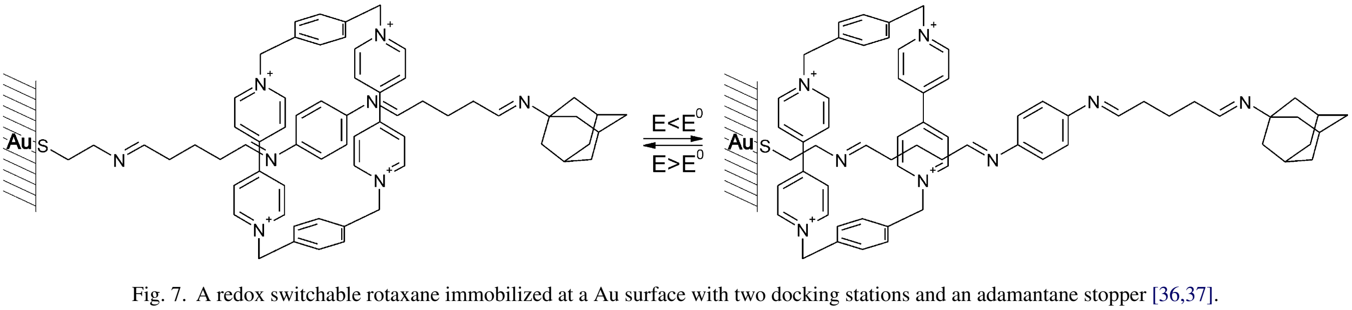

Fig. 7. A redox switchable rotaxane immobilized at a Au surface with two docking stations and an adamantane stopper [36,37].

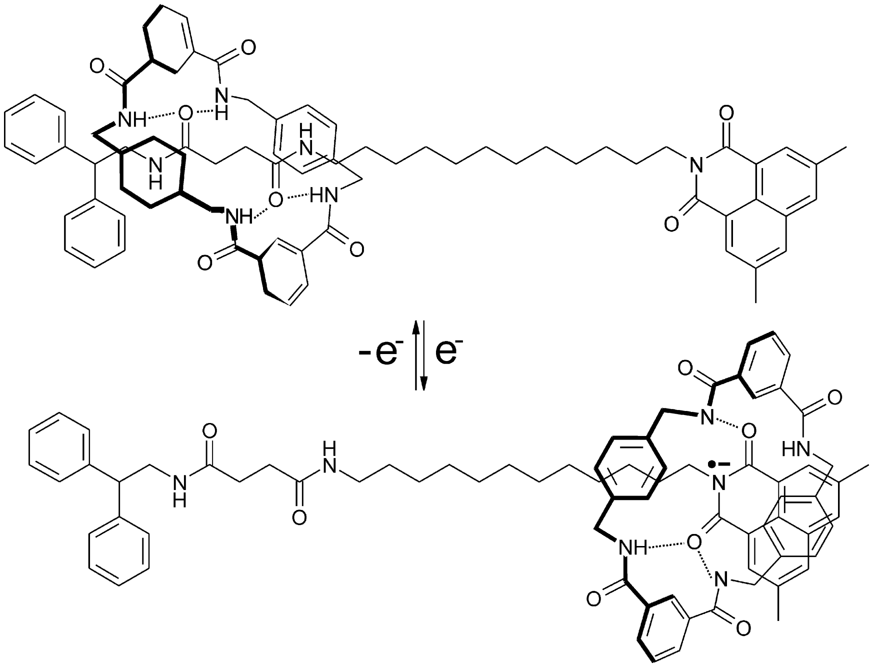

Fig. 8. An electrochemically switchable, hydrogen-bonded rotaxane that has the ring in the neutral state located at the succinamide docking station, while in the reduced form the ring shuttles to the naphthalimide docking station [39].

state of the naphthalimide moiety. The relative binding affinity of the two docking stations is altered by 8 orders of magnitude by reduction of the naphthalimide which triggers the translocation of the ring originally positioned at the succinamide station to the naphthalimide station. CV demonstrated that a new oxidation wave was observed for the rotaxane compared to the axle without the ring and that the shuttling is reversible at room temperature. Lowering the temperature to 213 K revealed the cathodic wave since the ring is now moving slowly on the electrochemical time scale.

Stoddart et al. reported catenanes and rotaxanes that have two docking stations to which an interlocked macrocycle can bind (Fig. 9) [40]. The redox state of one of the docking stations determines to which docking station the macrocycle binds. The catenane contains a macrocycle consisting of a tetrathiafulvalene (TTF) and a diooxynaphthalene (DPN) unit that serve as docking stations linked by ethyleglycol tethers [41]. The second interlocked macrocycle consists of a tetracationic cyclobis(paraquat-*p*-phenylene) ($CBPQT^{4+}$) unit. In the "rest" state, the TTF unit is complexed to the $CBPQT^{4+}$ ring, but electrochemical conversion of the TTF unit to the monocationic TTF^{+} or dicationic TTF^{2+} form leads to electrostatic repulsion between the $CBPQT^{4+}$ unit and the positively charged TTF unit. Therefore, the $CBPQT^{4+}$ moiety translocates along the ring to the neutral DPN moiety. The movement can be reversed by reduction of the TTF docking station.

Using a similar strategy, Stoddart et al. prepared rotaxanes composed of an axle with two bulky stoppers and a TTF and DPN linked by ethylene glycol units with or without an additional rigid terphenylene spacer (Fig. 9A–D). The switching behavior of these molecules was studied in solution in great detail by electrochemistry, ^{1}H NMR spectroscopy, and UV/vis spectroscopy [42].

A disulfide tethered rotaxane (Fig. 9D) was immobilized on Au and the redox-switching behavior was studied by CV at different temperatures [43]. According to CV, the $CBPQT^{4+}$ ring is located at the DNP center instead of the TTF unit in about one out of 10 molecules. A metastable state is observed at high scan rates, in which the ring moved back to a reduced TTF unit too slowly compared to the electrochemical time scale. Therefore, in the first scan the waves corresponding to encapsulated TTF units were observed, while subsequent scans were dominated by the free TTF units. The metastable state has a half life time of 11.7 s at 288 K and of 5 min at 263 K.

Additionally, Langmuir–Blodgett films (LB-films) of amphiphilic catenanes [44] (Fig. 9E) and rotaxanes (Fig. 9B) [45,46] could be prepared. The shuttling behavior of a similar rotaxane was also studied in LB-films since in solution the molecules are randomly distributed, while the movement of the ring becomes unidirectional upon surface-confinement. The TTF end is a hydrophobic stopper while the stopper on the DNP end is hydrophilic, or vise versa. The shuttling of the $CBPQT^{4+}$ after chemical oxidation and reduction could be followed by surface pressure-area isotherm analysis, X-ray reflectometry, and X-ray photoelectron spectroscopy (XPS). Additionally, the shuttling in LB-films at the water–air interface of a different rotaxane lacking the terphenyl moiety could be simulated by molecular dynamics [47].

The translation of molecular scale motion into the movement of macroscale objects is one of the challenges to achieve true molecular machinery or molecular actuators. Stoddart et al. also described a so-called molecular muscle based on a [3] rotaxane comprised of two pairs of complementary TTF and NP recognition sites [48]. Each NP site is enclosed by one $CBPQT^{4+}$ unit and the two complementary parts are linked by a rigid spacer. The distance between the two rings can be varied electrochem-

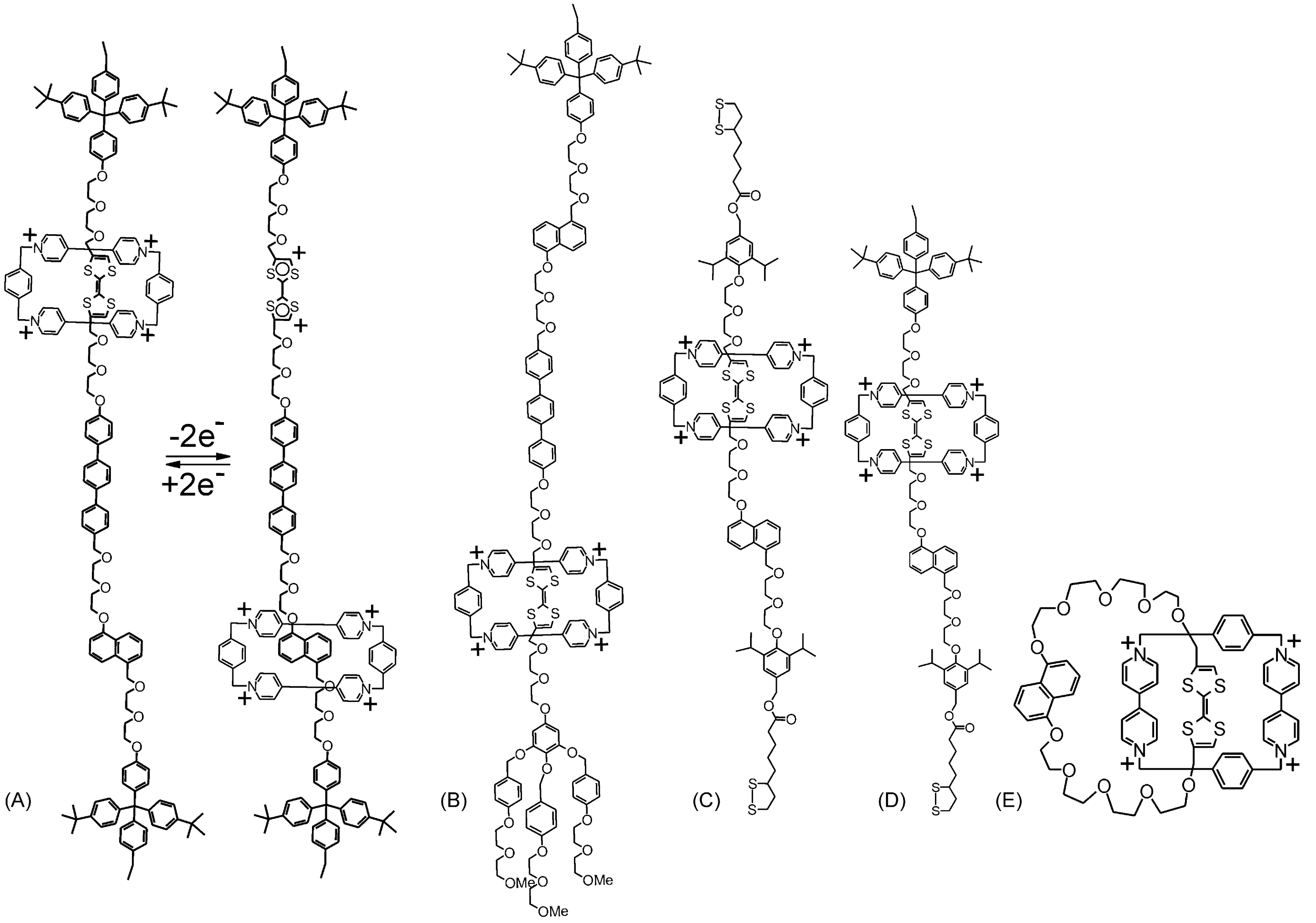

Fig. 9. The redox triggered movement of the CBPQT^{4+} ring is shown for a rotaxane consisting of a rigid terphenyle spacer (A); in the rest state the ring interacts with TTF unit, but electrochemical oxidation of TTF unit forces the ring to move to the DPN docking station due to electrostatic repulsion. The amphiphilic rotaxane used to for the preparation of LB-films (B) and disulfide functionalized rotaxanes at both (C) or one (D) stopper used for immobilize at metal surfaces. A typical catenane consisting of a DPN and a TTF docking stations between which the CBPQT^{4+} ring can shuttle (E) [6].

ically from 4.2 to 1.4 nm, provided that the molecule adopts a fully stretched conformation. Both cyclophane rings were functionalized with a disulfide tether which allowed immobilization of the rotaxane on one side of Au-coated cantilevers. Oxidation and reduction of the artificial muscle resulted in reversible bending of an AFM cantilever.

The electrochemical release of small guest molecules trapped in a maze of channels inside nanoporous silica particles was recently demonstrated [49]. A rotaxane (similar to the one shown in Fig. 9) with a OH-functionality at one of the stoppers was used for immobilization at nanoporous silica particles with highly ordered channels of 1.5–2.0 nm in diameter. The orientation of the rotaxane was such that the TTF unit was located in the upper part of the molecule and the DNP at the lower part of the molecule with respect to the particle. The channels were loaded with Ir(ppy)$_3$ or rhodamine B and the TTF unit was oxidized in order to close the channel by moving the CBPQT^{4+} down to the DNP group. The particles loaded with guest molecules could withstand wash procedures. However, the reduction of the TTF^{2+} unit opened the pores since the ring shuttles back the TTF unit and initiates the release of the guest molecules.

The incorporation of redox-active supramolecular systems in molecular scale junctions is an attractive approach to device miniaturization. Molecular electronic devices were prepared using LB-films of rotaxanes (Fig. 9B) and catenanes (Fig. 9D) and the rotaxanes with the disulfide functionalized stoppers (Fig. 9C) [50]. Devices were prepared by using LB-films of either the rotaxanes or only the dumbbell shaped axles at Pt electrodes, followed by deposition of Ti top electrodes. Both types of devices gave similar (I, V)-characteristics [51]. The switching behavior in these devices was dominated by the properties of the electrode/molecule interface. However, functionalization of both stoppers with disulfides allowed the immobilization of a single molecule between two Pt electrodes [52]. The devices prepared with a silicon bottom electrode and a titanium top electrode clearly showed controlled conductivity due to the shuttling.

3. Self-assembly and disassembly controlled by electrochemistry

Controlling non-covalent interactions in supramolecular chemistry and self-assembly is a powerful approach in bottom-up nanofabrication to construct novel materials for potential applications in, for instance, molecular electronics and sensors. The interactions that are most frequently encountered in supramolecular complexation are hydrophobic interactions, Van der Waals interactions, hydrogen bonds, electrostatic interaction, and π–π stacking. In this section, an overview is given of the electrochemically induced association and dissociation of supramolecular complexes and materials held together by different types of interactions.

3.1. Host–guest complexation

Cyclodextrins (CDs) and cucurbutirils (CBs) are water soluble host molecules which form stable inclusion complexes with a variety of guest molecules including redox-active guests such as Fc, cobaltocene (Cob), and viologen (V). The interplay of the cavity size and the nature of the redox-active guest molecules allows precise control over the host–guest complex formation, stoichiometry, and thermodynamics.

CDs are water soluble naturally occurring host molecules produced by enzymatic conversion of starch. CDs contain a hydrophobic cavity to which small molecules can bind in aqueous media [53]. CDs consist of linked glucose units to yield a chiral macrocycle and the size depends on the number of glucose units. The most common CDs are α-cyclodextrin (αCD), β-cyclodextrin (βCD), and γ-cyclodextrin (γCD), composed of 6, 7, and 8 glucose units, respectively. Synthetic procedures have been developed to chemically modify CDs selectively. For instance, the hydroxyl-groups at the upper and lower rim display different reactivities and also monofunctionalized CDs can be prepared. Fig. 10 shows the three different CD host molecules along with their characteristic dimensions.

Cucurbituriles are a class of host molecules that like CDs are able to form inclusion complexes with small guest molecules in water. The supramolecular chemistry of cucurbiturils has recently been reviewed [54–56]. Cucurbiturils are synthesized by an acid-catalyzed condensation reaction of glycoluril and formaldehyde. Cucurbiturils are abbreviated as CB[*n*] and *n* indicates the number of glycoluril units (Fig. 10). The CB[*n*] family span a wide range of cavity size ranging from CB[6] [57], CB[5], CB[7], and CB[8] [58], and CB[10] [59,60]. Two CBs which contain one inverted glycoluril unit, i.e. *i*CB[6] an *i*CB[7], have been isolated [61]. The family CB[*n*] hosts is similar to CDs in the sense that the cavity sizes of CB[6], CB[7], and CB[8] are similar to αCD, βCD, and γCD (Fig. 10). However, the chemical composition and binding properties are different. CBs are achiral and have an equatorial plane of symmetry which is not present in CDs. Thus, CDs have two cavity openings of different sizes with the smaller opening lined by primary OH-groups and the large opening by twice the number of secondary OH-groups, while CBs have two identical cavity openings lined with carbonyls. In the case of CDs, primarily hydrophobic interactions are responsible for the formation of stable inclusion complexes with a variety of organic and organometallic compounds. The hydroxyl groups located at the upper and lower rim do not play a profound role in the complexation of guests [62]. On the contrary, the interactions of CB with guest molecules rely on two types of interaction: (i) ion–dipole interactions between the positive charges of the guests and the carbonyl groups at the cavity openings, and (ii) hydrophobic interactions. In Fig. 10 the structure of CB[*n*] is shown along with a Table summarizing the dimensions of CB[*n*] with *n* = 5–8.

The oxidation state of the guest can strongly affect the stability of CD and CB[*n*] host–guest complexes. One of the first examples of a redox-controlled host–guest complex is the βCD–Fc inclusion complex [63]. A detailed electrochemical study by Matsue et al. of ferrocene carboxylic acid (FcA^-) in the presence of βCD showed that the peak oxidation potential shifted to higher potentials and the currents decreased upon complexation [64]. These findings were attributed to a CE mechanism, i.e. dissociation of the inclusion complex occurs prior oxidation of FcA^-. Also, the currents for the inclusion complex are lower than for the free Fc species due to a lower diffusion constant of the complex. The oxidation mechanism is outlined

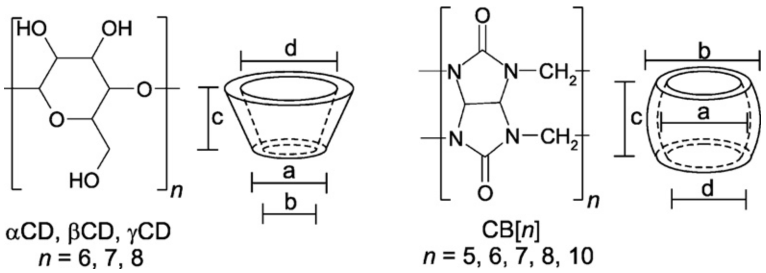

Fig. 10. Chemical structure of cyclodextrins (CDs) and cucurbiturils (CBs) along with the molecular dimensions

	αCD[a]	βCD[a]	γCD[a]	CB[5][b]	CB[6][b]	CB[7][b]	CB[8][b]
Cavity (Å)	5.3	6.5	8.3	4.4	5.8	7.3	8.8
	4.7	5.3	7.5	2.4	3.9	5.4	6.9
Height (Å)	7.9	7.9	7.9	9.1	9.1	9.1	9.1
Outer diameter (Å)	14.6	15.4	17.5	13.1	14.4	16.0	17.5

[a] Values taken from Ref. [62c].

[b] Values taken from Ref. [56].

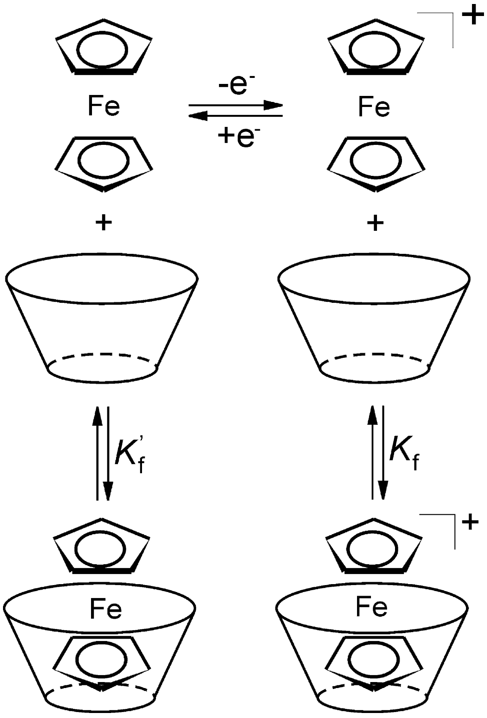

Fig. 11. Electrochemical oxidation of ferrocene and its inclusion complex with β-cyclodextrin [64].

in Fig. 11. Experimental evidence for the direct oxidation of the Fc-βCD complex could not be found, thus $K_f \gg K_f'$ (Fig. 11). The oxidized form of FcA^- does not bind to βCD. This is in sharp contrast to the binding of FcA^- to sulfonatocalix[6]arene which causes a negative shift of the peak oxidation potential and much smaller effect on the peak currents [65]. This indicates that the host interacts more strongly with the oxidized form of FcA^-. This can be explained by the anionic character of both guest and host in the reduced form. Kaifer et al. reported later that Fc-ammonium salts also can bind effectively to βCD [66].

Cobaltocenium (Cob^+) is a highly stable 18-valence electron complex like Fc which can be reduced to the neutral Cob species. Kaifer et al. showed that reduction in the presence of βCD induces the formation of Cob-βCD host–guest complexes and thus Cob^+ is in that sense complementary to Fc [67].

Dendrimers are highly monodisperse polymers bearing multiple functional end groups at the periphery of the molecule [68]. Ideally, dendrimers are defect free, highly branched macromolecules with a well-defined three-dimensional structure. The dendrimers have internal cavities to which guest molecules can bind, but also binding to the periphery of the molecules is possible. Due to these interesting properties, dendrimers have found application in a variety of fields [69]. Dendrimers have been prepared with a variety of end groups of which especially metallo-dendrimers have attracted considerable interest [70,71].

The decoration of dendrimers with redox-active guest functionalities leads to the redox-controlled formation of large supramolecular assemblies. Poly(propylene imine) (PPI) dendrimers bearing Fc guest functionalities have been prepared [72]. A third generation (G3) PPI-$(Fc)_{16}$ is shown in Fig. 12. PPI Dendrimers decorated with Fc units are virtually insoluble in aqueous media, but complexation of the Fc moieties to βCD resulted in large water soluble supramolecular multisite inclusion complexes of well-defined stoichiometries [73]. Addition of stronger competitive guest, i.e. 2-naphthalenesulfonate, resulted in precipitation of the dendrimers indicating that dendrimers do form multisite inclusion complexes with βCDs. Furthermore, CVs showed one reversible oxidation wave indicating that all end groups are electrochemically similar. The βCD-driven solvation of the apolar dendrimers was effective up to generation 3 under neutral conditions. Only in the case of the G3-PPI-$(Fc)_{16}$ two oxidation waves were recorded in CV spectrum. These

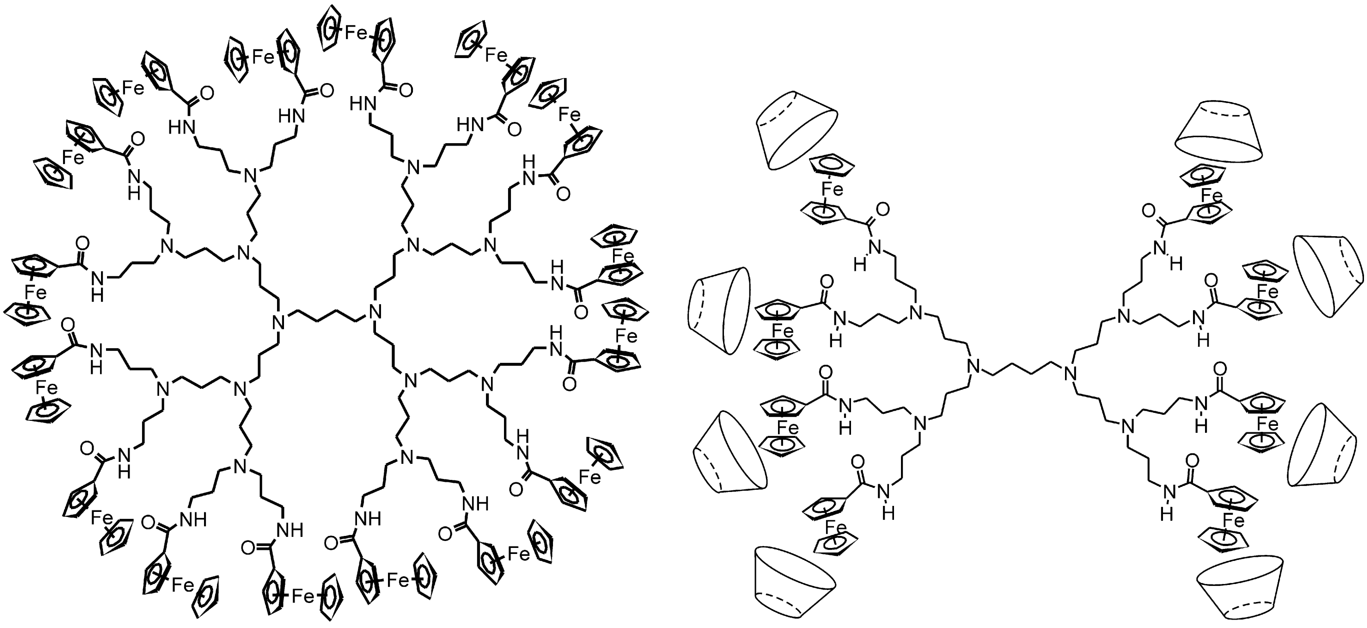

Fig. 12. A third generation poly(propylene imine) (PPI) dendrimer decorated with ferrocene moieties (left) [72]. Second generation PPI dendrimer with the ferrocene end groups complexed to β-cyclodextrin resulting in a water soluble supramolecular assembly (right) [73].

waves were attributed to non-complexed and complexed Fc moieties in neutral aqueous media. The solubility of the dendritic Fc–βCD complexes is significantly higher in acidic solutions [74]. Upon protonation of the core amines of the dendrimers, the dendrimers adopt a fully extended conformation due to electrostatic repulsion, which allowed the solubilization up to G5 of the Fc-decorated dendrimers by complexation of all end groups with βCD, except G5 to which about 40 βCDs could complex [75].

PPI dendrimers of G1 to G4 bearing up to 32 cobaltocenium (Cob^+) end groups have been prepared with all end groups in the cationic form. Electrochemical reduction of Cob^+ to Cob triggers the Cob–βCD complex formation resulting in large, water soluble dendrimer-βCD assemblies [76]. Reduction of the dendrimers in the absence of βCD resulted in the precipitation of the dendrimers.

The preparation PPI dendrimers containing both Cob^+ and Fc moieties are reported using equimolar amounts of each metallocene resulting in statistical mixtures of products [77,78]. A monomeric compound composed of both metallocenes linked by a small positively charged tether resulted in a three-state host–guest system of which the binding to βCD can be electrochemically controlled [79]. The fully oxidized form is not able to bind to βCD, but the fully reduced form binds to two βCDs, and the mixed Fc–Cob^+ binds to one βCD.

For applications in, for instance, molecular electronics and nanofabrication, it is important to control the positioning of molecules at surfaces. Recently, the electrochemically controlled delivery of redox-active Fc dendrimers to a so-called “molecular printboard” (Fig. 13) was reported [75]. The molecular printboard is comprised of heptathioether-functionalized βCD which forms densely packed SAMs on Au [80]. βCD monolayers on SiO_2 were also prepared [81]. The Fc dendrimer-βCD assemblies form stable monolayers at the βCD SAMs due to the formation of multivalent interactions. The stoichiometry of the immobilized dendrimers could be quantified. Electrochemical conversion of the Fc moieties to Fc^+ resulted in an effective desorption of the dendrimers from the molecular printboard, even in the case of the G5 having 7 Fc-βCD interactions with the molecular printboard. The immobilization of Fc-dendrimers at molecular printboards at SiO_2 could also be electrochemically controlled [82]. Biferrocene (BFc) consists of two directly linked Fc moieties which are strongly electrochemically communicating, and has three different oxidations states [83]. BFc also forms strong inclusion complexes with βCD and BFc-decorated PPI dendrimers form, like the Fc dendrimers, water soluble dendrimer-βCD assemblies [84]. The dendrimers could be immobilized at the βCD host surface and oxidation of the BFc moiety to the mixed valence state already caused effective desorption of the dendrimers from the molecular printboard [84].

The steric hindrance of large molecules employed in host–guest chemistry has a profound influence on the binding strength of the host–guest complexes. Newkome-type dendritic

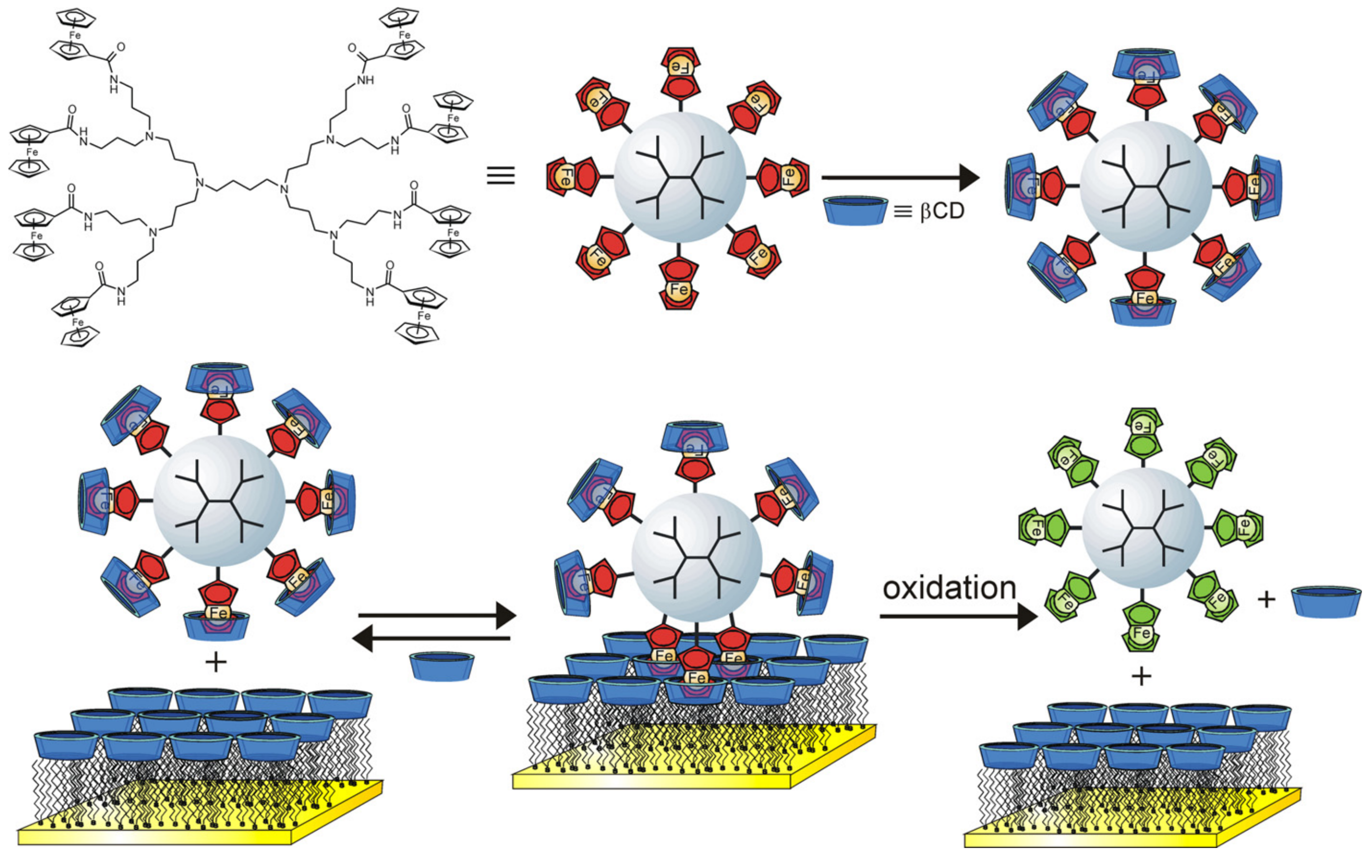

Fig. 13. Formation of a dendrimer-β-cyclodextrin assembly (top) and the electrochemically controlled adsorption at the β-cyclodextrin host surface [75].

wedges containing carboxylic acids at the periphery and a Fc center in the focal point which can bind to βCD. The influence of the increasing steric hindrance by increasing generation on the thermodynamic binding properties was studied [85]. The binding constant of the Fc group with βCD is $950\,M^{-1}$ for G1, but decreases sharply to 250 and $50\,M^{-1}$ for G2 and G3, respectively. These K_{ass} values were obtained by fitting the CV responses and are in accordance with a shift to higher potential in the case of G1. The K_{ass} value for G1 is comparable to other Fc–βCD inclusion complexes, but it is quite low for G2 and G3. This suggests that for G2, and even more for G3, the growing dendron partially surrounds the Fc moiety and interferes in the formation of the Fc–βCD inclusion complexes. An opposite trend was observed in a study using the same dendrimers in their binding to CB[7] [86]. An interaction of CB[7] could not be observed at pH 7 due to the deprotonated form of the carboxylic acid end groups repelling the negatively charged carbonyls at the rim of CB[7] in the case of G1. However, G2 and G3 do bind to CB[7]. Thus, the fact that the number of anodic charges increases by increasing generation, and complex formation is still favorable, indicates that the charges are located sufficiently far away and do not hinder the complexation. Lowering the pH to 2 resulted in the encapsulation of the Fc moiety by CB[7] in de case of G1.

Cationic guests form stable inclusion complexes with CBs. Kaifer et al. reported that Fc^+ and Cob^+ form highly stable 1:1 inclusion complexes with CB[7] with a K_{ass} larger than $10^6\,M^{-1}$ [87]. The electrochemical reduction of Fc^+ or Cob^+ only resulted in a modest loss in binding affinity. The ratio of binding constants for Fc/Fc^+ was only 0.4 as could be elucidated by the modest shift of −22 mV in the half-wave oxidation potential. The authors also claim that the redox mechanism does not proceed via a CE mechanism, as in the case of the Fc–βCD inclusion complex (Fig. 11), but via direct oxidation of the Fc-CB[7] complex. However, the highest scan rate used was only 2 V/s, while in the case of Fc-βCD scan rates up to 50–200 V/s were used [64], or low temperatures, to elucidate the redox mechanism. At high scan rates or low temperatures the rate of the chemical reaction becomes rate limiting and hampers the electrochemical reaction. The large association constants for both reduced guests ($K_{ass} > 4 \times 10^5\,M^{-1}$ and $K_{ass} > 3 \times 10^5\,M^{-1}$ for Fc and Cob respectively) supports the hypothesis that dissociation of the inclusion complex is not necessary. It is known that even strong host–guest complexes (for instance, Ad-βCD with $K_{ass} \approx 10^5\,M^{-1}$) are dynamic and form and dissociate 10^4 times a second [88].

Kim at al. reported a comparative study between the binding behavior CD and CB hosts to simple cationic and anionic Fc derivatives, and Fc methanol to CB[7] [89]. The authors were able to determine the crystal structure of Fc–CB[7]. The binding constant was found to be $3 \times 10^9\,M^{-1}$ for Fc methanol and $2–4 \times 10^{12}\,M^{-1}$ for the cationic Fc derivatives. The negatively charged FcA^- did not show significant binding to CB[7], while the neutral FcAH does. This demonstrates the influence of the presence of the carbonyl oxygens which are partially negatively charged and thus repel the binding of negatively charged guests, but favor the binding of positively charged guests. This is in sharp contrast to βCD since βCD is able to form inclusion complexes with all Fc derivatives with a K_{ass} in the range of $10^3–10^4$.

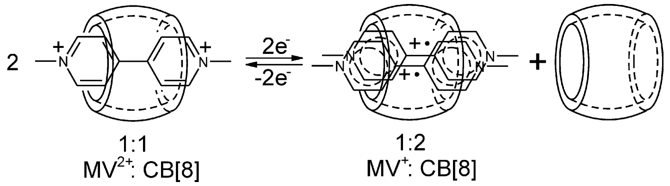

Fig. 14. The electrochemically controlled complexation of methyl viologen dication (MV^{2+}) with curcubituril[8] forming 1:1 complexes while the reduced methyl viologen cation (MV^+) forms 1:2 complexes.

Changing the redox state of the guest not only alters the binding strength of the host–guest inclusion complexes, but also can control the binding stoichiometry. Methyl viologen dication (MV^{2+}) and monocation (MV^+) form stable inclusion complexes with CB[7] and CB[8] with $K \approx 10^5\,M^{-1}$ in aqueous media [90,91]. In contrast, MV^{2+} does not form stable inclusion complexes with βCD, while the monocationic species MV^+ and the neutral form of MV do ($K_{ass} \approx 10^4\,M^{-1}$) [92]. This example illustrates one of the main differences in the binding properties of CDs vs. CBs: CDs form stable inclusion complexes with neutral guests, while CBs form inclusion complexes with cationic guests. CB[7] only forms 1:1 complexes with MV^+, CB[8] can form 1:2 complexes, and MV^{2+} form 1:1 complexes with both hosts. The 1:1 complex of MV^{2+} with CB[8] changes to a 1:2 complex upon reduction of the MV^+ to MV^+ (Fig. 14) [91]. Kaifer et al. showed dimerization of dendritic wedges with MV^{2+} in the focal point upon reduction to MV^+ in the presence of CB[8] [93]. CB[8] can also form 1:1:1 complex with 2,6-dihydroxynaphthalene ($Np(OH)_2$) and MV^{2+} which is stabilized by charge transfer interaction between the electron rich and electron deficient guests inside the hydrophobic cavity [94]. An equimolar mixture of the 1:1:1 complex in the presence of MV^{2+} could be electrochemically reduced resulting in the conversion of all MV^{2+} to MV^+ resulting in the formation of a 1:2 complex of CB[8] with two MV^+ units [95]. In contrast, reduction of the MV^{2+} in the presence of dopamine resulted in a ternary complex of MV^+, dopamine, and CB[8] [96]. A guest containing both a MV^{2+} and a napthalen-2-yloxy unit linked to each other by a small tether formed a 1:1 complex with CB[8] resulting in a locked conformation. Reduction of the complex in the presence of 1 equivalent of MV^{2+}, which was reduced simultaneously, resulted in the formation of a 1:1:1 complex of CB[8] with one MV^+ from solutions and the guest with the napthalen-2-yloxy unit located outside the cavity. Thus, the locked conformation could be electrochemically altered to an unlocked conformation.

A different type of redox host molecules is based on the concept of molecular tweezers which are able to bind to guests that are not available for binding to ring-shaped hosts [97]. Vögtle et al. described aromatic molecular tweezers that can bind dendrimers with a viologen (V) core up to G3 (Fig. 15) [98]. The V moiety was functionalized with one or two Fréchet type dendrons resulting in asymmetric or symmetric dendrimers, respectively. The molecular tweezer is composed of a naphthalene and four benzene units which completely quenched the fluorescence of the dendrimers upon binding. The tweezer binds

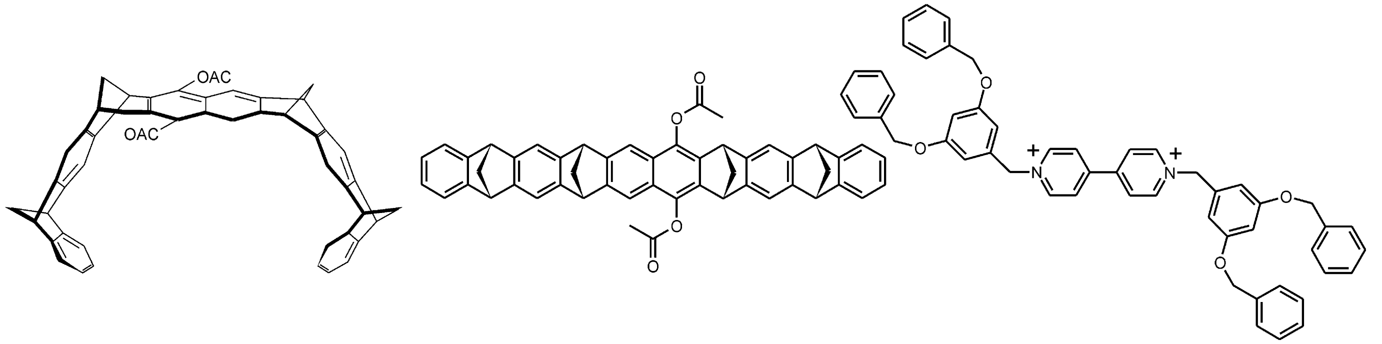

Fig. 15. A side view of the molecular tweezer (left) and the chemical structure (middle) and a first generation Newkome-type dendrimers with a viologen in the focal point [98].

to the dendrimers and dendritic wedges to the V moiety in a 1:1 manner and the K_{ass} was $3.4 \times 10^4\,M^{-1}$ for the G1 wedge and $2.7 \times 10^4\,M^{-1}$ for the G1 dendrimer and decreased with increasing generation to $1.6 \times 10^4\,M^{-1}$ and to $0.9 \times 10^4\,M^{-1}$ for the G2 and G3, respectively. The first reduction wave of V was shifted to more negative potential values while the second wave was unaffected showing that the complexes are stabilized by electron donor-acceptor interactions and dissociate upon reduction.

3.2. Hydrogen bonding

The controlled formation and/or disruption of hydrogen bonds mediated by electrochemisty is another way to control supramolecular assembly. Smith et al. reported redox-dependent formation of a dimmer of diarylurea and nitrobenzene (Fig. 16) [99] or dinitrobenzene [100]. The interaction between the urea and nitrobenzene is negligible in the oxidized state, but reduction leads to the formation of a strong complex ($K_{ass} = 10^5\,M^{-1}$). Arylureas form hydrogen bonds with *o*-quinones but electrochemical reduction of the quinones to their radical anions increased the K_{ass} 2000 fold [101].

Phenyl-urea terminated dendrimers constitute an example of a polyfunctional molecules to which phenanthrenequinone can bind resulting in large hydrogen bonded supramolecular assemblies (Fig. 17) [102]. CV data showed a shift of 90 mV of the oxidation wave upon complexation. This shift indicates a stabilization energy of 8.7 kJ/mol of the radical anionic state of the quinone corresponding to a 30-fold increase of binding affinity. CV data showed irreversible behavior at large scan rates (5 V/s) which became reversible at low scan rates (25 mV/s).

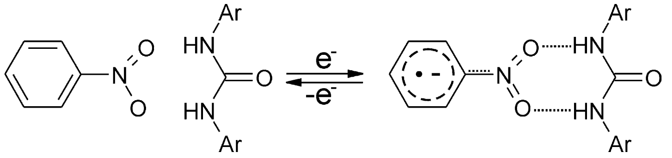

Fig. 16. Electrochemically controlled hydrogen bond formation of nitrobenzene with diarylureas [99].

Fc moieties can also be used to electrochemically induce host–guest complexation and read-out the properties of the host–guest complex. Tucker and co-workers have shown that Fc receptors comprised of two amidopyridyl groups located at the 1,1′- or 1,3-positions can bind urea and barbiturate derivatives via hydrogen bonding in organic solvents (Fig. 18) [103]. The receptors bearing two amidopyridyl groups at the same

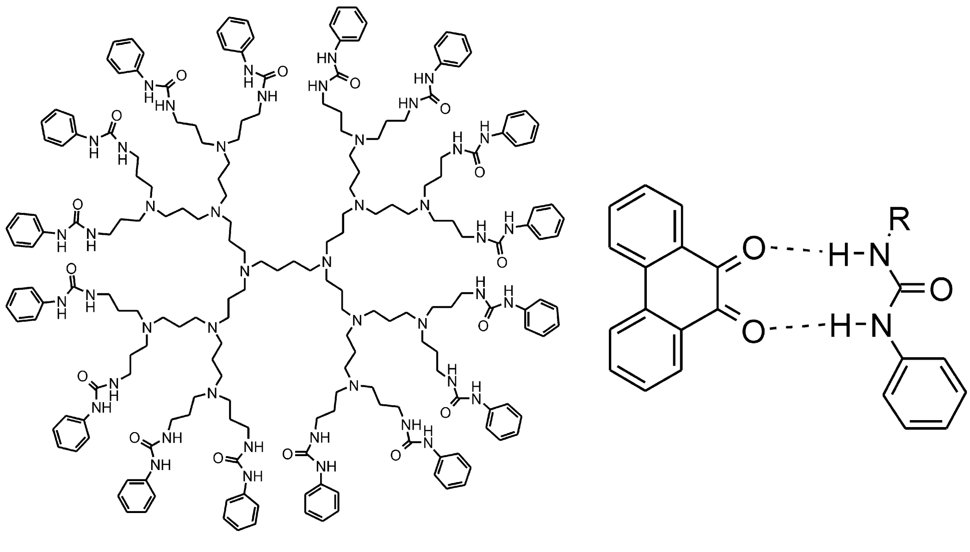

Fig. 17. Phenyl urea terminated PPI dendrimer interacts via hydrogen bonds with phenanthrenequinone. The supramolecular complexation can be electrochemically controlled [102].

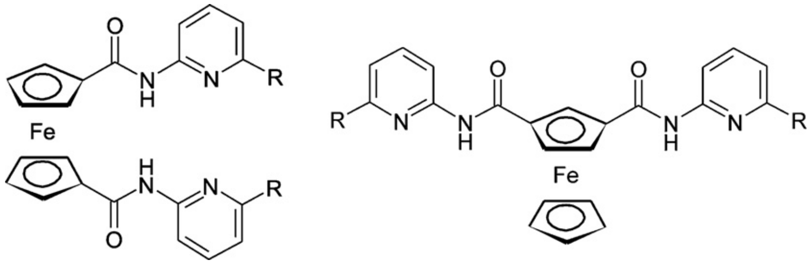

Fig. 18. Ferrocene receptors with two amidopyridyl groups located at the 1,1′-position (left) or 1,3-position (right) [103].

cyclopentadienyl (Cp) ring of the Fc gave larger K_{ass} values since they form a more planar cavity to bind the planar guests. Electrochemical conversion of Fc to Fc^+ decreased the binding strength by a factor 10 owing to the electron withdrawing effect of the Fc^+ moiety making the amide moiety a better hydrogen bond donating group. Similar receptors based on bis-amidopyridine Fc and Cob^+, respectively, were compared to study the influence of the effect of the positive charge controlled by the electrochemical redox state of the metal center and the binding carboxylic acids [104] or aminoacids, [105] all forming 1:1 complexes. Both Cp rings functionalized with an amidopyridine of Cob or Fc centers display a similar electrochemically controlled hydrogen bond formation with guest molecules. The difference in the K_{ass} for the oxidized and reduced form is 20.

Hydrogen bonded systems can also have a profound influence on the mechanism of the redox processes. Rotello and co-workers reported electrochemically controlled hydrogen bonding of isobutylflavin and 2,6-amidopyridines (Fig. 19A). The binding efficiency increased by a factor of 500 upon reduction of the flavin unit. Flavin is a cofactor that is normally non-covalently bound to apoenzymes [106]. Flavin undergoes a one-step reduction process and a two-step reoxidation process. The first process is the reversible formation of the flavin anion radical while the second wave arises in the cyclic voltammogram from an ECE process since the flavin anion can deprotonate flavin in solution resulting in a protonated flavin radical. This species can undergo a second reduction to give a fully reduced flavin anion which is reoxidized at lower potentials than the unprotonated flavin anion. Upon binding to amidopyridine this second oxidation wave is not observed since the complex formation prevents the ECE mechanism to take place. Recently, a Fc derivative that can form quadruple bonded hydrogen bonded 1:1 complex consisting of two identical halves (Fig. 19B) has been reported. The two identical Fc moieties were strongly electrochemically communicating due to the formation of hydrogen bonds [107].

Hydrogen bonds can also be used to control the adsorption of molecules at surfaces. Phenanthrenequinone binds strongly to ureas [108] and thioureas [109] by forming two hydrogen bonds which can be modulated by altering the redox state of the quinone. A self-assembled monolayer (SAM) of a disulfide phenanthrenequinone binds phenyl urea terminated PPI dendrimers by forming multiple interactions. Upon oxidation the dendrimers bind to the surface 2000 stronger ($K_{ass} = 2.4 \times 10^3\ M^{-1}$) while for a monovalent model compound a smaller increase of binding strength was observed. Introducing a Fc moiety at the amidopyridine gave an additional electrochemical control over the binding to phenanthrenequinone and flavin [110]. Not only the reduction of the phenanthrenequinone or flavin moiety increased the complex stability, but also the oxidation of the Fc centers.

The design and self-assembly of molecular capsules received considerable attention [111]. A well-established methodology for capsule formation is the dimerization of two identical calix[4]arenes functionalized with four urea groups on the upper rim [112]. Capsule formation can be electrochemically controlled by introducing Fc groups at the upper rim via a urea linkage [113]. Fc in the neutral form allowed the formation of a dimer in a head-to-head fashion. However, oxidation of the Fc moieties caused dissociation of the dimer (Fig. 20A). Model compounds in which the Fc moieties were replaced by charged amino groups showed no capsule formation. Thus, the disrup-

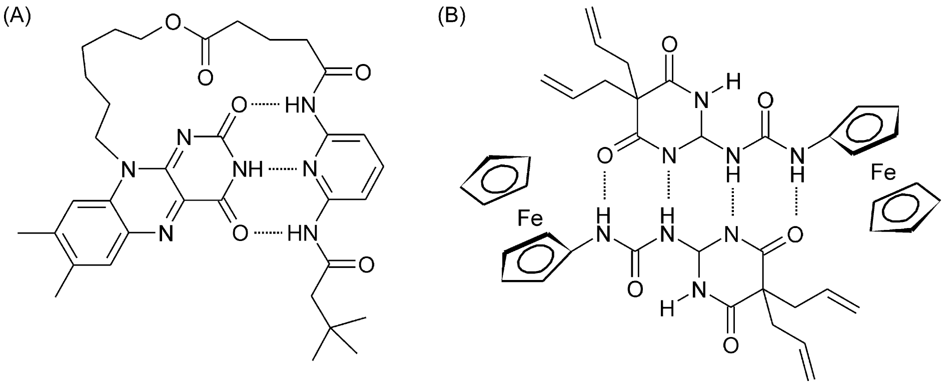

Fig. 19. Flavin covalently linked to a 2,6-amidopyridine moiety forming intramolecular hydrogen bonds (A) [106]. A ferrocene derivative that forms quadruple hydrogen bond motif (B) [106].

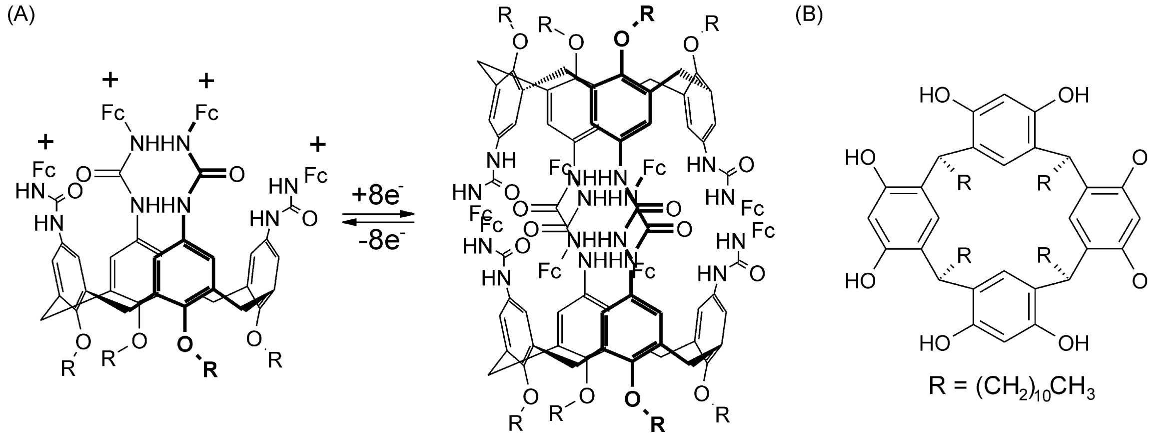

Fig. 20. Calixarene functionalized with ferrocene (Fc): in the reduced form the urea functionalities form hydrogen bonds with a second calixarene, while in the oxidized form the dimer dissociates due to the repelling cationic charges (A) [113]. Resorcinarene that forms a capsule with ferrocenium (Fc^+) (B) [116].

tion of the Fc-capsules is due to the positive charges generated by oxidation of the Fc centers.

The example described above described the dissociation of a capsule upon electrochemical oxidation of Fc. In contrast, oxidation of Fc in the presence of resorcinarene (Fig. 20B) drives capsule formation. Resorcinarene can form capsules consisting of six molecules in an octahedral geometry held together by hydrogen bounds by the OH groups of the upper rim and residual water molecules [114]. The capsule formation is induced by cationic groups [115]. Kaifer et al. showed that electrochemically generated Fc^+ is a suitable guest for the capsule formation [116]. Six host molecules complex to one Fc^+. The formation of the complex has a profound influence on the redox behavior of Fc, since the reduction required an overpotential of more than 500 mV and gave rise to a new anodic wave. Recently, Kaifer reported that stable resorcinarene capsules could be formed in CH_2Cl_2 without the presence of cations which could incorporate Cob^+ [117].

3.3. Metal coordination

Although one would assume that supramolecular assemblies held together by metal coordination are sensitive to the redox state of the metal centre(s), only very few examples of supramolecular assembly under redox-control are available in the literature. The assembly and disassembly of a dicopper helicate complex can be induced by the reversible conversion of Cu^+ to Cu^{2+} (Fig. 21) [118]. In the case of a bis-iminoquinoline quadridentate ligand the Cu^{2+} ions form a 1:1 square planer complex with the ligand while Cu^+ forms a 2:2 tetrahedral complex with two ligands resulting in a double helix. Quaterpyridines also coordinate to Cu^+ and form a double helical structures consisting of two ligands and Cu^+, which disassembled into a monomeric structure upon electrochemical conversion to Cu^{2+} [119]. Even larger helicates could be obtained by using quinque- and sexipyridine ligands [120].

3.4. Electrostatic interactions

Electrostatic interactions are profoundly affected by electrochemical conversion of neutral molecules into ions, and vice versa. Fc-terminated dendrimers (Fig. 12) have been used in molecular recognition of negatively charged ions [121,122]. Fc-decorated dendrimers or dendritic wedges are electrochemical exo-receptors for inorganic anions, oxo-anions and biological molecules [123]. The neutral dendrimers can only form hydrogen bonds with the anionic guests, but the oxidized form of the dendrimers also can have electrostatic interactions to enhance the binding. The presence of the Fc^+ also could polarize the N–H fragment further enhancing its H-bond donating tendencies. Usually, the binding of anions is stronger and the selectivity increases by increasing generation. This is the so-called “dendritic effect” which is caused by surface saturation of the higher generation dendrimers, bringing the Fc termini in close proximity of each other, resulting in smaller surface holes. Astruc et al. reported on Fc dendritic wedges immobilized on Au

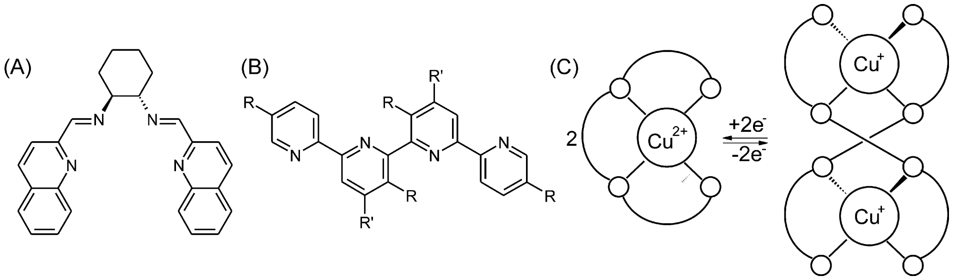

Fig. 21. Bis-iminoquinoline [118] (A) and quaterpyridine (R = H or CH_3, R′ = H or SCH_3) [119,120] (B) ligands for Cu^{2+} that form helicates upon reduction of Cu^{2+} (C).

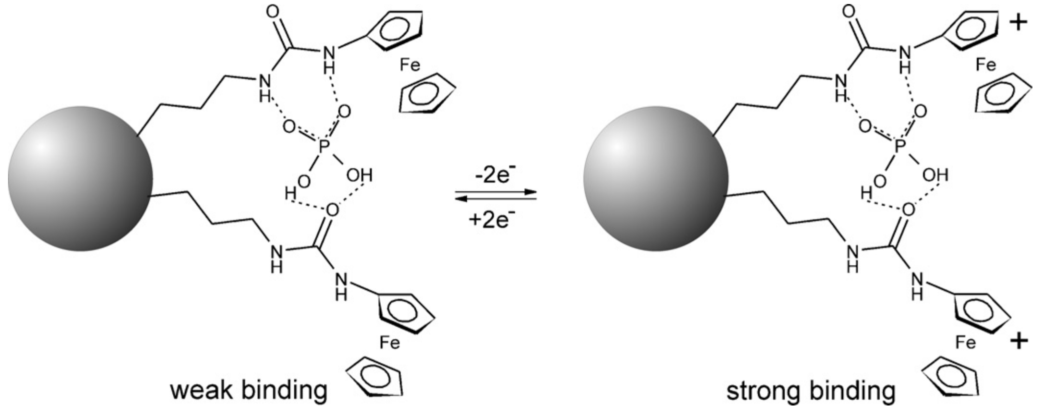

Fig. 22. Proposed binding mode of $H_2PO_4^-$ forming 2:1 complexes with two ferrocenyl ureas of dendrimer or dendritic wedges, or dendritic wedges immobilized at Au nanoparticles [127].

nanoparticles [124–126] and dendrimers [124,125]. The binding of $H_2PO_4^-$, HSO_4^-, Cl^-, Br^- and NO_3^- to Fc terminated dendrimers with 3, 9 and 18 Fc end groups was followed by titrations of the anions to the dendrimers followed by CV [124]. The largest shift in oxidation potential was found for $H_2PO_4^-$. After addition of 1 equivalent the CV remained unchanged indicating 1:1 binding stoichiometry of the $H_2PO_4^-$ to amidoylferrocenyl groups.

Modification of the linkages of the Fc units to the dendritic core has a profound influence on the binding stoichiometry to anions. Fc functionalized PPI dendrimers linked via urea moieties were also used in recognition studies of $H_2PO_4^-$ and compared to HSO_4^- and Cl^- in DSMO as solvent [127]. A large shift in oxidation potential of 112 mV was found for $H_2PO_4^-$, while HSO_4^- and Cl^- gave shifts of 40 and 16 mV, respectively. In competition experiments with $H_2PO_4^-$ in the presence of equimolar amount of HSO_4^- or Cl^- a shift of oxidation potential of 116 mV nicely demonstrated the selectivity for $H_2PO_4^-$. Titration of $H_2PO_4^-$ showed that the potential already shifted to a maximum value at 0.5 equivalents of $H_2PO_4^-$ per Fc moiety indicating that each $H_2PO_4^-$ is bound by two end groups of the dendrimers, involving a double hydrogen bond as depicted in Fig. 22 [128].

Replacing the Cp of the Fc moieties by pentamethylcylcopentadienyl (Cp*) leads to Fc* redox centers with a higher stability and lipophilicity [129]. This prevents precipitation on the electrodes after oxidation in CH_2Cl_2. The scope of anions that can be bound by these dendrimers was limited to phosphates and sulfates, but could be extended to Cl^- and Br^- by introducing $[Fe(\eta^5\text{-}C_5Me_5)(\eta^6\text{-}N\text{-alkylaniline})]^+$ units [130]. The recognition, which depends on the synergy between the $X^-\cdots HN$ hydrogen bond, the electrostatic interactions, and the shape of the peripheral cavities formed by the dendrimer branches and tripods, could be followed by ^1H NMR spectroscopy.

Besides dendrimers, also dendrons containing of Fc moieties attached to Au nanoparticles linked by $Si(Me)_2$ or amides were used in recognition studies of small anions and ATP^{2-}. Dendrons containing of 3 or 9 Fc groups were immobilized onto gold nanoparticles by thiol linkages resulting in particles containing up to about 360 Fc groups (Fig. 23) [126]. The recognition was followed by CV showing a new wave that was attributed to complex formation. HSO_4^- is recognized only by the amido Fc bearing colloids and the interaction is weaker compared to the interaction with $H_2PO_4^-$ ion due to lower negative charge density on the oxygen atoms in HSO_4^- than $H_2PO_4^-$ ion. The dominant interaction is hydrogen bonding between the partially

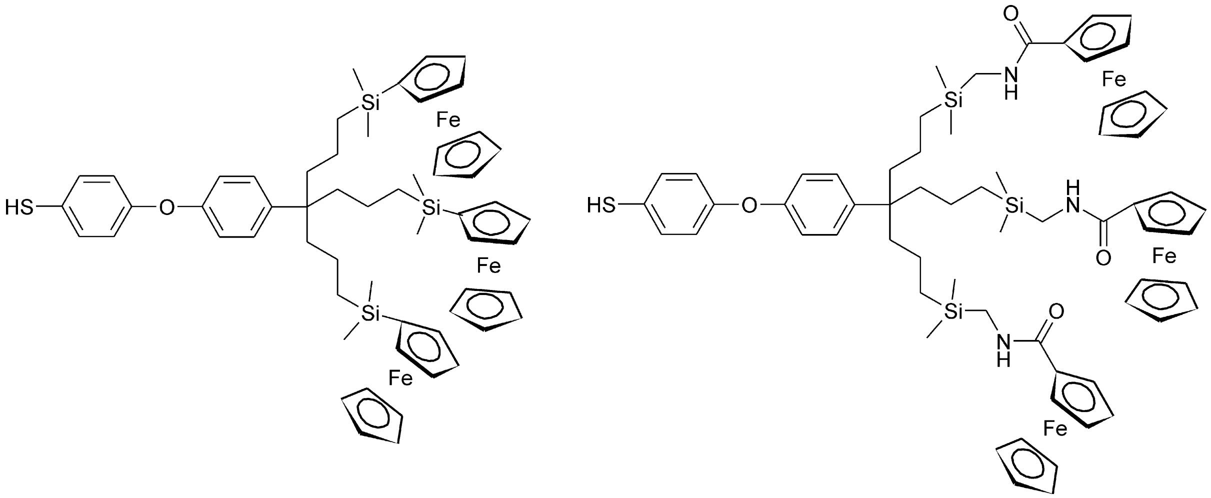

Fig. 23. First generation dendritic wedges with ferrocene linked by $Si(Me)_2$ or amido moieties used to immobilize at Au nanoparticles [126].

positively charged N-atom in the amido group and the O-atoms of the anions. The Si-atom of the silylferrocene colloids is partially positively charged and this could be the explanation for the difference in selectivity of the two colloids.

Recently, Astruc et al described PPI dendrimers decorated with transition metal clusters of $[\{CpFe(\mu_3\text{-}CO)\}_4]$ as exo-receptors for ATP^{2-} and $H_2PO_4^-$ [131]. The dendrimers are stable toward oxidation of the tetra-iron cluster (Fe_4^0 to Fe_4^+ and Fe_4^+ to Fe_4^{2+}) and reduction (Fe_4^0 to Fe_4^-). These dendrimers recognized ATP^{2-} better than $H_2PO_4^-$, while the opposite holds for the metallocene dendrimers described above.

Smith et al. reported a series of dendrimers having the Fc moieties in the focal point which were receptors for Cl^- [132,133]. Fc was decorated with two Newkome type of branches of G0, G1, and G2 and the binding to chloride was studied by CV and ^1H NMR. The binding to chloride decreased with increasing generation and the dendrimers recognized chloride better than bromide indicating a negative dendritic effect.

So far, only examples were given of covalently bound dendrimers as receptors for simple anions and ATP. Hydrogen bonded assemblies were reported of amine terminated PPI dendrimers of generation 1 to 5 and interacting with dendrons. The dendrons consisted of a *p*-phenyl hydroxyl at the focal point and three terminal double bonds or amidoferrocenyl groups resulting in large assemblies consisting of 192 end groups [134]. Primary amines and alcohols formed three complementary O–H–N bonds in a 1:1 stoichiometry, which is the basis of the self-assembly between the dendrimers and dendrons. These supramolecular dendrimers bind ATP^{2-} and $H_2PO_4^-$ strongly according to CV titrations. Binding of the anions results in the appearance of a new wave at less anodic potentials. As the concentration of anion increases, the new wave increases at the cost of the original wave. At 0.5 equivalent of anion per end group, the original Fc wave almost completely disappeared of and the CV was dominated by the new wave indicating that the anions form 2:1 complexes with the dendritic end groups. A positive dendritic effect in the binding of $H_2PO_4^-$ to the dendrimers was observed as the binding constant increased from $3.4 \times 10^3\ M^{-1}$ for the dendron to $67 \times 10^3\ M^{-1}$ for G2 and higher generations. In the case of ATP^{2-} a negative dendritic effect was observed as $K_{ass} = 2.8 \times 10^3\ M^{-1}$ for G2 decreased to $1.3 \times 10^3\ M^{-1}$ for G3 and higher.

Amidoferrocene is one of the most widely used receptors to bind to simple anions and to electrochemically read out the sensing properties both at surfaces and in solution [135–138]. Beer et al. recently showed that monolayers of 1,1′-bisubstituted disulfide Fc at Au recognize anions consistently better compared to having the receptor in solution (Fig. 24) [139]. In solution, a cathodic shift for Cl^-, Br^-, and $H_2PO_4^-$ was 40, 20, and 210 mV, while for the surface confined system shifts of 100, 30, and 300 mV were found, respectively. Thus, the surface confined receptors show a sensing amplification which is associated with surface preorganization of the host pseudo macrocycle.

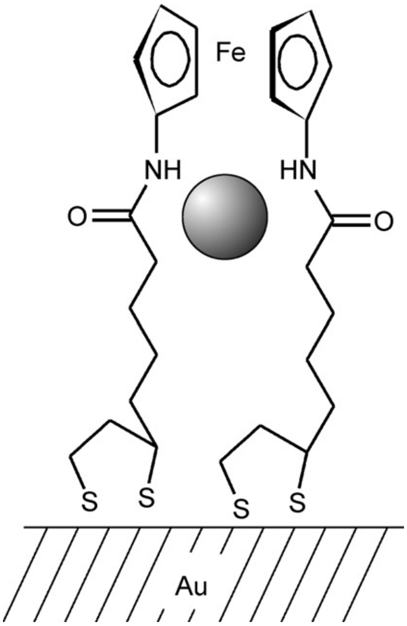

Fig. 24. Surface enhanced anion binding due to surface induced preorganization of the 1,1′-bissubstured ferrocene host [139].

The surface enhanced recognition became even more apparent in the binding of perrhennate anion (ReO_4^-) in aqueous media. A cathodic shift of 15–20 mV was observed, while in solution no electrochemical sensing was observed. In $CH_2CN/CHCl_3$ mixture, phosphate was selectively bound by the receptor in competition experiments with perrhennate, while in water perrhennate was selectively sensed.

Moutet et al. reported receptors based on a single or multiple Fc moieties that electrochemically bind anions including F^-. An increase in the number of amidoyl Fc centers increased the binding strength of the oxidized receptors with the anions F^-, $H_2PO_4^-$, ATP^{2-}, and HSO_4^- and gave better electrochemical responses compared to the monovalent receptors [140]. The same group also reported a Fc based receptor based on a cyclam framework (Fig. 25) [141]. Like the amidoyl Fc receptors, the cyclam-based receptor binds the anions by hydrogen bonds which are reinforced upon electrochemical conversion of Fc to Fc^+. Alkylation of the amines reduced the binding since hydrogen bond formation is not possible with anions. Complexation of Cu^{2+} gave a receptor that recognized F^- selectively from other halogens.

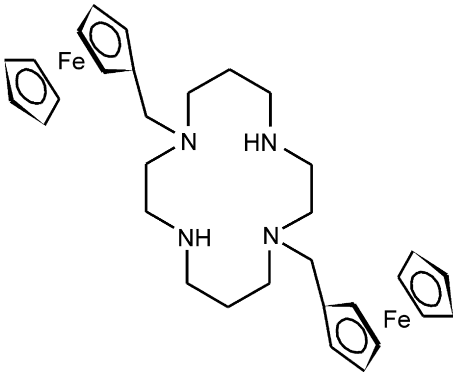

Fig. 25. Anion receptor based on a cyclam framework with ferrocene substituents [141].

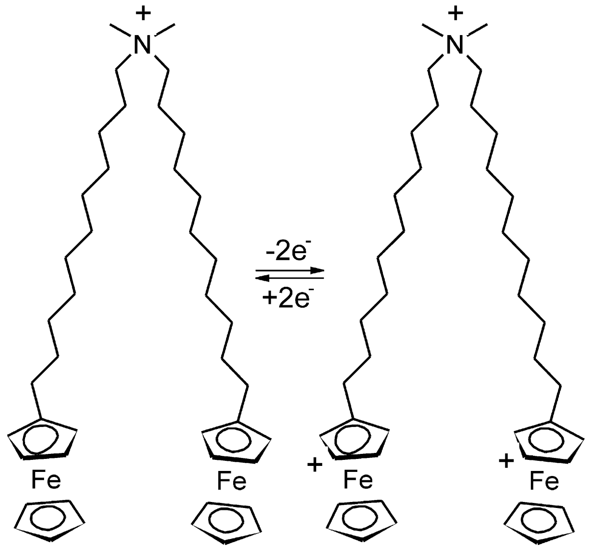

Fig. 26. Ferrocene surfactant BFDMA [142].

Vesicles are potentially useful in drug delivery since water soluble compounds may be entrapped inside the inner aqueous phase, while sparingly water soluble compound can be captured inside the bilayer. For many applications it is desired that vesicle formation can be controlled so that the release of substances trapped by the vesicle can be triggered by an external stimulus. The group of Abe et al. reported ammonium surfactants with Fc head groups, i.e. bis(11-ferrocenyl(undecyl))-dimethylammonium bromide (BFDMA) which form vesicles of 500–2000 nm in diameter (Fig. 26) [142]. Electrochemical oxidation of the Fc head group results in disintegration of the vesicles into smaller aggregates and micelles. The authors were able to release glucose, trapped in the inner aqueous phase, and benzene, trapped in the bilayer of the vesicles, into the bulk. Vancso et al. have recently demonstrated that the permeability of polymer microcapsules with walls containing poly(ferrocenylsilanes) responds to the oxidation state of Fc: oxidation leads to a swelling of the polymer due to electrostatic repulsion and to an increased permeability [143].

The Fc lipid BFDMA has also been used to complex to DNA and facilitates the transport of DNA across cell membranes [144]. It is well known that cationic lipids form lipoplexes with DNA and can mediate transfection. BFDMA is monocationic, but oxidation of both Fc moieties result in an lipid having a charge of 3+. The Fc lipid determines the efficacy of transfection since the cationic 3+ form can mediate DNA transport, while the monocationic form is not. Transfection experiments were conducted using a plasmid encoding enhanced green fluorescent protein (EGFP) and a COS-7 cell line. Lipoplexes were formed with either reduced or oxidized BFDMA and the plasmid followed by incubation with the cells. Cells that were incubated with the lipoplexes formed with the oxidized form of BFDMA showed only expression of the protein comparable to background levels, while lipoplexes formed with the reduced form were transfected and showed significant expression of EGFP.

4. Conclusions

Nature exploits the concepts of self-assembly and supramolecular chemistry at a level of complexity far beyond the chemist's capabilities. For applications in molecular scale fabrication, nanoelectronics, sensing, or molecular machines and actuators, a detailed understanding of molecular recognition and self-assembly, as well as the control of recognition and assembly by external stimuli is essential. At present it is possible to synthesize supramolecular assemblies, even of the size of small proteins, where the assembly and disassembly of components can be exactly controlled by altering the binding affinity of the recognition elements. From a technological point of view, electrochemical control is a logical choice since it is compatible with state-of-the-art silicon-based electronic circuitry. However, the incorporation of relatively complex and fragile supramolecular assemblies in molecular scale electronic devices as well as unambiguous proof that the device output characteristics are controlled by the molecules or change of the molecules upon external stimuli is still a major issue. A deeper understanding of self-assembly and recognition processes will give rise to redox-responsive supramolecular systems that are promising in sensor applications, data storage, molecular machinery, and adaptive materials.

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