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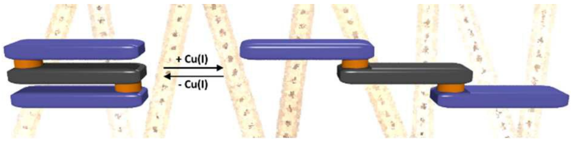

A bis(ferrocene) three tiered molecular folding ruler can be induced to undergo a large scale extension and contraction process either chemical or better electrochemical methods.

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A Ferrocene Based Switchable Molecular Folding Ruler

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A 2,2'-bipyridine-appended bis(ferrocene) three tiered molecular folding ruler, can be switched from a folded conformation to an extended conformation by the addition of [Cu(CH_3CN)$_4$](PF_6) and 6,6'-dimesityl-2,2'-bipyridine. This extension and contraction process could be triggered either chemically or electrochemically and was reversible.

Nanoscale molecular machines are critical for the functioning of biological systems.[1] Inspired by these systems chemists have begun to create synthetic analogues.[2] Molecular machines based on both mechanically interlocked architectures (MIAs) and non-interlocked systems have been developed and the pioneering work in this area led to the award of the 2016 Nobel prize in Chemistry to Sauvage, Stoddart and Feringa.[3] While MIAs have been exploited to generate some impressive synthetic machines, including synthetic rotary motors,[4] molecular muscles,[5] and a sequence-specific peptide synthesiser[6] there have been increasing efforts to generate non-interlocked systems, as they are potentially synthetically more accessible. In particular, systems incorporating metal ions are becoming more and more common due to the useful kinetic and thermodynamic properties of the coordination bonds.[7] Non-interlocked synthetic machines have been exploited to develop rotary motors,[8] molecular walkers[7c, 9] and robots.[10] More recently, non-interlocked rotary motors have also been used to "drive" nanocars across surfaces,[11] and contract[12] and expand[13] gels.

Sandwich complexes such as ferrocene (**fc**),[14] metallocarboranes[15] and lanthanide bis(porphyrinate)s[16] have been used as rotary components in a range of non-interlocked molecular machines due to their molecular ball-bearing[17] properties.[18] However, the vast majority of these sandwich systems only contain one molecular ball-bearing unit and switch from a stacked (*syn*) to unstacked (*anti*) state (Figure 1a). The exception is the elegant polymeric molecular folding ruler of Takeuchi and co-workers.[16e] The authors developed a polymer containing zinc porphyrin units as a recognition site for a ditopic guest molecule, and cerium(IV) bis(porphyrinate) rotatable joints. The system was designed to extend and contract upon treatment with a chemical stimulus in a similar fashion to muscles. In its natural state the cerium(IV) bis(porphyrinate) polymer adopts an extended conformation, and the addition of 1,4-diazabicyclo[2.2.2]octane (DABCO) was supposed to induce the folding of the "ruler" into a contracted stacked form. Unfortunately, while UV-vis spectroscopy confirmed the binding DABCO to the zinc porphyrin sites, dynamic light scattering experiments indicated that there was little contraction observed, with the average polymer size remaining approximately 12 nm in diameter. The re-"extension" of the polymer was achieved via protonation of the DABCO guest with trifluoroacetic acid.

Herein, inspired by the design of the polymeric folding ruler,[16e] we build on our previous work with ferrocene rotors[14e, 14f] and report a triple tiered diferrocene molecular folding ruler (Figure 1, **difcbipy**). Additionally, we examine the switching from a stacked (*syn*, *syn*) to an extended (*anti*, *anti*) conformation, driven by the complexation and decomplexation of a copper 6,6'-dimesityl-2,2'-bipyridine fragment to the 2,2'-bipyridyl (**bipy**) binding sites of **difcbipy**. The system was studied using a combination of nuclear magnetic resonance (NMR), and UV-vis spectroscopies, cyclic voltammetry (CV) and density functional theory (DFT). Similar to our previously reported monoferrocene rotary switch,[14f] a combination of electrostatic and steric repulsion destabilises the *syn*, *syn* conformation of **difcbipy** upon complexation generating the *anti*, *anti* rotamer. This extension and contraction process was completely reversible and could be triggered either chemically or electrochemically.

The triple tiered diferrocene folding ruler (**difcbipy**) was synthesised from 1-(5-yl-ethynyl-2,2′-bipyridine)-1′-iodo-ferrocene[14f] and 1,4-diethynyl-2,5-bis(hexyloxy)benzene in modest yield (12%) synthesised using modified literature procedures (ESI†).[19] ^{1}H NMR spectroscopy, density functional theory (DFT) calculations and X-ray crystallography were used to determine the preferred conformation of **difcbipy** (ESI†). The proton signals associated with the internal pyridyl (H_{d-f}, $\Delta\delta$ = 0.1-0.12 ppm) and phenyl rings ($\Delta\delta$ = 0.18 ppm) of **difcbipy** were shifted upfield relative to those of the singly armed model compounds (1-(5-yl-ethynyl-2,2'-bipyridine)ferrocene and 1,4-diethynyl-2,5-bis(hexyloxy)benzene (**S4**), suggesting that **difcbipy** adopted a stacked (*syn*, *syn*) conformation in solution (ESI†). This was further supported by computational modelling of the system. DFT calculations (CAM-B3LYP/6-31G(d), DMF solvent field) were used to determine the

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relative energies of a series of different rotational conformers of **difcbipy** (the angle (α) between the bipy and phenyl "arms" of **difcbipy** was varied from -180˚ to 180˚ and the compound energy minimised). These calculations showed, as expected, that the stacked, fully eclipsed (*syn*, *syn*) rotamer (initial angle α = 0˚) was the lowest energy conformation for difcbipy by 10 kJ mol^{-1} (Fig. 2a, ESI†). Additional evidence for stacked (*syn*, *syn*) conformation was obtained from X-ray crystallography (Fig. 2b and ESI†). The molecular structure of **difcbipy** clearly showed that the bipyridyl and phenyl substituents are stacked (centroid-centroid distance 3.737 Å) and the ferrocene cyclopentadiene (Cp) rings are eclipsed, with a dihedral angle of 3.98˚ between the substituents, consistent with the ^{1}H NMR spectral and computational data (Fig. 2b and ESI†).

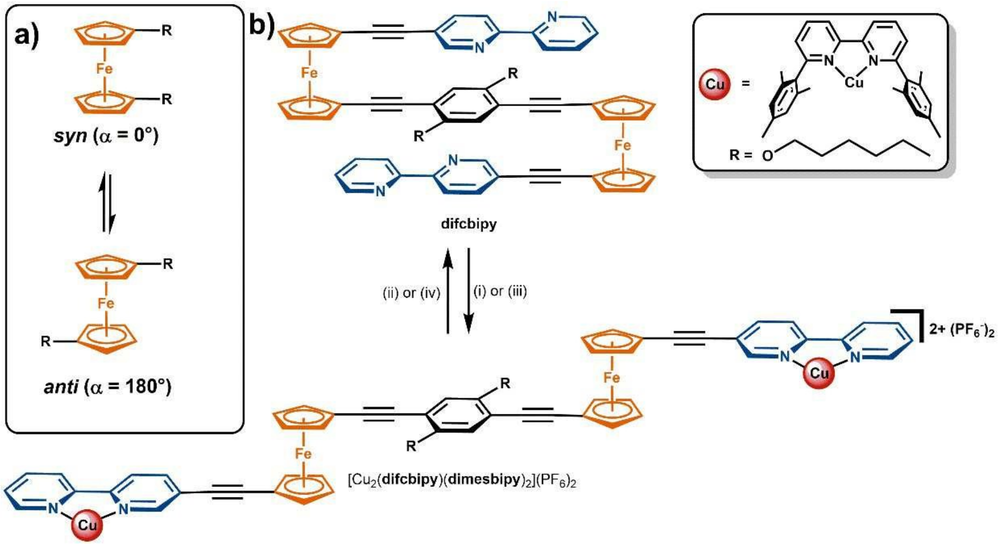

Figure 1. a) Generic stimuli responsive switching of ferrocene (**fc**) rotor molecules b) Synthesis of the dicopper(I) complex $[Cu_2(\textbf{difcbipy})(\textbf{dimesbipy})_2](PF_6)_2$ from **difcbipy** and the chemical and electrochemical switching. (i) $[Cu(CH_3CN)_4](PF_6)$ (2 eq.), **dimesbipy** (2 eq.), $CDCl_3$, 298 K; (ii) **cyclam** (2 eq.), $CDCl_3$, 298 K; (iii) +2e$^-$, acetone, 0.1 M NBu_4PF_6 ; and (iv) **terpy** (2 eq.), -2e$^-$, acetone, 0.1 M NBu_4PF_6.

We chose to use the copper(I) 6,6'-dimesityl-2,2'-bipyridine[20] complex $[Cu(\textbf{dimesbipy})(CH_3CN)_2]^+$ developed by Schmittel and co-workers to unfold the **difcbipy** (Fig. 1b). The complex is well known to cleanly form heteroleptic complexes such as $[Cu(\textbf{bipy})(\textbf{dimesbipy})]^+$ and we[14f] and others[21] have previously used the motif to generate switchable systems. Reaction of **difcbipy** in acetone solution with $[Cu(CH_3CN)_4](PF_6)$ and the sterically bulky bipyridine ligand 6,6'-dimesityl-2,2'-bipyridine[20] (**dimesbipy**) was accompanied by a colour change from orange to red indicative of complexation (Fig. 1b and ESI†).[14f, 22] ^{1}H NMR, ^{13}C NMR, and IR spectroscopy, combined with HRESI-MS and elemental analysis, confirmed the formation of the expected dicopper(I) complex $[Cu_2(\textbf{difcbipy})(\textbf{dimesbipy})_2](PF_6)_2$. The mass spectrum of the complex displayed two peaks at m/z = 981.3261 $[Cu_2(\textbf{difcbipy})(\textbf{dimesbipy})_2]^{2+}$ and m/z = 2107.6128 $[Cu_2(\textbf{difcbipy})(\textbf{dimesbipy})_2(PF_6)]^+$ consistent with the clean formation of the dicopper(I) complex (ESI†).

Due to the combination of electrostatic and steric repulsion generated upon complex formation it was expected that the **difcbipy** would switch conformation from the *syn*, *syn* to the *anti*, *anti* rotamer.[14f] An examination of the ^{1}H NMR spectra of the complex $[Cu_2(\textbf{difcbipy})(\textbf{dimesbipy})_2](PF_6)_2$, the diferrocene folding ruler **difcbipy** and the corresponding model compound **S4** provided experimental support for this conformation switch on complexation. As discussed above, the proton resonance of the central phenyl unit of **difcbipy** was shifted upfield relative to those of the model compound **S4**, indicating that the triple tiered diferrocene folding ruler phenyl rings adopts a stacked (*syn*, *syn*) conformation in solution (ESI†). Upon complexation to the $[Cu(\textbf{dimesbipy})]^+$ the proton signals of the phenyl unit shift downfield to a value that was almost identical to that observed for the model compound **S4** indicating that the phenyl arm of the dicopper(I) complex is no longer π-stacked (ESI†).

DFT calculations (CAM-B3LYP/6-31G(d), DMF solvent field) were used to examine the relative energies of different rotational conformers of the dicopper(I) complex $[Cu_2(\textbf{difcbipy})(\textbf{dimesbipy})_2](PF_6)_2$ (ESI†). The resulting energy plot revealed that the *anti*, *anti* rotamer (α = 180˚) was the lowest energy conformation (ESI†). Futhermore, as the angle (α) between the central phenyl and terminal bipy "arms" of the folding ruler complex was reduced the energy increased. The energies of conformations with α ≤ 100˚ were so high that these rotamers would not be readily accessible, presumably due to the electrostatic and steric repulsion (ESI†). Thus it can be surmised that the bipy arms of the rotor must have extended to at least 100˚ away from the central phenyl arm in solution, generating an *anti*, *anti* rotamer. Disappointingly, we were unable to generate X-ray quality single crystals of $[Cu_2(\textbf{difcbipy})(\textbf{dimesbipy})_2](PF_6)_2$ despite extensive efforts.

Having confirmed that **difcbipy** (*syn*, *syn*) and the corresponding dicopper(I) complex (*anti*, *anti*) would adopt two different conformations we next examined if we could cleanly and reversibly switch between the folded and extended conformations. Addition of two equivalents of 1,4,8,11-tetraazacyclotetradecane (cyclam) to an chloroform ($CDCl_3$) solution of $[Cu_2(\textbf{difcbipy})(\textbf{dimesbipy})_2](PF_6)_2$ caused an immediate colour change from red to orange (Fig. 1b (ii), ESI†) and the precipitation of a white solid, indicating that the Cu(I) ions had been removed from the ferrocene complex.[21a, 21b] ^{1}H NMR and UV-vis spectroscopy and ESMS (ESI†) confirmed that only the free **difcbipy** and **dimesbipy** were present in solution.

Addition of two equivalents of $[Cu(CH_3CN)_4](PF_6)$ to the solution regenerated the characteristic red colour of the complex

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$[Cu_2($**difcbipy**$)($**dimesbipy**$)_2](PF_6)_2$, and the ^1H NMR spectrum (ESI†) indicated that the complex had quantitatively re-formed. This chemically driven *syn*, *syn*-to-*anti*, *anti* switching process could be repeated a number of times (>5) indicating that switching was completely reversible (ESI†). However, the method led to the build-up of waste by-products (Cu(II)-cyclam) which could potentially lead to the loss of function.[23] Therefore we also examined whether the electrochemical Cu(I)/Cu(II) switching process developed by Sauvage *et al.*[24] could be exploited to extend and contract **difcbipy**.

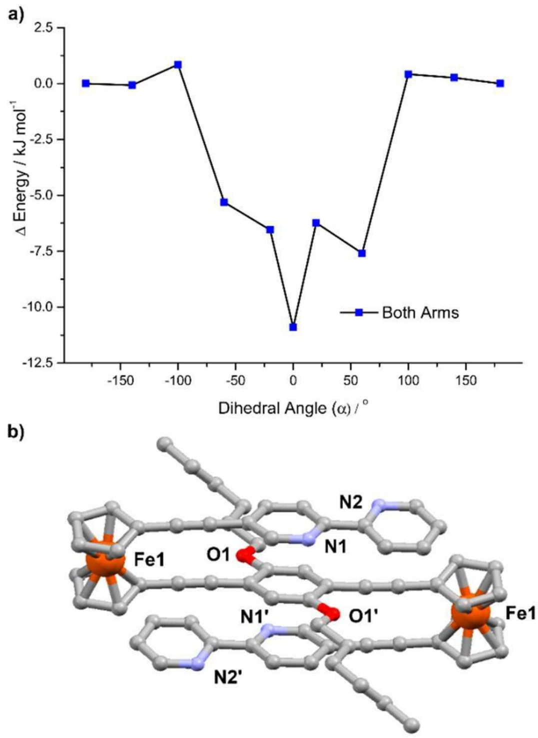

Figure 2. a) A plot showing the calculated (DFT, CAM-B3LYP, DMF solvent field) relative energy of the different conformers of **difcbipy** across a range of dihedral angles, b) a ball-and-stick representation of the solid state structure of **difcbipy**. Hydrogen atoms of the complex are omitted for clarity. Additional crystallographic details can be found in the ESI†.

CV (100 mV s^{-1}, acetone, 0.1 M NBu_4PF_6) experiments showed that the $[Cu_2($**difcbipy**$)($**dimesbipy**$)_2](PF_6)_2$ complex displays two chemically reversible processes at 0.66 and 0.80 V respectively (Fig. 3 red/brown trace) while the **difcbipy** displays a single ferrocenyl based chemically reversible processes at 0.73 V. By comparison with the related previously prepared model systems[22, 25] the first oxidation process of $[Cu_2($**difcbipy**$)($**dimesbipy**$)_2](PF_6)_2$ was assigned to the $Cu^{II/I}$ couple while the second oxidation process is ferrocenyl based.

The CV experiment with $[Cu_2($**difcbipy**$)($**dimesbipy**$)_2](PF_6)_2$ was then carried out in the presence of two equivalents of 2,2′:6′,2″-terpyridine (**terpy**). The anodic potential sweep showed the two peaks corresponding to the $Cu^{II/I}$ 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 $[Cu_2($**difcbipy**$)($**dimesbipy**$)_2]^{4+}$ complex was observed. Instead proceeding in the cathodic direction, a peak corresponding to the reduction of the pentacoordinated $[Cu($**dimesbipy**$)($**terpy**$)](PF_6)_2$ complex was observed at -0.15 V (Fig. 4 black trace). This electrochemical behaviour is very similar to that observed previously by us with our monoferrocene rotor system[14f] and Sauvage *et al.*[24a, 24b] in their molecular machines.

Bulk electrolysis in the presence of two equivalents of **terpy** was accompanied by a colour change from deep red/brown to orange, the same as was observed for the chemical switching process with cyclam (ESI†). Spectroelectrochemistry (acetone, 0.1 M Bu_4NPF_6, OTTLE cell, ESI†) of the $[Cu_2($**difcbipy**$)($**dimesbipy**$)_2](PF_6)_2$ complex confirmed that during the bulk oxidation the MLCT band (λ_{max} = 460-470 nm) decreases until a spectrum consistent with "free" **difcbipy** is generated. ESI-MS analysis of the **terpy** and $[Cu_2($**difcbipy**$)($**dimesbipy**$)_2](PF_6)_2$ mixture before bulk electrolysis displayed peaks due to the $[Cu_2($**difcbipy**$)($**dimesbipy**$)_2(PF_6)]^+$, $[Cu_2($**difcbipy**$)($**dimesbipy**$)_2]^{2+}$ and $[$**terpy**$+H]^+$ ions. After oxidation the mass spectrum only contain peaks consistent with $[Cu($**terpy**$)($**dimesbipy**$)]^{2+}$, $[$**difcbipy**$+H]^+$ and $[$**difcbipy**$+Na]^+$ ions.

Combined these results suggest that, upon oxidation or reduction of the copper ions, the $[Cu($**dimesbipy**$)]^{n+}$ fragments are set in motion, as was observed in the monoferrocene rotor system.[14f] Upon oxidation of $[Cu_2($**difcbipy**$)($**dimesbipy**$)_2]^{2+}$ to $[Cu_2($**difcbipy**$)($**dimesbipy**$)_2]^{4+}$, the resulting tetrahedrally coordinated Cu(II) ions are unstable and this leads to the migration of the $[Cu($**dimesbipy**$)]^{2+}$ fragment to the **terpy** ligands generating the more stable five-coordinate $[Cu($**terpy**$)($**dimesbipy**$)]^{2+}$ complex.[14f] Similarly, upon reduction of the Cu(II) back to Cu(I) the $[Cu($**terpy**$)($**dimesbipy**$)]^+$ complex is unstable as the copper(I) ions are in the pentacoordinate trigonal bipyramidal environment. As such the $[Cu($**dimesbipy**$)]^+$ fragments migrate back to the **difcbipy** regenerating the complex $[[Cu_2($**difcbipy**$)($**dimesbipy**$)_2]^{2+}$, and returning the copper(I) ions to the preferred tetrahedral coordination environment. This results in an electrochemically induced extension and contraction of the diferrocene molecular folding ruler **difcbipy**.

Herein we have shown that a 2,2'-bipyridine-appended triple tiered diferrocene molecular folding ruler **difcbipy** can be switched from a folded/stacked (*syn*, *syn*) to an extended/unstacked (*anti*, *anti*) conformation upon the addition of $[Cu(CH_3CN)_4](PF_6)$ and **dimesbipy** to the rotor units. This switching is driven by a combination of electrostatic and steric repulsion which destabilizes the folded conformation upon copper(I) complexation and generates the extended rotamer. The 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 electrochemical switching, in the presence of **terpy**, provides a clean reversible method for the extension and contraction of the diferrocene molecular folding ruler. Furthermore, the extension and contraction of the diferrocene molecular folding ruler is of a larger magnitude than that observed for previously reported ferrocene switches.[18]

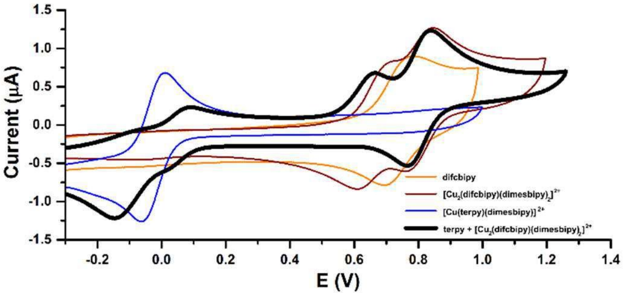

Figure 3. CVs (100 mV s^{-1}, acetone, 0.1 M Bu_4NPF_6) of the **difcbipy** (–), $[Cu_2($**difcbipy**$)($**dimesbipy**$)_2](PF_6)_2$ (–), $[Cu($**terpy**$)($**dimesbipy**$)](PF_6)_2$ (–), and $[Cu_2($**difcbipy**$)($**dimesbipy**$)_2](PF_6)_2$ in the presence of **terpy** (–).

The findings presented suggest that the molecular "folding ruler" design of Takeuchi and co-workers[16e] could potentially be exploited to develop stimuli responsive (nano)molecular actuators. We are currently trying to improve the synthesis of the ferrocene based folding ruler unit and develop methods to incorporate them into condensed phases in order to transfer the molecular level motion into useful work.

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†Electronic Supplementary Information (ESI) available: the supplementary information contains the experimental procedures, ^{1}H and ^{13}C NMR, HR-ESI-MS, UV-Vis, electrochemical and crystallographic data. CCDC reference number 1527569. See DOI: 10.1039/b000000x/

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