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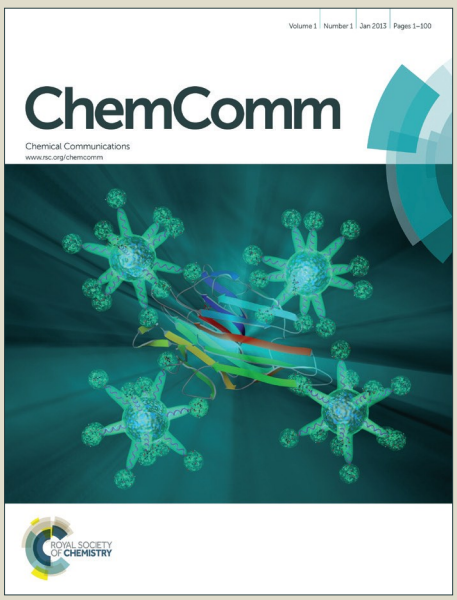

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Ferrocene is the prototypical organometallic sandwich complex and despite over 60 years passing since the discovery and elucidation of ferrocene's structure, research into ferrocene-containing compounds continues to grow as potential new applications in catalysis, biology and the material sciences are found. Ferrocene is chemically robust and readily functionalized which enables its facile incorporation into more complex molecular systems. This coupled with ferrocene's reversible redox properties and ability function as a "molecular ball bearing" has led to the use of ferrocene as a component in wide range of interlocked and non-interlocked synthetic molecular machine systems. This review will focus on the exploitation of ferrocene (and related sandwich complexes) for the development of non-interlocked synthetic molecular machines.

Introduction

Molecular machines are ubiquitous in nature and are responsible for everything from the production of adenosine triphosphate (ATP), the energy currency of life, to the muscular contractions and expansions that generate controlled motion.[1] Chemists have taken inspiration from these biomolecular systems to develop progressively more sophisticated switchable synthetic molecular machines. These machines can be broadly categorised as either mechanically interlocked, wherein two or more covalently discrete moieties are locked together due to a mechanical bond, or non-interlocked.[2]

The majority of synthetic systems developed are based on mechanically interlocked architectures (MIAs)[3] and exploit supramolecular interactions in order to switch between states. There have been some spectacular successes, including synthetic rotary motors,[4] molecular muscles,[5] elevators[6] and sequence-specific peptide synthesis machines.[7] However, for the most part these successes have been obtained using complex and difficult to synthesize MIAs. While the development of template[3] and active-template[8] methods for the synthesis of MIAs has enabled the generation of a vast array of interlocked architectures, the synthesis of molecular machines based MIAs remains challenging and laborious and this has led to increasing efforts to develop potentially synthetically more accessible non-interlocked systems.[2u, 2v, 9] In particular, non-interlocked systems incorporating metal ions[10] are becoming increasingly common due to the favourable kinetic and thermodynamic properties of the coordination bonds.[11]

Ferrocene (**Fc**, Figure 1), an 18 electron organometallic complex comprised of an iron(II) ion sandwiched between two cyclopentadiene (**Cp**) ligands, has been known and studied for over 60 years.[12] Ferrocene compounds have been applied in a range of areas, including biological and medicinal chemistry,[13] catalysis,[14] molecular sensing,[15] and electroactive materials.[16] The ready synthesis, reversible electrochemistry[17] and molecular ball-bearing[18] properties of **Fc** derivatives have made them attractive building blocks for the development of non-interlocked synthetic molecular machines.[19]

The iron(II) ion of **Fc** is sandwiched between the two **Cp** ligands, and acts as an "atomic ball-bearing" enabling the **Cp** rings to freely rotate (the barrier to rotation is 0.9(3) kcal mol^{-1}, with the eclipsed conformation preferred).[20] The short distance between the planes of the **Cp** rings (3.3 Å, Figure 1) means that the substituents of 1,1'-disubstituted **Fc** are in close proximity. Substituents that are able to engage in supramolecular interactions (hydrogen bonding[21] and π-π interactions[22]) often favour the formation of the *syn*-conformation. As such, 1,1'-disubstituted **Fc** can potentially be controllably switched between the *syn* and *anti* conformations (Figure 1).

Additionally, it is well established that **Fc** can undergo reversible oxidation to ferrocenium (**Fc**$^+$). This oxidation only results in a minor structural change of the **Fc** unit, with a slight lengthening of the Fe-C bonds by approximately 0.1 Å,[23] but induces a positive charge. It can be envisioned that this positive charge can lead to electrostatically driven molecular motion in appropriately designed systems.

These properties coupled to the extensive and robust synthetic chemistry of **Fc** have led to a surge in interest in the exploitation of this organometallic unit as a component of molecular machines. Ferrocene has been incorporated into both MIA and non-interlocked machine-like systems. For example, MIA systems where the **Fc** is used as a redox active stopper unit or binding station on a rotaxane thread,[24] or as part of a

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macrocycle,[25] have been reported. However, this review focuses on non-interlocked molecular machines that contain **Fc** (and related sandwich complexes).

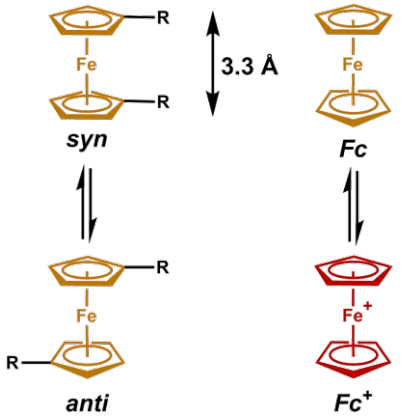

Figure 1 The conformational conversion of 1,1'-disubstituted **Fc** a di-substituted **Fc** between the *syn* and *anti* forms, and the reversible oxidation of **Fc** to **Fc**$^+$.

Exploiting ferrocene's reversible redox chemistry to induce molecular motion

Molecular Rotors

As mentioned above, **Fc** can undergo reversible oxidation to **Fc**$^+$ and Kume and co-workers have exploited this property to develop an electrostatically driven ferrocene-containing rotor (Figure 2).[26] The system is made up of two components: a stator consisting of a di-anthracenyl phenanthroline ligand and a ferrocenyl rotor comprised of a pyridyl-pyrimidine ligand with bulky anthracene and ferrocenyl substituents attached (Figure 2a). The stator and rotor ligands are coordinated to a copper(I) centre and in the reduced state the pyrimidine is coordinated to the copper(I) such that the sterically cumbersome anthracene attached to the pyrimidine unit is directed away from the anthracenyl units of the phenanthroline ligand, causing the **Fc** to be close proximity to the copper(I) centre (Figure 2b). Oxidation of the **Fc** to **Fc**$^+$ causes an electrostatic repulsion between the positively charged copper and the similarly positive **Fc**$^+$, resulting in a rotation of the pyridinium such that the nitrogen adjacent to the anthracenyl group binds to the copper(I) instead (Figure 2a). On reduction of the **Fc**$^+$ back to **Fc**, the pyrimidine rotates back to the initial conformation to relieve the steric clash between the three anthracenyl groups.

Schmittel and co-workers[27] have developed a similar electrostatically driven ferrocene-containing rotor. The rotor consists of a stator containing a zinc porphyrin unit and a dimesityl substituted phenanthroline, and a rotor arm containing a pyridinyl pyrimidine (Figure 3). The redox-active switching stimulus is a separate **Fc** appended phenanthroline. The stator is complexed to a copper(I) centre within the dimesityl phenanthroline unit, and in the oxidised **Fc**$^+$ state, the rotor arm is also complexed to the same copper(I) centre.

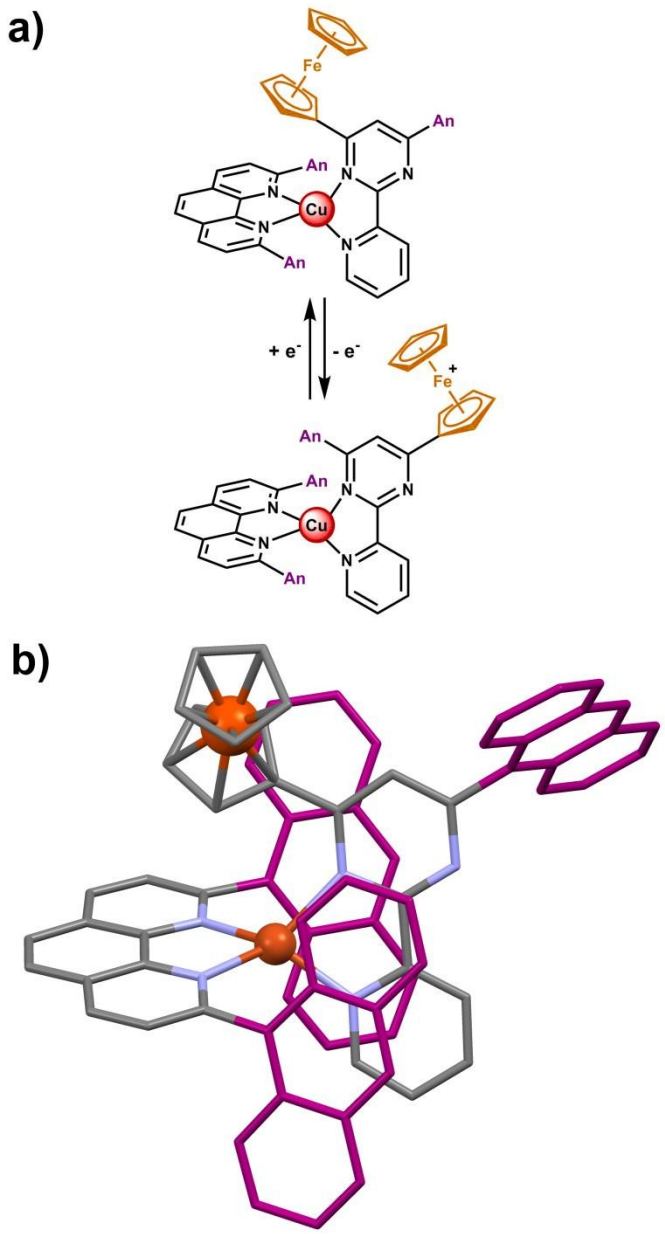

Figure 2 a) The redox-driven rotation of the pyrimidine rotor relative to the stator, and b) the crystal structure of the reduced species depicting the **Fc** in close proximity to the copper(I) centre. The carbon atoms of the di-anthracenyl phenanthroline are shown in yellow to aid clarity.

On reduction of the **Fc**$^+$ to **Fc**, the electrostatic repulsion between the copper(I) and the **Fc** is nullified, and the ferrocene-appended phenanthroline displaces the rotor arm and complexes to the copper(I) dimesityl pocket, causing the pyridinyl pyrimidine arm to rotate away and form a complex with the zinc porphyrin unit. Oxidation of the **Fc** regenerates electrostatic repulsion and causes the decomplexation of the ferrocene-appended phenanthroline ligand, resulting in reformation of the initial rotor complex conformation.

A more complex switching cascade between three separate switches has also been developed that relies on this same **Fc**

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based switching process, combined with the oxidation and reduction of the copper(I) centre.[28]

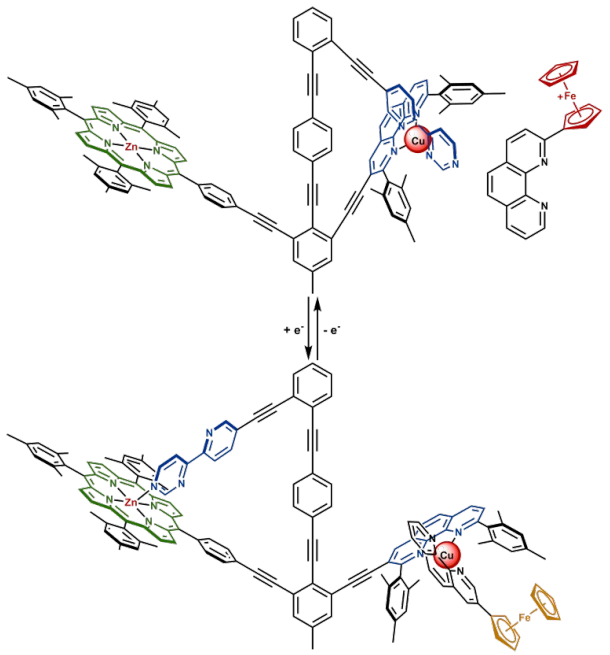

Figure 3 The redox-triggered switching of the porphyrin containing molecular rotor.

Rapenne and co-workers have published a series of papers concerning efforts to develop a surface bound ferrocene-based rotor. The proposed system involved a pentameric rotor unit coordinated through a ruthenium(II) centre to a surface-bound tripodal stator.[17a-c, 17e, 29] This rotary machine was initially designed to contain five **Fc** units appended at the periphery of the rotor (Figure 4a). Placement of the proposed rotor between an anode (electron source) and cathode (electron sink) would allow the oxidation of the **Fc** adjacent to the cathode. The resulting electrostatic repulsion between the cathode and the positively charged $\mathbf{Fc}^+$ would then cause the rotor to rotate such that the $\mathbf{Fc}^+$ could be reduced at the anode, while simultaneously causing a second **Fc** to be oxidised at the now-adjacent cathode (Figure 4b). Each of these successive oxidations and reductions would result in a unidirectional 72° rotation, allowing the eventual complete rotation of the rotor.

Recently, Rapenne and co-workers have successfully bound a pentameric rotor onto a gold surface through thiol pendant arms attached to the stator.[17a] In this design iteration of the rotor, one of the **Fc** arms has been truncated to a simple methyl group, as the high degree of symmetry in the previously proposed structure would not allow for imaging of the rotation (Figure 4c). In this less symmetric analogue, the unidirectional clockwise and anticlockwise rotation of the rotor was followed through scanning tunneling microscopy (STM) imaging. Unlike the initially proposed machine, the rotation was induced by electronic excitation rather than electrostatic repulsion, as excitation of the electrons resulted in a ratchet-like potential energy surface, where if the ferrocenyl arm was excited an anticlockwise rotation was favoured, while excitation of the truncated arm resulted in clockwise rotation.

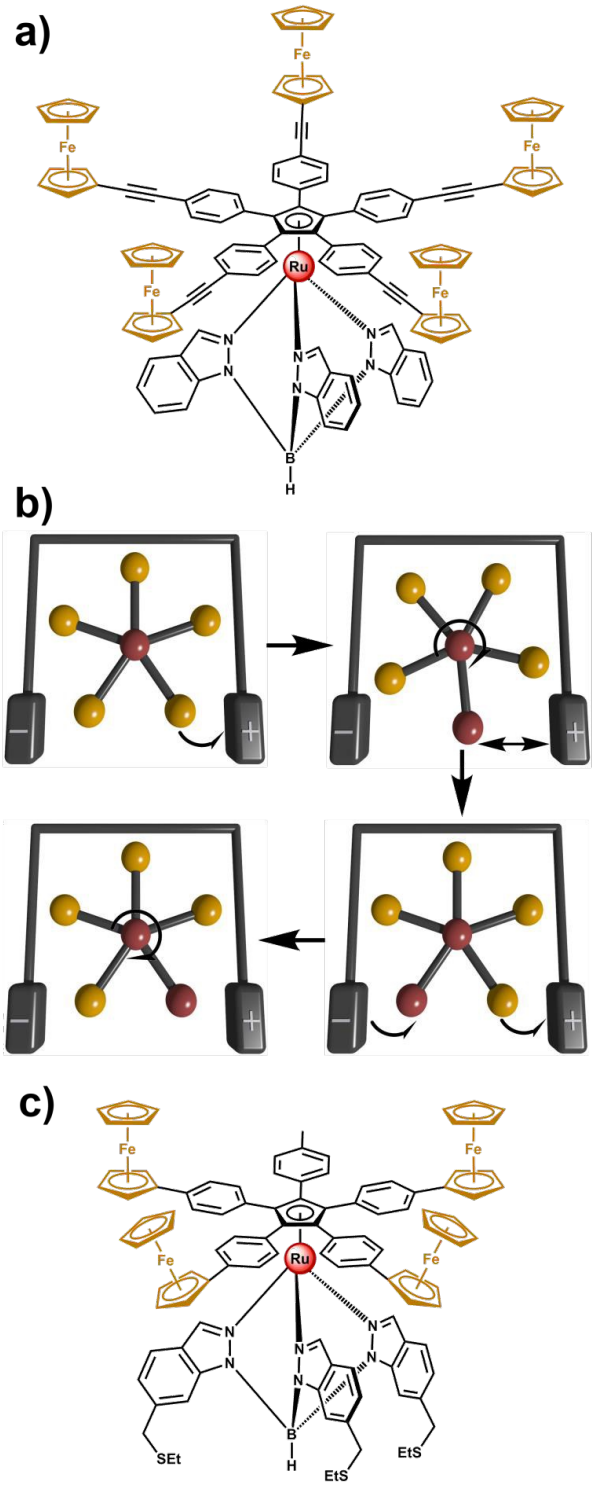

Figure 4 a) Rapenne's proposed ferrocene-containing rotor, b) a single 72° turn of the electrostatically-driven unidirectional rotational cycle, and c) the structure of the eventually realised surface-bound rotor.

Electrostatically driven supramolecular self-assembly

Biological molecular machines, such as the highly complex bacterial flagella, are known to self-assemble,[30] and self-

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assembly is widely viewed as a highly effective way of synthesising large supramolecular architectures such as molecular cages,[31] metal-organic frameworks,[32] and molecular machines.[33] A range of ferrocene-containing materials have been shown to display redox driven self-assembly/disassembly.

Kaifer and Moon have generated a self-assembled cage that can be reversibly assembled and dissembled upon **Fc** oxidation.[34] The cage is made up of two tetraurea-substituted calix[4]arenes, previously shown to self-assemble due to hydrogen bonding by both Rebek and Bohmer,[35] with four **Fc** units appended to the upper rim of each subunit (Figure 5a). Oxidation of the eight **Fc** units was shown to lead to dissociation of the dimeric cage due to the electrostatic repulsion between the $\mathbf{Fc}^+$ groups (Figure 5b). Reduction of the $\mathbf{Fc}^+$ led to the re-formation of the cage, thus it was proposed that such a stimuli-responsive molecular cage could potentially be exploited as a redox active drug delivery agent. The same concept could also be applied for the generation of other molecular machine structures requiring controllable assembly-disassembly.

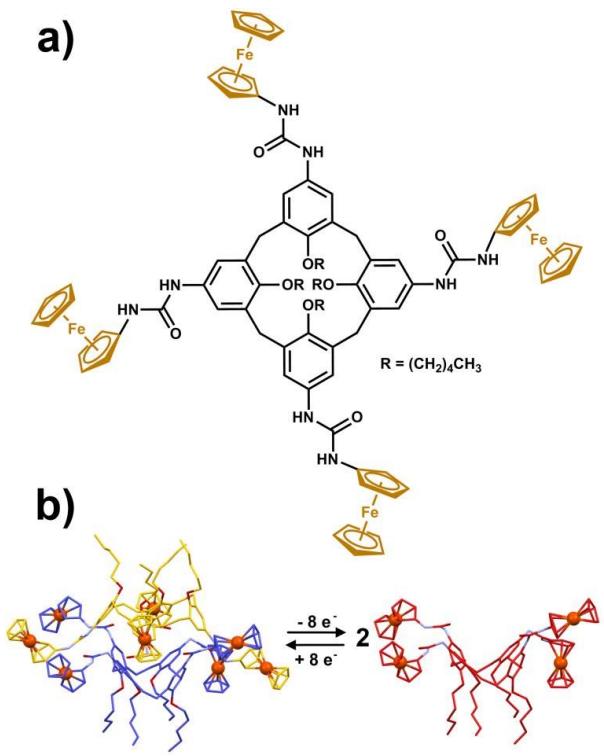

Figure 5 a) The monomer of the redox responsive molecular cage, and b) the energy minimised molecular models of the cage dimer and the tetraferrocenium monomer, with each monomer coloured separately and hydrogens omitted for clarity.

The redox activity of **Fc** has also been shown to impact the structural morphology of a fluorene-ferrocene copolymer in a 1:1 mixture of methanol and hexane.[36] In the fully reduced state, the copolymer self-assembles into twisted ribbons, while oxidation of the **Fc** units causes the large-scale rearrangement of the polymer such that it forms discrete micelles. This is proposed to be due to the aversion of the charged $\mathbf{Fc}^+$ units to the non-polar solvent, thus causing the polymer to collapse in on itself to form a micelle structure with the hydrophobic alkyl groups attached to the fluorene units extending out into solution.

Heinze *et al.* have created a redox-switchable ferrocene-containing foldamer, where the fully reduced oligomeric **Fc** amide strands exist in a folded conformation due to complementary hydrogen bonds between the amide groups.[37] Oxidation of the **Fc** to $\mathbf{Fc}^+$ results in electrostatic repulsion between the charged groups, uncoupling the hydrogen bonding and resulting in a fully extended conformation, according to modelling studies.

A redox-active metallogelator has recently been developed by Afrasiabi and Kraatz.[38] The gelator consists of a ferrocene-peptide conjugate, and undergoes a sol-gel transition in response to sonication-induced self-assembly. The reverse gel-sol transition can be triggered via a variety of stimuli, including ultrasound, light, heat, and oxidation of the **Fc** unit. The ability of the gelator to undergo the gel-sol transition under so many different input stimuli allows the application of these compounds in basic logic gate operations.

Using the molecular "ball-bearing" properties of ferrocene to generate controlled rotary motion.

The ability of **Fc** to act a molecular "ball-bearing" has been harnessed by a number of groups to develop synthetic rotors and switches.

Molecular Rotors

The rotary behaviour of a diferrocenyl species on a gold(111) surface has been investigated by Erker *et al.*.[39] The high temperature (350-400 K) deposition and annealment of the diferrocenyl compound onto the gold resulted in one of the **Fc** units losing a **Cp** ligand and becoming immobilised on the surface (Figure 6). STM imaging of the surface revealed wheel-like structures, where the partially degraded **Fc** unit acted as a surface-bound stator, and the attached oligoethylene chain and pendant **Fc** rotated rapidly around it. The rotation was found to be thermally activated, and could be halted by cooling the rotor to 20 K. The rotors were only observed when prepared at high temperatures, suggesting that the partial thermal decomposition of one of the **Fc** units is necessary in order to generate the surface bound stator.

Two-State Switches

One of the simplest ferrocene-based switches was developed by Wang *et al.*, using the common ferrocenyl building block 1,1'-ferrocene dicarboxylate.[40] In the fully deprotonated form, the two negatively charged carboxylates electrostatically repel one another, causing the attached **Cp** rings to rotate and give an *anti*-conformer of the **Fc** (Figure 7). Protonation of one carboxylate group causes the **Cp** rings to rotate such that the added proton can hydrogen-bond between the two carboxylate groups, giving a *syn*-like conformer where the angle between the two substituents was calculated to be 68°. Deprotonation

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causes the system to switch back to its initial *anti* state. Similar protonation-driven ferrocene-based switches have been developed by Higuchi *et al.*[22d] and Milyukov *et al.*,[41] using amines and phosphinic acids as the protonatable groups, respectively.

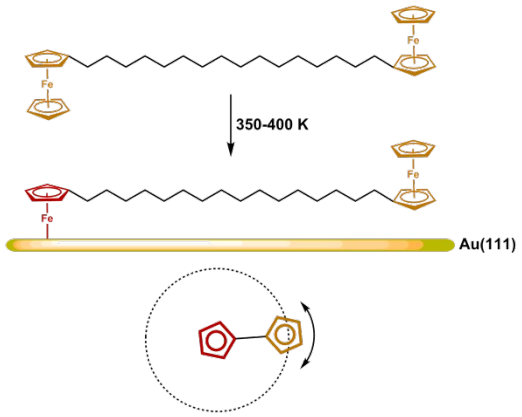

Figure 6 The annealing of the ferrocene-based rotor onto a gold surface.

A related system was generated by Heinze and co-workers, where a **Fc** substituted with two amide groups initially adopts an eclipsed *syn*-conformation due to complementary hydrogen-bonding between the two substituents (Figure 8).[42] The addition of chloride causes the **Fc** to rotate by 95° (according to DFT calculations) in order to accommodate the anion binding between the two N-H groups of the amides. The chloride ions could be removed through addition of an excess of thallium cations, causing the switch to rotate to its initial conformer.

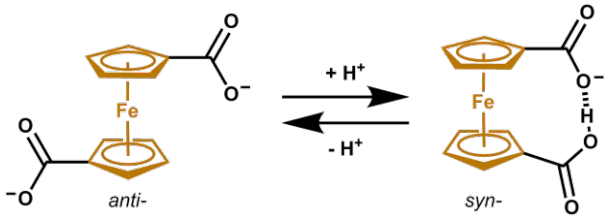

Figure 7 Protonation/deprotonation-driven switching of Wang's two-state switch.

Bosnich and co-workers have harnessed the propensity for 1,1'-diaryl substituted **Fc**s to adopt a *syn* conformation through π-π interactions in order to create rotary two-state switches.[43] It has been well established in the literature that 1,1'-diaryl substituted **Fc** compounds preferentially adopt a π-stacked conformation in both solution and solid state due to favourable electrostatic interactions between the π-clouds of the two aromatic substituents.[44] Bosnich postulated that this could potentially be exploited generate controlled rotational motion through charge-induced repulsion between the two aryl substituents resulting in the formation of a two-state switch.

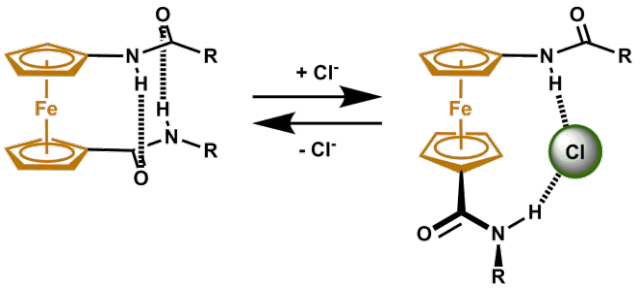

Figure 8 Anion-driven switching of Heinze's two-state switch.

The first generation system consisted of a 1,1'-dipyridylferrocene, where the two pyridine substituents were found to π-stack in the same manner as previous literature examples (Figure 9a). It was then rationalised that protonation of the two pyridines would cause them to electrostatically repel one another and rotate away from each other. Initially, triflic acid was used to proton the pyridines and generate positive charge on the substituents. However, the triflate counterion it was found to form a strong hydrogen bond to the pyridine N-H, thus quenching the charges and resulting in no electrostatic repulsion and negligible rotation (1.94°) (Figure 9b).

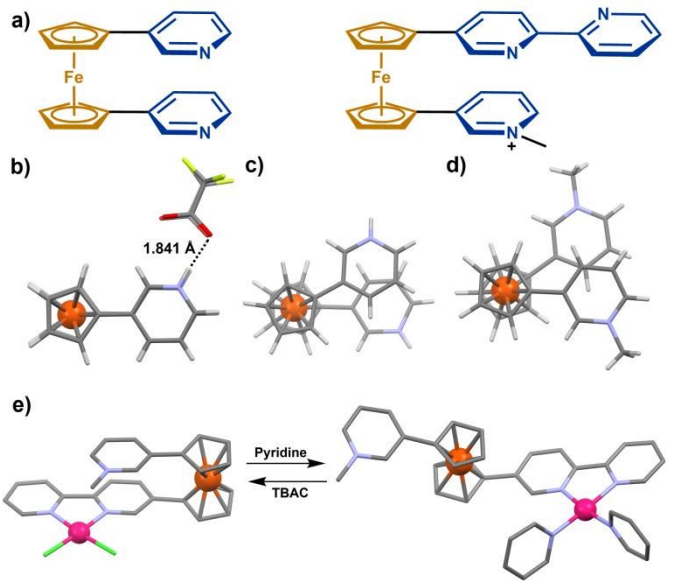

Figure 9 a) Bosnich's first and second generation two-state switches and the solid state structures of b) protonated 1,1'-dipyridylferrocene quenched by a triflate counterion with the O-H hydrogen bond labelled, c) protonated 1,1'-dipyridylferrocene as a SbF_6 salt, and d) methylated 1,1'-dipyridylferrocene as a SbF_6 salt, and e) the reversible rotation of the second generation two-state switch.

Protonation using $HSbF_6$ which contains a bulky non-coordinating SbF_6^- counterion was attempted. In this case a 29.62° rotation of the pyridine "arms" was observed (Figure 9c). Dimethylation (to introduce the positive charge) of the pyridine rotor resulted in a similar degree of rotation (37.52°) (Figure 9d). These results indicated that a 1+/1+ charge repulsion was not sufficient to completely overcome the attractive π-π stacking interactions.

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It was apparent that a higher charge was necessary in order to achieve full rotation of the ferrocenyl substituents; hence a second generation system was developed (Figure 9a). This system was comprised of an unsymmetrically substituted **Fc**, with a methylated pyridine attached to one **Cp** ring, and a bipyridine unit coordinated to palladium(II) dichloride attached to the other. This resulted in a 0/1+ charged compound which was once again found to π-stack in both solution and solid state, as evidenced by both ^{1}H NMR spectroscopy and X-ray crystallographic studies (Figure 9e). The negatively charged chloride ligands of the palladium could be exchanged for neutral pyridines upon treatment of the rotor with $AgSbF_6$ and pyridine, resulting in a 1+/2+ tricationic system. The electrostatic repulsion between the two substituents in this system was found to be sufficient to fully decouple the π-stacking, causing the substituents to rotate almost completely away from one another (~160°) and adopt the *anti*-conformation. Addition of chloride ions to the system displaced the pyridine ligands from the tricationic species regenerating the neutral palladium(II) dichloride complex and restoring the initial π-stacked conformer.

The work by Bosnich has been recently developed further by Crowley and co-workers with the synthesis of a ferrocene-based switch where the **Fc** is doubly substituted with bipyridine units via alkyne linkers (1,1'-di(5-yl-ethynyl-2,2'-bipyridine)ferrocene (diebipyFc), Figure 10a).[45] Like Bosnich's system, it relies on the favourable π-stacking between the two substituents to attain its contracted state. Unlike Bosnich's system, it requires the complexation of copper(I), along with a dimesitylbipyridine (dimes) co-ligand,[46] to achieve the extended state. A combination of electrostatic and steric repulsion destabilises the *syn* conformation upon complexation of the copper(I) dimesitylbipyridine units and lead to the formation of the *anti* rotamer. This extension process was completely reversible and contraction could be triggered either chemically, or more importantly, electrochemically. Addition of 1,4,8,11-tetraazacyclotetradecane (cyclam) to dicopper(I) rotor removes the copper ions from the rotor complex restoring the π-stacked *syn* conformation of the 1,1'-di(5-yl-ethynyl-2,2'-bipyridine)ferrocene. While the chemical switching is fully reversible the process generates chemical by-products that need to be removed from the system. Conversely, the electrochemical switching process enables clean, reversible interconversion between the *syn* and *anti* rotamers.

The electrochemical switching of the dicopper(I) rotor complex was carried out in the presence of a 2,2′:6′,2″-terpyridine (terpy) ligand and oxidation or reduction of the copper ions sets the $[Cu(dimes)]^{n+}$ fragments in motion. Upon oxidation of $[Cu_2(diebipyFc)(dimes)_2]^{2+}$ to $[Cu_2(diebipyFc)(dimes)_2]^{4+}$, the resulting tetrahedrally coordinated Cu(II) ions are unstable and this leads to the migration of the $[Cu(dimes)]^{n+}$ fragment to the terpy ligands generating the more stable five-coordinate $[Cu(terpy)(dimes)]^{2+}$ complex and free 1,1'-di(5-yl-ethynyl-2,2'-bipyridine)ferrocene (Figure 10b). Similarly, upon reduction of the Cu(II) back to Cu(I) the $[Cu(terpy)(dimes)]^{2+}$ complex is unstable as the copper(I) ions are in the pentacoordinate trigonal bipyramidal environment. As such the $[Cu(dimes)]^{+}$ fragments migrate back to the ferrocene rotor regenerating the complex $[Cu_2(\mathbf{1a})(\mathbf{3})_2]^{2+}$ and returning the copper(I) ions to the preferred tetrahedral coordination environment. While both the chemical and electrochemical switching processes are fully reversible chemical waste/by-products (Cu(II) cyclam complexes) that need to be removed from the system are generated in the chemically driven system. Conversely, the electrochemical switching process enables clean, reversible interconversion between the *syn* and *anti* rotamers.

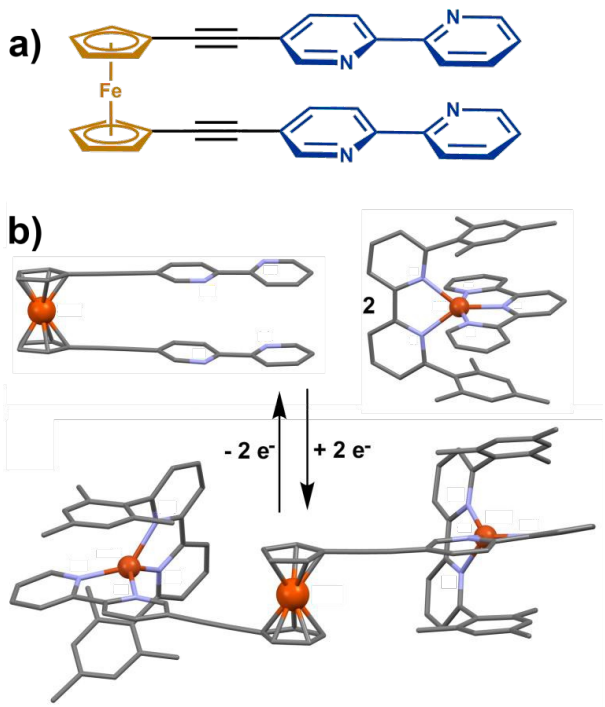

Figure 10 a) The structure of Crowley's ferrocene-based switch, and b) the electrochemical switching, with the crystal structures of the species of interest depicted (terpyridine omitted for clarity).

In the conceptual reverse, Bucher and co-workers[47] have shown that 1,1'-disubstituted **Fc** rotors functionalized with cationic 4,4'-bipyridinium "arms" can be exploited to produce redox-switchable systems. Initially, the di-4,4'-bipyridinium rotors exist in the *anti*, charge repelled conformation due to electrostatic repulsion between the substituents of the **Fc** (Figure 11a). A two electron reduction of the **Fc** rotors leads to the formation of bipyridinium radicals on each arm of the rotor. These radicals then form an intramolecular π-dimer complex generating the *syn* stacked rotamer. ^{1}H NMR evidence suggested that the 4+ system was not π-stacked, as expected, and X-ray crystallography of one of the iterations showed an extension angle of 75.63° (Figure 11b). The non-methylated 2+ analogue of the same system displayed an almost identical extension angle of 88.89° (Figure 11c). Formation of the contracted species was supported by DFT calculations and UV-Vis spectroscopy, but was found to only

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be achieved when using rigid, conjugated linkers between the **Fc** and the bipyridine arms.

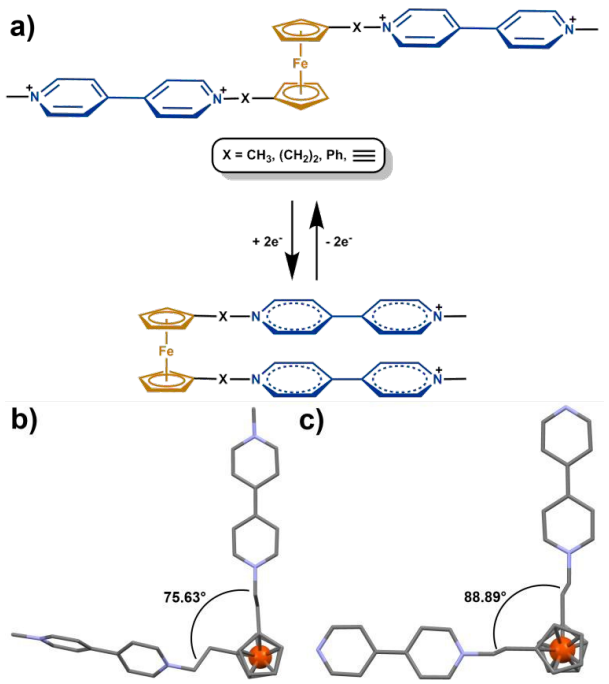

Figure 11 a) The redox switching of Bucher's two-state switch and the crystal structures of b) a tetracationic "extended" system, and c) a dicationic non-methylated system. Solvent, counterions and hydrogens are omitted for clarity.

These same compounds have been thoroughly investigated by Qiu *et al.* in a computational study for their application in non-linear optics.[48] A **Fc** system disubstituted with buckybowls was also investigated by the same group.[49] The energy of the different rotational conformers was calculated, and it was found that the energy required to switch between the closed state and the open state was 14.8 kcal mol^{-1}.

Takeuchi and co-workers have also developed a redox switchable system.[50] The authors synthesised a 1,1'-disubstituted **Fc** where the substituents are redox active naphthalenediimide groups (Figure 12a). The solid state structure of the rotor molecule (Figure 12b) shows that the naphthalenediimide groups adopt the *syn* π-stacked conformation (as expected) with a dihedral angle of just 8.98°. However, calculations suggest that in solution the *anti* (open) conformation is 1.4 kcal mol^{-1} more stable than the *syn* π-stacked rotamer. With such a low barrier to rotation the rotor adopts an equilibrium between the both the *syn* and *anti* conformers in solution. Upon reduction to give the radical anion species, the contracted state is "locked in" due to the strengthening of the π-π interactions (Figure 12a). A second reduction gives the dianionic species that exists in an equilibrium between the extended and contracted conformations, where the contracted form is preferred due to the pseudo-pairing of the radicals on each substituent.

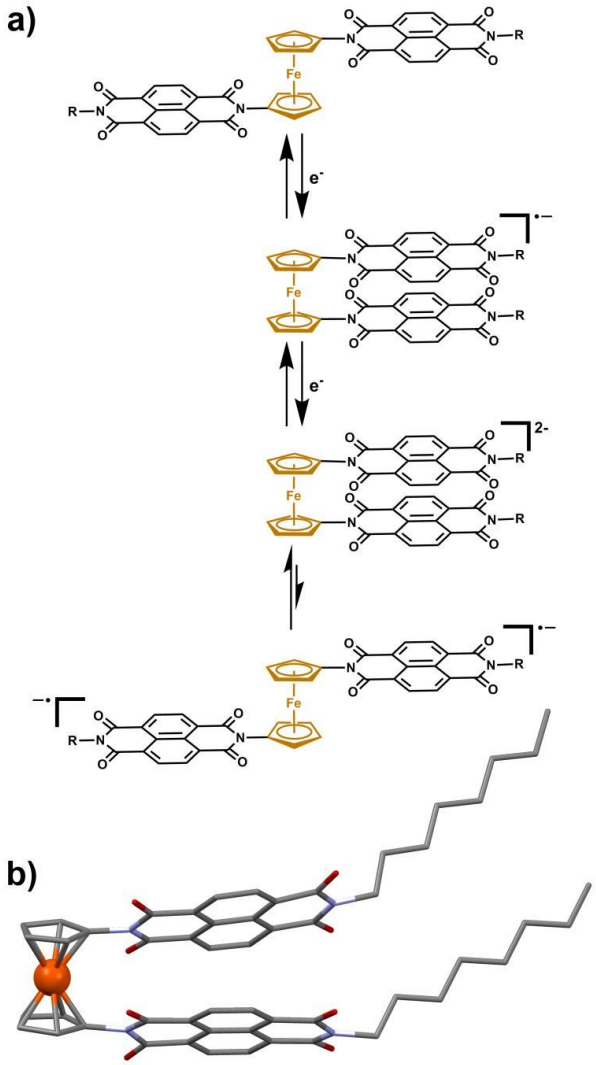

Figure 12 a) The proposed redox-induced switching of Takeuchi's two-state switch, and b) the solid-state structure of the fully reduced species.

A zinc porphyrin appended ferrocene-based "tweezer" synthesised by Rath *et al.* is also capable of acting as a two-state switch (Figure 13).[51] A single equivalent of a ditopic chiral guest is capable of forming a complex between the two zinc porphyrin units, locking the tweezers into a "contracted" state, while an excess of guest causes each zinc unit to bind an individual guest molecule, causing the **Fc** to rotate such that the porphyrin units are no longer stacked.

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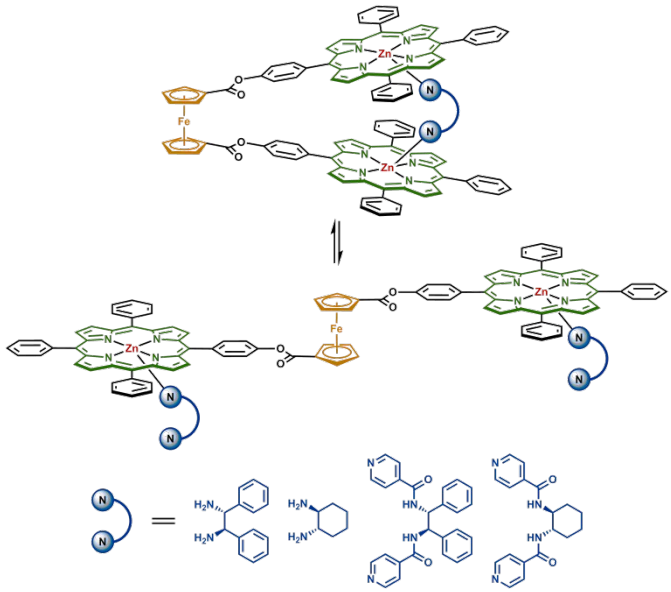

Figure 13 The opening and closing of a ferrocene-based tweezer complex, where the favoured conformation is dictated by the stoichiometry of the ditopic guest.

Molecular Brakes

Tian *et al.* has developed a molecular brake in which an external stimulus halts the rotational motion of the "ball-bearing"-like **Fc** unit.[52] A 1,1'-disubstituted **Fc** where the substituents are the bulky photoactive benzo[e]indoline groups initially adopts the *anti* conformation as evidence by the solid state structure and DFT calculation and the substituted **Cp** rings freely rotate about the **Fc** pivot. On addition of Zn^{2+} ions, the rotation is halted and the molecule is "locked" into a U-shaped *syn* configuration. This process was found to be completely reversible, as addition of EDTA to remove the Zn^{2+} regenerated the free rotation of the **Fc** rotor.

McGlinchey and co-workers have also generated a ferrocene-based molecular brake where ferrocenyl units were attached to anthracenes and triptycenes, effectively hindering the rotation of the aromatic propeller units.[19b, 53] In this case, the **Fc** is utilised purely for its steric bulk. On attachment of one bulky **Fc** to triptycene the rotational barrier of the triptycene was found to be 16.8 kcal mol^{-1},[19b] significantly higher than the 2.3 kcal mol^{-1} rotational barrier of triptycene when bound to a silica surface in the same position as the **Fc**.[54] More interestingly, the di-substituted 9,10-diferrocenyltriptycene was found to act as a molecular dial (Figure 14b). The di-substituted compound could exist as two distinct rotamers, with the **Fc** units eclipsed (meso rotamer) or staggered (rac rotamer). These two states could slowly interconvert in a stepwise manner, resulting in a slow rotary dial with three possible "settings" (Figure 14a).

The steric effect of **Fc** on ferrocenyl-pentaphenylbenzene and pentanaphthylbenzene have also been investigated and found to again slow the rotation of the propeller-like groups.[55]

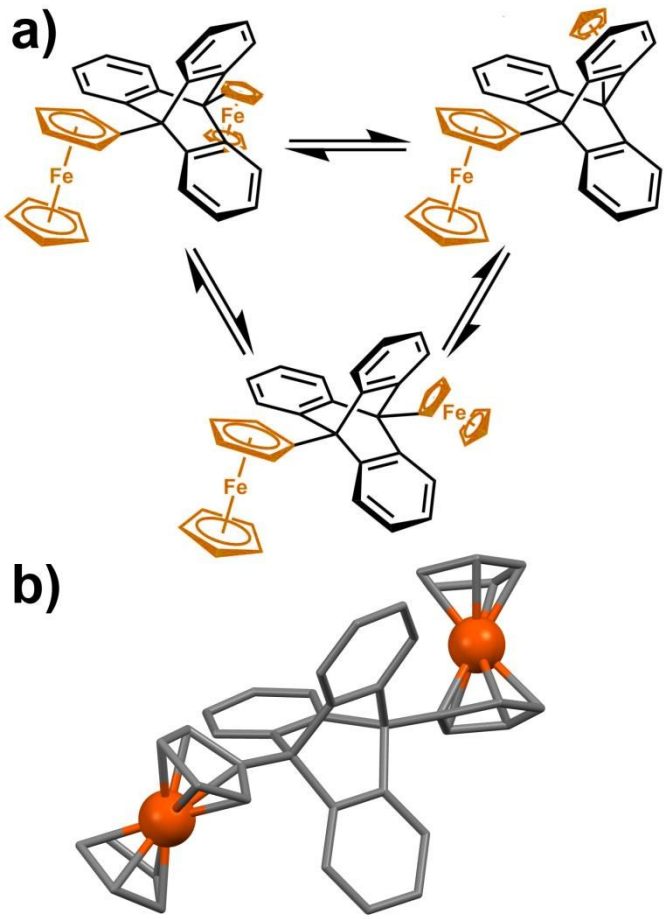

Figure 14 a) The interconversion between the three "settings" of McGlinchey's molecular dial, and b) the solid-state structure of the meso-rotamer of the di-ferrocenyltriptycene.

Molecular "Scissors"/"Pliers"

In an impressive series of papers Aida and co-workers have used of **Fc** as a pivot unit to create a range of molecular machines including molecular mimics of macroscopic scissors and pliers.[19a, 56] These molecular "scissors" feature a **Fc** pivot joint, a photoisomerisable azobenzene strap, and two phenyl "blades" (Figure 15b).[56b] Irradiation of the "closed" *trans*-isomer with UV light (350 nm) causes the azobenzene strap to isomerise and give the *cis*-isomer, where the phenyl "blades" rotate away from one another – a motion reminiscent of scissors opening (Figure 15a). Application of visible light (>400 nm) causes photoisomerism back to the "closed" *trans*-form of the "scissors".

The authors then exploited their "molecular scissors" to generate a second generation molecular machine that mimicked the action of macroscopic pliers.[56a] These "molecular pliers" contained the same **Fc** pivot joint and photoisomerisable azobenzene "handle", but instead of phenyl "blades" zinc(II)-containing porphyrin units were appended to each **Cp** ring of the **Fc** unit. Opening and closing of these "pliers" proceeded in an identical fashion to the "scissors", requiring UV light to open and visible light to close. The extra functionality

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introduced to these "pliers" allowed them to bind guest molecules, such as 4,4'-biisoquinoline, between the porphyrin units, and the process of opening and closing the pliers acted to distort the bound guest rotamer, adding an additional pedal-like motion to the overall conformational change (Figure 15c).

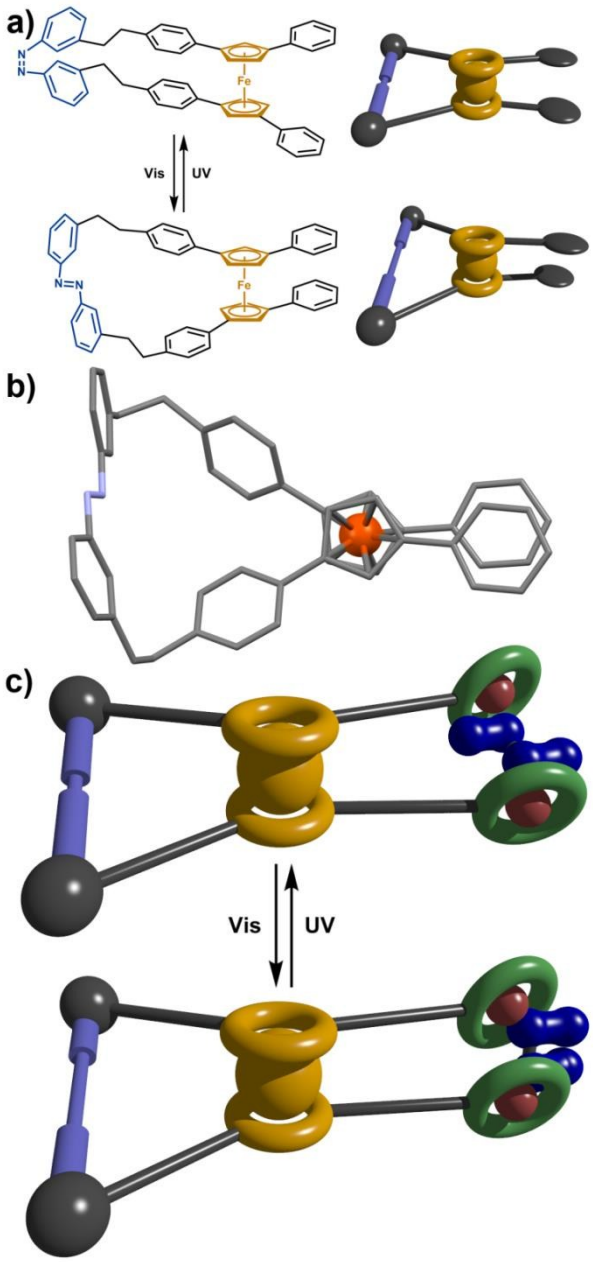

Figure 15 a) The photoisomerism of the azobenzene strap causing the molecular "scissors" to open and close, b) the crystal structure of the trans-isomer of the scissors, showing the overlapped phenyl "blades" in the "closed" state, and c) the photoinduced opening and closing of the molecular "pliers", showing the distortion of a bound 4,4'-biisoquinoline guest. Porphyrin rings are shown in green, zinc(II) in red, and the guest molecule in dark blue. The remainder of the molecule is identical to the molecular "scissors".

A version of the "molecular scissors" where the azo-benzene strap has been replaced by a rhodium phosphine complex has also been developed (Figure 16b).[57] In this case, diphenylphosphoryl azide (DPPA) and an aldehyde act as a "fuel" for the scissors, and the catalytic decarbonylation of the aldehyde causes the rhodium complex to interconvert between the *trans* and *cis* form (Figure 16a). As a result, the methoxyphenyl "blades" open and close continuously until the reactants/fuel is exhausted.

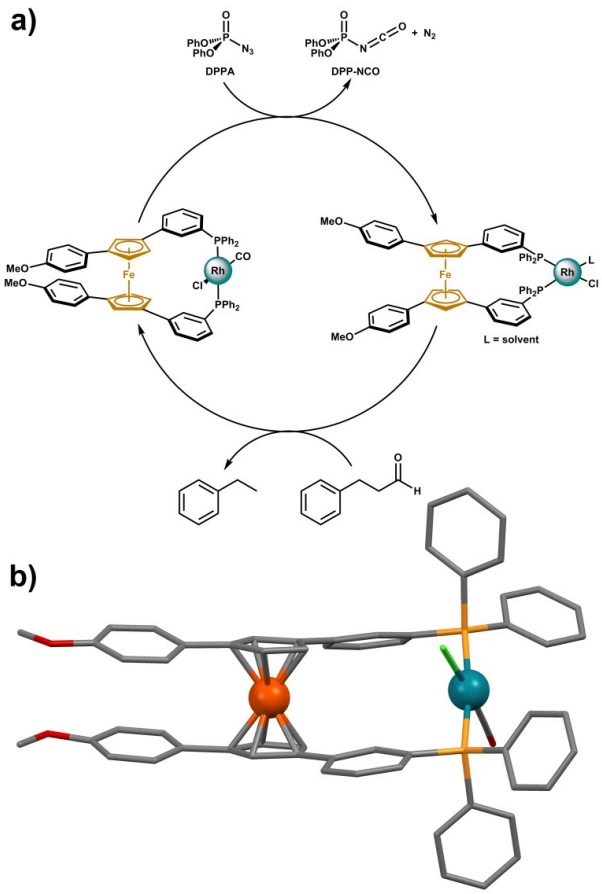

Figure 16 a) The proposed reaction cycle of the catalytically driven scissors, and b) the crystal structure of the scissors, with the rhodium phosphine complex in the *trans*/closed configuration.

Other rotary molecular "ball-bearing" machines

Whilst **Fc** is the most commonly exploited molecular "ball-bearing" unit, other sandwich complexes display similar behaviour. Lanthanide bis(porphyrinate)s and metallocarboranes have both been used to generate rotary machines.

Molecular Spring

The construction of a "molecular spring" has been achieved by Takeuchi and co-workers through a combination of both **Fc** and cerium bis(porphyrinate) rotatable joints (Figure 17a).[58] The native form of the spring is "extended", with the **Fc** units distanced (computational modelling gives an Fe-Fe distance of 3.2 nm), and contraction is stimulated by the addition of a chiral carboxylic acid – 1*R*,2*R*-cyclohexanedicarboxylic acid (Figure 17b). Six equivalents of the carboxylic acid chelate to

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the peripheral pyridines of the cerium bis(porphyrinate), inducing a large conformational change to the rotational centres. This rotation is transferred through the rigid framework to the **Fc** units, which also rotate, giving the "contracted" form where the **Fc** units are much closer together (computational modelling gives an Fe-Fe distance of 0.5 nm).

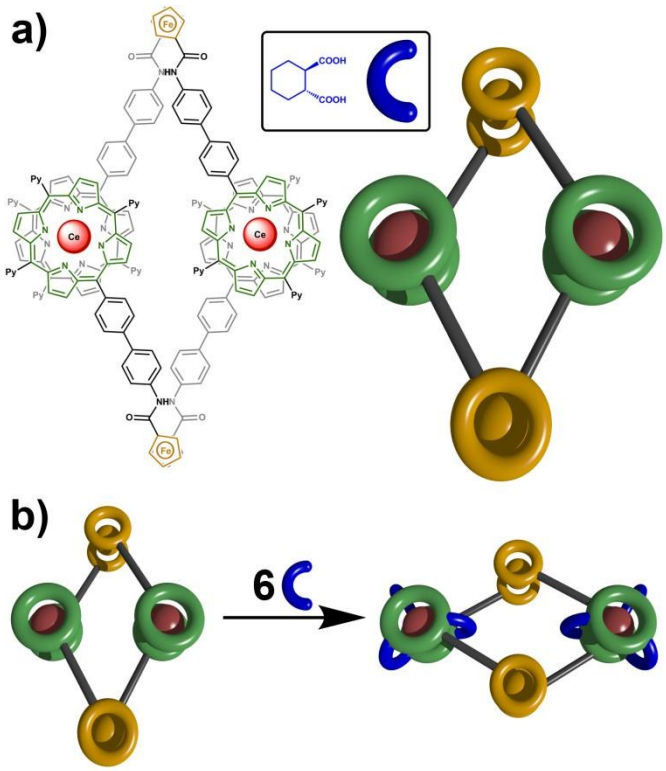

Figure 17 a) The structure of the molecular spring and dicarboxylic acid along with their cartoon representations, and b) the spring contraction mechanism.

Molecular Rotor

A surface-bound rotor system synthesised by Otsuki and co-workers contains a pendant **Fc**, but uses a cerium bis(porphyrinate) as the rotatable unit attached to the surface (Figure 18).[59] The surface used in this case was highly ordered pyrolytic graphite, and the adhesion to the surface was achieved through the use of long alkyl chains that packed in a lamellar pattern. The **Fc** appended to the porphyrin was used as a "beacon", allowing the rotation of the porphyrin to be tracked by STM. Consecutive scans of the same surface revealed the **Fc** units could reorient in 90° steps, suggesting that the porphyrins were capable of rotating to four distinct positions, with the likelihood of rotation dependent on the neighbouring molecules.

A similar surface-bound cerium bis(porphyrinate) rotor has been developed by Noji *et al.*.[60] In this case, the "bottom" porphyrin was adhered to an amino-modified glass substrate via active-ester-terminated succinyl linkers, while the "top" porphyrin, with azide-terminated triethyleneglycol linkers, was attached to an alkyne-decorated magnetic bead. The bead was large enough to track via optical microscopy, and, like Otsuki's rotor, was found to rotate in 90° intervals. The energy required to achieve rotation was found to be greater than 1.8 kcal mol^{-1} at 298 K, but it could also be made to forcibly rotate using magnetic tweezers.

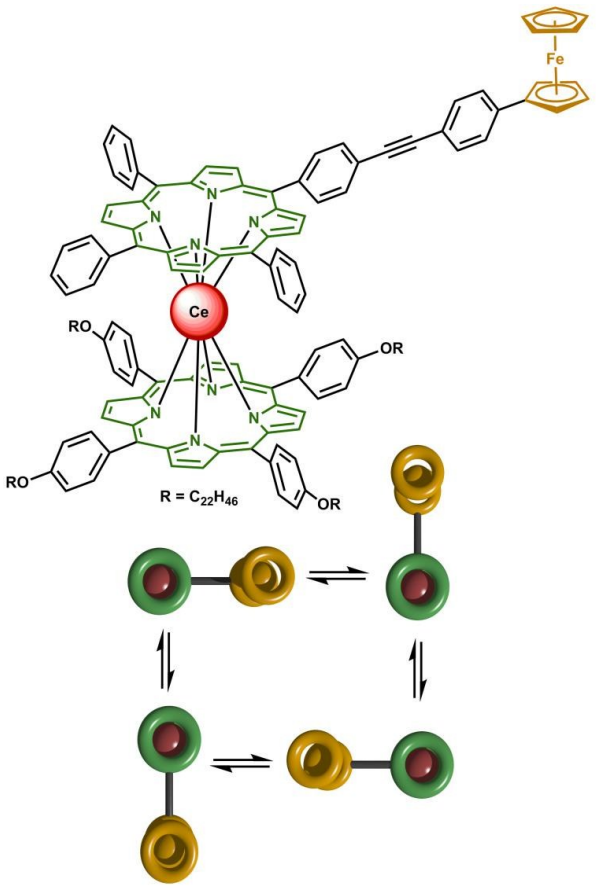

Figure 18 Otsuki's molecular rotor and the 90° rotations it is capable of.

Folding Ruler

A prominent example of a cerium bis(porphyrinate)-based machine is Takeuchi's folding ruler.[61] This "ruler" is a polymer containing zinc porphyrin units as a recognition site for a ditopic guest molecule, and cerium(IV) bis(porphyrinate) rotatable joints between each of the zinc porphyrin sites. In its natural state this polymer adopts an extended conformation, and the administration of 1,4-diazabicyclo[2.2.2]octane (DABCO) was supposed to induce the folding of the "ruler" into a contracted stacked form (Figure 19). Complete contraction is not achieved as the DABCO is thought to only bind a maximum of every second tier and binds uncontrollably such that loops and "tangles" form. Dynamic light scattering reveals a negligible change in average polymer size on contraction, maintaining an approximately 12 nm diameter, with the only real change being the size distribution narrowing slightly on exposure to the DABCO. Re-"extension" is achieved via removal of the guest through protonation, by addition of trifluoroacetic acid.

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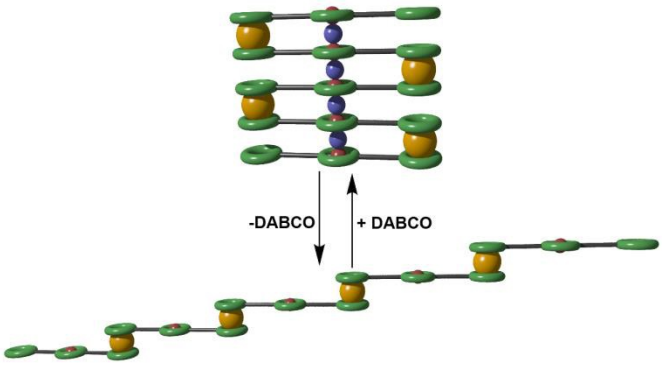

Figure 19 Idealised extension and contraction of Takeuchi's polymer-based "folding ruler". Cerium(IV) is depicted in yellow, porphyrin in green, zinc in red, and the DABCO guest in blue.

Molecular Gear

Both cerium and lanthanum bis(porphyrinates) have been utilised by Takeuchi *et al.* to create molecular gears.[62] These gears consist of a top rotor consisting of a quadruply appended porphyrin coordinated to the cerium or lanthanum, and a side rotor, consisting of a quadruply appended rhodium porphyrinate complexed orthogonal to the initial bis(porphyrinate), such that the two rotor interdigitate (Figure 20). In this manner, the rotation of the top rotor is transferred to the side rotor, resulting in the coordinated rotation of an interlocked molecular gear. The synchronised rotation of the rotors can be decoupled such that they rotate independently through addition of triethylamine. This is due to only seven of the eight pyrrole groups of the cerium bis(porphyrinate) being coordinated, thus leaving the remaining pyrrole highly susceptible to deprotonation. The base-induced deprotonation increases the π-π interactions between the two porphyrins, which in turn subtly changes the conformation of the cerium bis(porphyrinate) enough to allow the rotors to slip out of gear. Subsequent addition of trifluoroacetic acid causes the rotors to once again become mechanically interlocked and rotate simultaneously. A triply interlocked gear has also been produced, where the addition of base results in a slower rotational rate compared to the acidified rotor, rather than a decoupling of rotation.[62c]

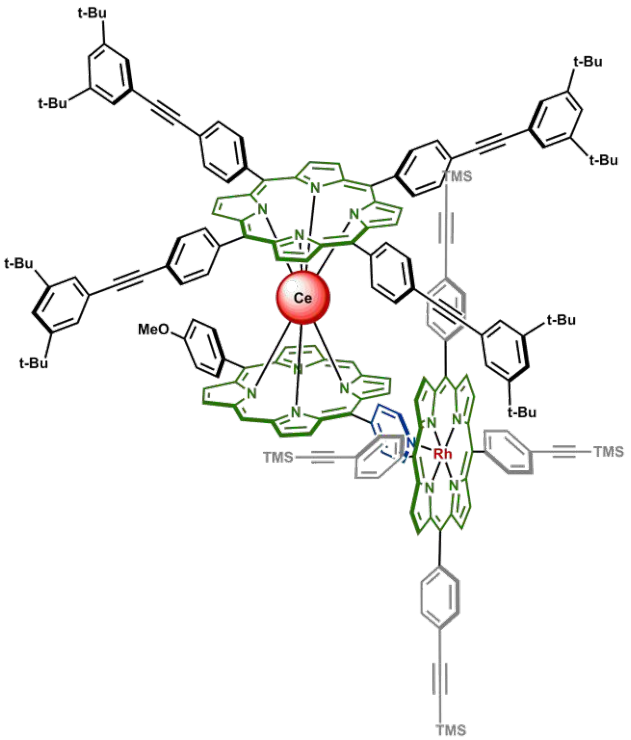

Figure 20 The structure of one of Takeuchi's molecular gears showing the two interlocking rotors.

Carborane-Based Rotor

Other sandwich complexes, such as *nido*-carboranes, also have potential as components of molecular machines. Hawthorne and co-workers have explored the use of both nickel and cobalt carboranes to develop rotary switches.[2x, 63] Nickel(III) coordinates to two carborane polyhedrons via the B_3C_2 face in a *transoid* manner, as the carbon vertices have a reduced concentration of negative charge compared to the antipodal boron vertices,[63b] thus any substituents attached on the carborane boron adjacent to the two carbon atoms will also be *trans* to each other (Figure 21).[63a] Oxidation of the metallocene to nickel(IV) via addition of aqueous $FeCl_3$ causes the carboranes to rotate to the *cisoid* geometry, bringing any attached substituents closer together. Electrochemical reduction of the nickel(IV) regenerates the *transoid* nickel(III) carborane and brings the substituents back to their initial locations. Cobalt carboranes were found to exhibit similarly reversible *transoid* to *cisoid* behaviour on oxidation/reduction.[63c]

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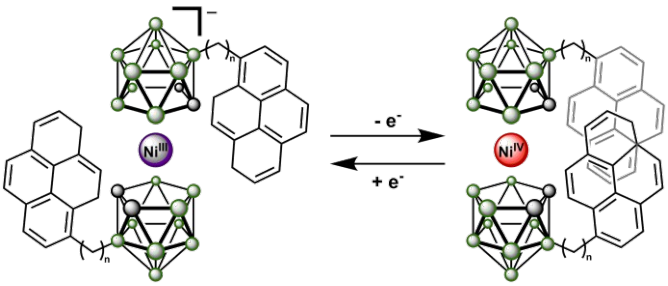

Figure 21 Redox controlled switching of a nickel carborane system with pendant pyrenes attached. Boron atoms are depicted in green, carbon in black.

Conclusions and outlook

Ferrocene's reversible redox properties and ability to act as a molecular "ball bearing" in combination with its robust synthetic chemistry has resulted in it being a highly attractive component for the generation of synthetic molecular machines. These properties have been exploited to create a range of non-interlocked machine systems, including switches, rotors, brakes, springs, and molecular "scissors" and "pliers". While these results clearly show that **Fc** is a useful building block for the development of synthetic molecular machine systems, there remain many challenges that need to be overcome before synthetic systems truly rival biological molecular machines. The design of the vast majority of **Fc** based systems has been inspired by macroscopic machines (e.g. brakes, springs, scissors and pliers). In order to generate systems that operate in the conditions present in the nanoworld it may be more effective (albeit difficult) to draw design principles from biological systems. Furthermore, most of the **Fc** systems described in this review are relatively simple conformational switches that operate under equilibrium conditions. Conversely, most biological molecular machines operate in non-equilibrium conditions and use the molecular motion to perform useful tasks.[2a, 2b] Finally, biological molecular motors are nearly always membrane (surface) bound (e.g. actin-myosin complex, kinesin, F_oF_1-ATPase and bacterial flagella) allowing them to transfer their molecular motion into work upon their surrounding environment, most of the **Fc** based machines generated to date operate exclusively in solution. It is widely appreciated that in order to harness the molecular level motion to perform useful work synthetic molecular machines need to be anchored on to surfaces.[2t] Indeed, it has been shown that surface bound synthetic molecular machines can be used to generate macroscopic motion.[5b, 64] Thus, more efforts are need to integrate these **Fc** based machines into condensed phases.

Although still a relatively young field, there have been many the spectacular successes in the development of both mechanically interlocked and non-interlocked molecular machines.[2] While **Fc** based molecular machines are not yet as well developed as other systems it seems that the useful properties of the **Fc** unit coupled with the imagination of chemists should enable more complex **Fc** containing machines capable of performing a range of tasks to be targeted in the near future.

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Notes and references

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† Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data. See DOI: 10.1039/b000000x/

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