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Chemically and electrochemically induced expansion and contraction of a ferrocene rotor†

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A 2,2'-bipyridine-appended ferrocene rotor, 1,1'-di(5-yl-ethynyl)-2,2'-bipyridine)ferrocene, can be switched from a folded/stacked (*syn*) conformation to an extended/unstacked (*anti*) conformation by the addition of $[\text{Cu}(\text{CH}_3\text{CN})_4](\text{PF}_6)$ and 6,6'-dimesityl-2,2'-bipyridine. This extension and contraction process was completely reversible and could be triggered either chemically or electrochemically.

All the cellular processes of life are carried out by biological (nano)-molecular machines.¹ Inspired by these systems chemists have begun to develop switchable synthetic molecular machines.² While there have been some spectacular successes, including synthetic rotary motors,³ molecular muscles,⁴ and sequence-specific peptide synthesis machines⁵ the vast majority of synthetic systems developed are based on complex and difficult to synthesise mechanically interlocked architectures (MIAs).⁶ The challenging and laborious synthesis of these MIAs has led to increasing efforts to develop potentially synthetically more accessible non-interlocked molecular machines.⁷ In particular systems incorporating metal ions are becoming more and more common due to the favourable kinetic and thermodynamic properties of the coordination bonds.⁸

The reversible electrochemistry⁹ and molecular ball-bearing¹⁰ properties of ferrocene (Fc) derivatives¹¹ have made them useful building blocks for the development of non-interlocked synthetic molecular machines.¹² We and others have exploited ferrocene to develop electrostatically driven two-state switches (Fig. 1).¹³ We have shown that pyridyl and 2,2'-bipyridyl (bpy) 1,1'-disubstituted ferrocenes^{13c} initially adopt the stacked *syn*-conformation due to the electronic preference of the ferrocene and favourable π - π interactions.

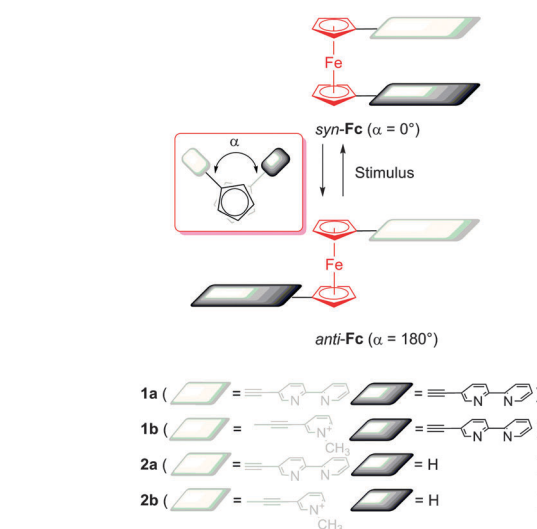


Fig. 1 Generic stimuli responsive switching with ferrocene (Fc) rotor molecules and the compounds **1a–b** and **2a–b** studied herein.

Introduction of charge to the ferrocene “arms”, either by protonation or metallation with Pd^{2+} ions, induced rotation to the *anti*-conformation to minimise the electrostatic repulsion between the cationic substituents of the ferrocene rotors.^{13c} Deprotonation or addition of chloride ions removed the electrostatic repulsion restoring the initial stacked *syn* conformation.^{13c} Other workers^{13a,b} have generated electrochemical switchable systems by incorporating redox-active organic arms into the ferrocene rotors.

Herein we build on our previous work^{13c} and develop ferrocene rotor systems that can be switched from the *syn* to *anti* conformation by the complexation/decomplexation of a copper 6,6'-dimesityl-2,2'-bipyridine fragment. A combination of electrostatic and steric repulsion destabilises the *syn* conformation upon complexation generating the *anti* rotamer. This extension and contraction process was completely reversible and could be triggered either chemically or electrochemically.

The ethynylferrocene rotors (**1a–b**) and model (**2a–b**) systems were readily synthesised using modified literature procedures (ESI†).¹⁴

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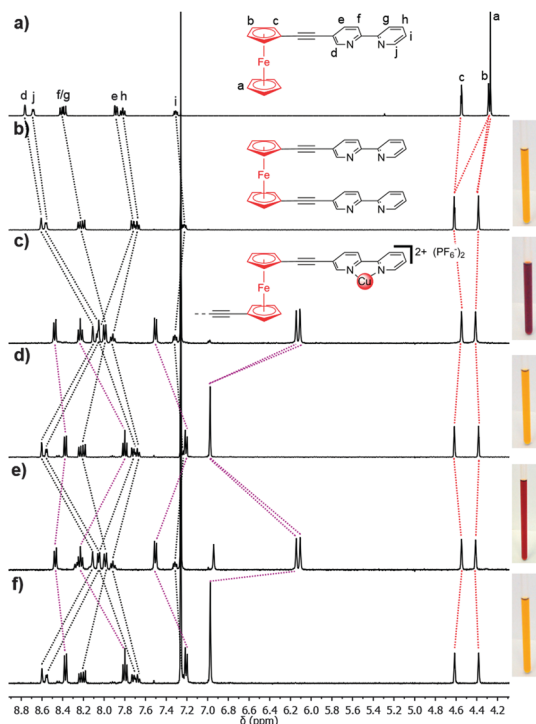


Fig. 2 ^1H NMR spectra (400 MHz, CDCl_3 , 298 K) of (a) **2a** (b) **1a** (c) the copper(I) complex $[\text{Cu}_2(\mathbf{1a})(\mathbf{3})_2](\text{PF}_6)_2$ (d) cyclam induced de-metallation/switching (e) addition of 2 eq. of $[\text{Cu}(\text{CH}_3\text{CN})_4](\text{PF}_6)$ (f) cyclam induced de-metallation/switching.

^1H NMR spectroscopy, density functional theory (DFT) calculations and X-ray crystallography were used to determine the preferred conformation of the ferrocene rotors (**1a–b**). The proton signals associated with the bipyridyl and pyridyl rings ($\text{H}_{\text{d-j}}$) of **1a–b** were shifted upfield relative to those of the singly armed model compounds **2a–b**, indicating that the di-armed ferrocene rotors adopt a stacked (*syn*) conformation in solution (Fig. 2a and b and ESI,† Fig. S38). This was further supported by computational modelling of the systems. DFT calculations (CAM-B3LYP, DMF solvent field)^{13b,15} were used to determine the relative energies of a series of different rotation conformers of **1a–b** (the angles between the ferrocene “arms” of **1a–b** was varied from -180° to 180° and the compound energy minimised). These calculations showed, as expected, that the stacked, fully eclipsed (*syn*) rotamers (angle = 0°) were the lowest energy conformations for both **1a** and **1b** by 3 and 6 kJ mol^{-1} , respectively (ESI,† Fig. S82 and S86). Additional evidence for the stacked (*syn*) conformation was obtained from X-ray crystallography (Fig. 3a and ESI†). The molecular structure of **1a** clearly showed that the bipyridine substituents are stacked (centroid–centroid distances 3.636 and 3.716 Å) and the ferrocene cyclopentadiene (Cp) rings are eclipsed, with a dihedral angle of 1.58° (Fig. 3a) between the substituents consistent with the ^1H NMR spectral and computational data.

Reaction of either **1a**, **1b** or **2a** in acetonitrile (CH_3CN) solution with $[\text{Cu}(\text{CH}_3\text{CN})_4](\text{PF}_6)$ and the sterically bulky bipyridine ligand 6,6'-dimesityl-2,2'-bipyridine¹⁶ (**3**) was accompanied by a colour change from yellow/orange to red/brown indicative of complexation (Scheme 1(i) and ESI†).¹⁷ ^1H NMR spectroscopy (Fig. 2c and ESI,†

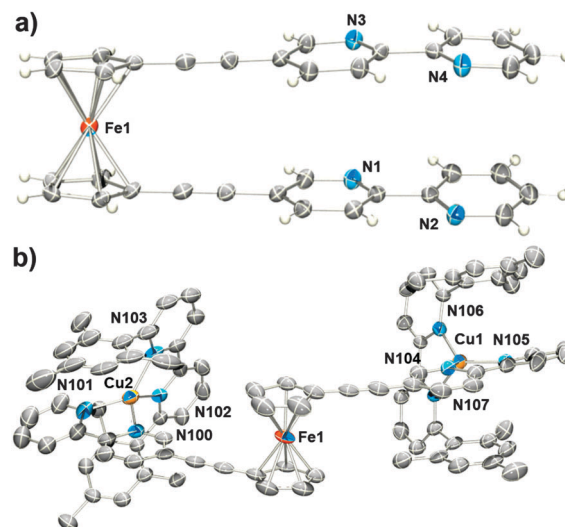
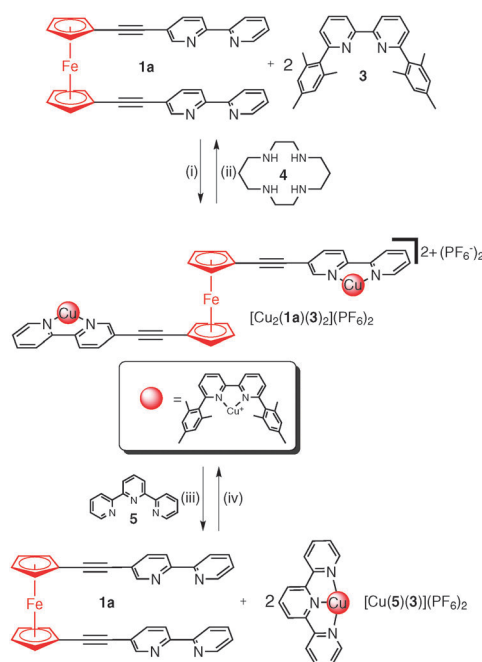


Fig. 3 ORTEP¹⁸ diagrams showing the solid state structures of the rotor **1a** (a), and the Cu(I) complex $[\text{Cu}_2(\mathbf{1a})(\mathbf{3})_2](\text{PF}_6)_2$ (b). The ellipsoids are shown at the 50% probability level. Counterions and hydrogen atoms of the complex are omitted for clarity. Additional crystallographic details can be found in the ESI.†



Scheme 1 Synthesis of the copper(I) complex of **1a** and the chemical and electrochemical switching. (i) $[\text{Cu}(\text{CH}_3\text{CN})_4](\text{PF}_6)$ (2 eq.), CDCl_3 , 298 K; (ii) cyclam **4** (2 eq.), CDCl_3 , 298 K; (iii) 2,2':6',2''-terpyridine (**5**) (2 eq.), -2e^- , acetone, 0.1 M NBu_4PF_6 ; and (iv) $+2\text{e}^-$, acetone, 0.1 M NBu_4PF_6 .

Fig. S41 and S42) and ESMS (ESI† Fig. S64–S67) confirmed the formation of the expected copper(I) complexes. Due to the combination of electrostatic and steric repulsion generated upon complex formation it was expected that the ferrocene rotor units (**1a** and **1b**) would switch conformation from the *syn* to the *anti* rotamer. An examination of the ^1H NMR spectra of the complex $[\text{Cu}(\mathbf{1b})(\mathbf{3})](\text{PF}_6)_2$, the rotor **1b** and the corresponding model compound **2b** provided experimental support for this *syn* to *anti* conformation switch



on complexation. As discussed above, the proton resonances of the methylpyridinium unit of **1b** are shifted upfield relative to those of the model compound **2b**, indicating that the di-armed ferrocene rotor adopts a stacked (*syn*) conformation in solution (ESI,† Fig. S38). Upon complexation to the copper(i) **3** complex the proton signals of the methylpyridinium unit shift downfield to values that are almost identical to those observed from the model compound **2b** indicating that the pyridinium arm of the copper(i) complex is no longer π -stacked (ESI,† Fig. S41). DFT calculations (CAM-B3LYP, DMF solvent field)^{13b,15} were used to examine the relative energies of different rotational conformers of the copper(i) complexes $[\text{Cu}_2(\mathbf{1a})(\mathbf{3})_2](\text{PF}_6)_2$, and $[\text{Cu}(\mathbf{1b})(\mathbf{3})](\text{PF}_6)_2$ (ESI,† Fig. S84 and S88). The resulting plot revealed that the minimum angle between the two arms could not be less than 60° , with the energy difference between higher angle conformations being negligible. Thus it can be surmised that the arms of the rotor must have extended to at least 60° in solution. Consistently, the molecular structure of $[\text{Cu}_2(\mathbf{1a})(\mathbf{3})_2]^{2+}$ as the perchlorate (ClO_4^-) salt (Fig. 3b and ESI†) showed that the $[\text{Cu}(\mathbf{3})]^+$ units had coordinated to both bipyridine arms of **1a** in the expected “pacman-like” arrangement. More importantly it confirmed that the rotor molecule was almost completely extended, with the angle between the two arms ranging from 142 – 145° (Fig. 3b and ESI†).

Having confirmed that the rotors **1a–b** (*syn*) and the corresponding copper(i) complexes (*anti*) adopt two different conformations we next examined if we could cleanly and reversibly switch between the rotor (**1a**) and rotor complex $[\text{Cu}_2(\mathbf{1a})(\mathbf{3})](\text{PF}_6)_2$. Addition of two equivalents of 1,4,8,11-tetraazacyclotetradecane (cyclam, **4**) to an acetone solution of $[\text{Cu}_2(\mathbf{1a})(\mathbf{3})_2](\text{PF}_6)_2$ caused an immediate colour change from red to orange (Scheme 1(ii), Fig. 2c and d and ESI†), indicating that the Cu(i) ions had been removed from the ferrocene complex.¹⁹ ^1H NMR and UV-vis spectroscopy and ESMS (Fig. 2c and d and ESI†) confirmed that only the free rotor **1a** and free 6,6'-dimethyl-2,2'-bipyridine ligand **3** were present in solution. Addition of two equivalents of $[\text{Cu}(\text{CH}_3\text{CN})_4](\text{PF}_6)_2$ to the solution regenerated the characteristic red colour of the complex $[\text{Cu}_2(\mathbf{1a})(\mathbf{3})_2](\text{PF}_6)_2$, and the ^1H NMR spectrum (Fig. 2e) indicated that the complex had quantitatively re-formed. This chemically driven *syn*-to-*anti* switching process could be repeated a number of times (>5) indicating that switching was completely reversible (ESI,† Fig. S47). However, the method led to the build-up of waste by-products (Cu(ii)-cyclam) which is uneconomical and could potentially lead to the loss of function.²⁰ Therefore we explored alternative switching methodologies. The electrochemical Cu(i)/Cu(ii) switching process developed by Sauvage *et al.*²¹ for the generation of a range of MIAs molecular switches and machines seemed ideal.²²

The CV (100 mV s^{-1} , acetone, $0.1\text{ M NBU}_4\text{PF}_6$) of the $[\text{Cu}_2(\mathbf{1a})(\mathbf{3})_2](\text{PF}_6)_2$ rotor complex displays two chemically reversible processes at 0.64 and 0.85 V respectively (Fig. 4 red/brown trace). By comparison with the previously prepared $[(3\text{-bpyFc})\text{Cu}(\mathbf{3})](\text{PF}_6)_2$ ¹⁷ and $[\text{Cu}(\mathbf{3})(\text{bpy})](\text{BF}_4)_2$ ²³ model systems the first oxidation process was assigned to the Cu^{III} couple while the second oxidation process is ferrocenyl based.²⁴ These assignments were further supported by two-step bulk electrolysis experiments. A stepwise oxidation was performed on the $[\text{Cu}_2(\mathbf{1a})(\mathbf{3})_2](\text{PF}_6)_2$ complex, oxidation at the potential of the first wave ($E_{\text{appl}} = 0.72\text{ V}$) passed 2.0 F mol^{-1} with the oxidized species $[\text{Cu}_2(\mathbf{1a})(\mathbf{3})_2]^{4+}$ proving stable at ambient temperature.

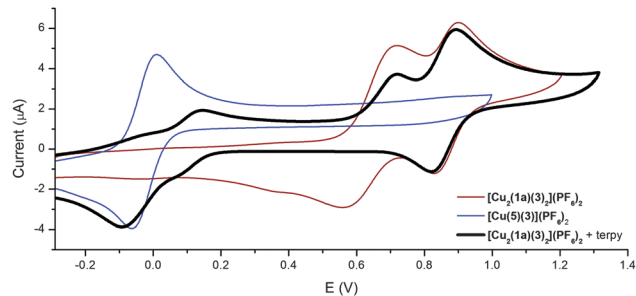


Fig. 4 CVs (100 mV s^{-1}) of the Cu(i) complex $[\text{Cu}_2(\mathbf{1a})(\mathbf{3})_2](\text{PF}_6)_2$, the Cu(ii) terpy complex $[\text{Cu}(\mathbf{5})(\mathbf{3})](\text{PF}_6)_2$, and $[\text{Cu}_2(\mathbf{1a})(\mathbf{3})_2](\text{PF}_6)_2$ in the presence of terpy in acetone.

The second step at $E_{\text{appl}} = 1.1\text{ V}$ passed only 1.0 F mol^{-1} , thereby confirming the transfer of two and one electrons, respectively. These results confirmed that the first process is the Cu(i) to Cu(ii) oxidation while the second is the oxidation of the ferrocene to ferrocenium.

The CV experiment was then carried out in the presence of two equivalents of 2,2':6',2''-terpyridine (**5**). The anodic potential sweep showed the two peaks corresponding to the Cu^{III} and ferrocenyl oxidation processes. On the reverse scan, only the reduction of the ferrocenium back to ferrocene is observed. No peak corresponding to the reduction of the $[\text{Cu}_2(\mathbf{1a})(\mathbf{3})_2]^{4+}$ complex was observed. Instead proceeding in the cathodic direction, a peak corresponding to the reduction of the pentacoordinated $[\text{Cu}(\mathbf{5})(\mathbf{3})](\text{PF}_6)_2$ complex was observed at -0.10 V (Fig. 4 black trace). This electrochemical behaviour is very similar to that observed by Sauvage *et al.*²¹ in their MIAs systems.

Bulk electrolysis in the presence of two equivalents of 2,2':6',2''-terpyridine (**5**) was accompanied by a colour change from deep red/brown to yellow, the same as was observed for the chemical switching process with cyclam (ESI,† Fig. S81). Spectroelectrochemistry (acetone, $0.1\text{ M NBU}_4\text{PF}_6$, OTTE cell, ESI,† Fig. S80) of the $[\text{Cu}_2(\mathbf{1a})(\mathbf{3})_2](\text{PF}_6)_2$ complex confirmed that during the bulk oxidation the MLCT band ($\lambda_{\text{max}} = 476\text{ nm}$) decreases until a spectrum consistent with “free” **1a** is generated. ESI-MS analysis of the 2,2':6',2''-terpyridine (**5**) and $[\text{Cu}_2(\mathbf{1a})(\mathbf{3})_2](\text{PF}_6)_2$ mixture before bulk electrolysis displayed peaks due to the $[\text{Cu}_2(\mathbf{1a})(\mathbf{3})_2](\text{PF}_6)_2$, $[\text{Cu}_2(\mathbf{1a})(\mathbf{3})_2]^{2+}$ and $[\mathbf{5} + \text{H}]^+$ ions. After oxidation the mass spectrum only contain peaks consistent with $[\text{Cu}(\mathbf{5})(\mathbf{3})]^{2+}$, $[\mathbf{1a} + \text{H}]^+$ and $[\mathbf{1a} + \text{Na}]^+$ ions.

Combined these results suggest that, upon oxidation or reduction of the copper ions, the $[\text{Cu}(\mathbf{3})]^{n+}$ fragments are set in motion. Upon oxidation of $[\text{Cu}_2(\mathbf{1a})(\mathbf{3})_2]^{2+}$ to $[\text{Cu}_2(\mathbf{1a})(\mathbf{3})_2]^{4+}$, the resulting tetrahedrally coordinated Cu(ii) ions are unstable and this leads to the migration of the $[\text{Cu}(\mathbf{3})]^{n+}$ fragment to the 2,2':6',2''-terpyridine (**5**) ligands generating the more stable five-coordinate $[\text{Cu}(\mathbf{5})(\mathbf{3})]^{2+}$ complex (Scheme 1(iii)). Similarly, upon reduction of the Cu(ii) back to Cu(i) the $[\text{Cu}(\mathbf{5})(\mathbf{3})]^+$ complex is unstable as the copper(i) ions are in the pentacoordinate trigonal bipyramidal environment. As such the $[\text{Cu}(\mathbf{3})]^{n+}$ fragments migrate back to the ferrocene rotor **1a** regenerating the complex $[\text{Cu}_2(\mathbf{1a})(\mathbf{3})_2]^{2+}$ and returning the copper(i) ions to the preferred tetrahedral coordination environment.

Herein we have shown that readily synthesised 2,2'-bipyridine-appended ferrocene rotor molecules can be switched from a



folded/stacked (*syn*) to an extended/unstacked (*anti*) conformation upon the addition of $[\text{Cu}(\text{CH}_3\text{CN})_4](\text{PF}_6)_2$ and 6,6'-dimesityl-2,2'-bipyridine to the rotor units. This switching is driven by a combination of electrostatic and steric repulsion which destabilizes the *syn* conformation upon copper(I) complexation and generates the *anti* rotamer. This extension and contraction process was completely reversible and could be triggered either chemically or electrochemically. The chemically driven process can be repeated multiple times but a large amount of Cu(II)-cyclam waste slowly builds up in solution. The switching of the rotor can also be triggered electrochemically. Oxidative bulk electrolysis of the $[\text{Cu}_2(\mathbf{1a})(\mathbf{3})_2](\text{PF}_6)_2$ rotor complex in the presence of two equivalents of 2,2':6',2''-terpyridine (**5**) was accompanied by a colour change from deep red/brown to yellow indicative of the translocation of the $[\text{Cu}(\mathbf{3})]^{2+}$ fragment to the 2,2':6',2''-terpyridine (**5**) ligands and the formation of *syn*-**1a**. Reduction of the mixture restored the original red/brown colour suggesting the $[\text{Cu}(\mathbf{3})]^+$ fragment has moved from the 2,2':6',2''-terpyridine (**5**) back to the rotor **1a** regenerating the extended *anti*- $[\text{Cu}_2(\mathbf{1a})(\mathbf{3})_2](\text{PF}_6)_2$ rotor complex. This electrochemical process provides a clean reversible method for the extension and contraction of the ferrocene rotors.

The findings presented here could enable the generation of new, readily accessible, non-interlocked, electrochemically switchable bistable molecular machines or catalysts.²⁵ Inspired by the molecular "folding ruler" of Takeuchi and co-workers²⁶ we are currently attempting to generate longer ferrocene oligomers that will undergo a larger molecular extension and contraction and exploit these molecules as (nano)molecular actuators.

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