Oxidation triggers guest dissociation during reorganization of an $\text{Fe}^{II}_{4}\text{L}_6$ twisted parallelogram†

Alex J. Plajer,‡ Felix J. Rizzuto,‡ Larissa K. S. von Krbek,§ Yohan Gisbert, Victor Martínez-Agramunt and Jonathan R. Nitschke

A three-dimensional $\text{Fe}^{II}_{4}\text{L}_6$ parallelogram was prepared from ferrocene-containing ditopic ligands. The steric preference of the bulky ferrocene cores towards meridional vertex coordination brought about this new structure type, in which the ferrocene units adopt three distinct conformations. The structure possesses two distinct, bowl-like cavities that host anionic guests. Oxidation of the ferrocene $\text{Fe}^{III}$ to ferrocenium $\text{Fe}^{IV}$ causes rotation of the ferrocene hinges, converting the structure to an $\text{Fe}^{IV}_{4}\text{L}_6$ species with release of anionic guests, even though the average charge per iron increases in a way that would ordinarily increase guest binding strength. The degrees of freedom exhibited by these new structures – derived from the different configurations of the three ligands surrounding a meridional $\text{Fe}^{II}$ center and the rotation of ferrocene cores – thus underpin their ability to reconfigure and eject guests upon oxidation.

The phenomenon of mer or fac coordination is exclusive to octahedral coordination geometries around metal vertices. Other geometries, such as square planar motifs, lead to the formation of entirely different polyhedra,21–23 while tetrahedral metal-binding pockets can lead to helicates or interlocked structures.28–34 Other metal coordination motifs that are tied to their own rules of isomerism could lead to new families of metal–organic polyhedra.

Among such motifs, metalloccenes35–44 can display conformational isomerism by rotation of the cyclopentadiene ligands with respect to one another. The different eclipsed and staggered conformations of metalloccenes offer a large range of possible dihedral angles between covalently-connected substituents, rendering such building blocks attractive in the synthesis of low-symmetry metal–organic assemblies.

We thus envisioned that the incorporation of metalloccene ligands into supramolecular capsules with octahedral metal ion vertices could enable the formation of low-symmetry products. Metalloccenes are furthermore redox-active, enabling potential stimuli-responsive behavior45–53 that may be used for different host–guest interactions,54–57 such as redox-triggered guest ejection or structural reconfiguration,55,56

Results and discussion

Here we show the use of a ferrocene-containing ditopic ligand to generate a low-symmetry $\text{M}_{4}\text{L}_6$ assembly, with electrochemical, magnetic, and optical functionality. Ferrocene is sterically demanding and can rotate, adopting conformers along the Cp–Fe–Cp axis. This flexibility enables a single ligand to adopt multiple rotational conformations, creating a new structure type: twisted parallelogram 1 (Fig. 1).
The reaction of A,$^{27}$ 2-formylpyridine, and Fe$^{	ext{II}}$(PF$_6$)$_3$ in CD$_3$CN (Fig. 1a) gave rise to a $^1$H NMR spectrum with six sets of ligand environments per diimine ligand L$^A$ (Fig. S1–S4†). All signals gave the same rate of diffusion by $^1$H DOSY NMR spectroscopy, consistent with the formation of a single species (Fig. S12†). Two-dimensional NMR spectra suggested that the structure contained two distinct mer coordination environments (Fig. S6–S11†). Low and high resolution ESI mass spectrometry corresponded to an Fe$^{	ext{III}}$L$_6$ assembly (Fig. S15 and S16†).

Employing preformed ligand L$^{	ext{azo}}$ (a congener of LA with diazo, instead of diimine, coordinating units) with Fe$^{	ext{II}}$(NTf$_2$)$_2$ during assembly resulted in the formation of a product L$^{	ext{azo}}$ that appeared isostructural to 1 by NMR and ESI-MS (Fig. 2a, ESI Section 2.2†). Single crystals of L$^{	ext{azo}}$ suitable for X-ray diffraction studies were grown. The crystal structure confirms the formation of an Fe$^{	ext{III}}$L$_6$ assembly with meridional coordination vertices (Fig. 2). As observed in solution, there are two distinct mer coordination environments in the solid state, imparting approximate $C_2$ symmetry. The two enantiomers co-crystallized, and are related by inversion symmetry in the crystal. They are composed of alternating $\Delta$ and $\Lambda$ pyridyl-imine Fe$^{	ext{III}}$ centers that frame a parallelogram. The overall scaffold can be visualized as two connected, twisted diamonds (Fig. 1c).

Of the many possible rotational conformers of L$^A$, only three were observed in 1: four of the six ferrocene units accommodate a slightly staggered conformation, with the phenylene substituents spread by 59$^\circ$ and 126$^\circ$, respectively, and two are in an eclipsed conformation, with phenylene units 72$^\circ$ apart (Fig. 1a, bottom). This new structure type is enabled by the bulky but flexible ferrocene linkers; mer-coordinated rigid ditopic linkers have been observed to form barrel-like or cubic assemblies instead.$^{19,21,28-40}$ The formation of 1 thus illustrates how the conformational flexibility associated with bis-coordinated metal-allocenes may lead to the formation of otherwise inaccessible supramolecular structure types.

Assembly 1 shows two distinct binding pockets for guests in the solid state, within which two anions are found. These pockets are defined by ferrocene subunits, which extend above and below the plane of the four mer-coordinated Fe$^{	ext{II}}$ vertices (Fig. 2b and c).

The $^{19}$F NMR spectrum of 1 showed two sets of PF$_6^-$ resonances, suggesting binding of PF$_6^-$ within 1 in slow exchange on the NMR timescale (Fig. S13†). We infer the presence of suitably-shaped anions to lock the rotation of the ferrocene units in 1 into a single configuration. When Fe$^{	ext{II}}$(OTf)$_2$ was used instead of the hexafluorophosphate salt, a broader $^1$H NMR spectrum was observed, with ESI mass spectra confirming the presence of assembly 1 (Fig. S14 and S17†). PF$_6^-$ was thus necessary to generate a sharp NMR spectrum, which corresponds to the solid-state configuration in Fig. 2. Due to the broad $^1$H NMR spectra of the assemblies formed with anions other than PF$_6^-$, we were unable to perform titrations that would provide accurate binding affinities for guests within 1.

Having confirmed the unique geometry of 1, we investigated its electrochemical properties. Ferrocene is a well-studied one electron reductant ($E = 0.4$ V vs. SCE; 0 V vs. Fe/Fc$^+$$^-$$^+$). Cyclic voltammetry experiments conducted in 0.1 M Bu$_4$PF$_6$/CH$_3$CN electrolyte revealed one redox process centered at $E^\text{1/2} = 0.3$ V, and one irreversible process at $E^\text{1/2} = 1.1$ V vs. Fe/Fc$^+$$^-$$^+$ (Fig. S18 and S19†). We assigned these processes to the oxidation of the ferrocene units, and to the oxidation of the Fe$^{	ext{II}}$ vertices, respectively. The observation that all ferrocene cores undergo
oxidation simultaneously suggests there is no electronic communication between metallocene cores within 1.

To assess the structural effects of oxidizing the ferrocene cores within 1, we added 6 equivalents of [NO]PF₆ (Fig. 3a) (a 1e⁻ oxidant, *E* = 0.87 V vs. Fe/Fe⁺), which can only oxidize the ferrocene units, and not the Fe³⁺ vertices,† to a solution of 1 in CH₂CN (Fig. 3). In contrast to the case for 1, where six ligand environments were observed in the diamagnetic region (ca. 0 to 10 ppm, Fig. 3b and S2†) of the NMR spectrum, the wide sweep ¹H NMR spectrum (ca. −60 to 300 ppm) of the oxidized product showed only one set of ligand environments (Fig. 3c and S23†). This spectrum was consistent with the formation of a highly-symmetric, paramagnetic species. High-resolution ESI-MS confirmed the formation of [FeL⁺] complex 2 (Fig. S27†). The spectra of complex 2 suggest the adoption of a conformation of the ferrocene moieties in which the phenylene linkers stack on top of each other (Fig. 3a). High resolution MS-MS studies on 2 furthermore revealed that the *z* = ±1 peak of 2 fragmented only into the oxidised ferrocene ligand L⁺; no protonated neutral ligand was observed (Fig. S28†). These observations indicated that the Fe³⁺(pyridylimine) vertices were not oxidised (i.e., they remained as Fe²⁺) following the oxidation of ferrocene to ferrocenium.

Attempted chemical reduction via treatment of 2 with 6 equivalents of tetrakis(dimethylamine)ethylene reductant did not result in the clean regeneration of 1. All paramagnetic NMR signals disappeared, but no clean NMR spectrum corresponding to 1 was observed, although some degree of reversibility was indicated by UV-vis titration (Fig. S33†). We infer that small amounts of free, insoluble Fe⁴⁺ products were generated during oxidation (and potential reaction with NO radicals), hampering reassembly.

To assess the electronic and optical effects of ferrocene oxidation, we titrated [NO]PF₆ into a CH₂CN solution of 1 and followed the UV-vis spectral progressions upon oxidation (Fig. 3d). The most pronounced change in the UV-vis spectra was the loss of the Fe⁴⁺(pyridylimine) MLCT bands at 500–600 nm, which brings about a color change from the purple of 1 to the orange of 2. A shifting crossover point was observed during the titration, as opposed to a regular isosbestic point. This observation indicated that the conversion of 1 into 2 was not a simple process, suggesting the presence of intermediates.

Similar spectral progressions were observed by UV-vis spectroelectrochemical measurements. An applied potential of +0.7 V vs. Ag⁺/Ag resulted in a decrease of the MLCT band, which regenerated upon relieving the applied potential (Fig. S30 and S31†). Unlike experiments involving chemical oxidation, which were allowed to equilibrate before collection of spectra, spectroscopy during electrochemical oxidation was done continuously, giving rise to differences in spectral progression between these two experiments. Both optical spectroscopy experiments suggest that the *mer*-Fe²⁺ metal centers transition from low to high spin upon oxidation of the ferrocene centres of 1.

Taken together, our NMR, MS-MS, optical and electrochemical data suggest that the Fe³⁺ center in 2 is high spin. Mononuclear 2 thus contains high spin pyridylimine-ligated Fe²⁺ (*S* = 2) and a low spin ferrocenium Fe³⁺ (*S* = 1/2). Loss and regeneration of the Fe³⁺ MLCT band upon oxidation and reduction, respectively, along with MS charge and stoichiometry evidence, suggest that the pyridylimine Fe²⁺ center switches from low to high spin upon oxidation of the ferrocene units. The overall *S* = 5/2 spin of the system was confirmed using the Evans method ([ESI Section 4.3†]).

Upon oxidation, we propose that 1 is destabilized by Coulombic repulsion between the Fe³⁺ ferrocenium centres, and between the ferrocenium centres and Fe²⁺ vertices, causing the disassembly of 1 to mononuclear complexes of 2. This disassembly process occurs in multiple steps, leading to the

![Fig. 3](image-url)
observed lack of an isosbestic point in the UV-vis titration – we hypothesize that a fast oxidation process causes a rapid change in the UV-vis spectra, followed by rearrangement and guest release, which is slow and manifests as a gradual transition in the UV-vis spectra (Fig. 3d). We previously observed that Coulombic repulsion between cationic ligands can prevent self-assembly.6,45

The disassembly process also destroys the pockets that bind PF6– anions, leading to their ejection.19F NMR spectroscopy after oxidation shows only one PF6– signal, at the chemical shift of the free anion, indicating that 2 does not interact strongly with PF6– (Fig. S24†). This observation appears counterintuitive: oxidation of 1 should render the assembly more positively charged and make anion binding more favorable. Here, however, destruction of the anion-binding cavities in 1 led to guest ejection in spite of the increased Coulombic attraction anticipated between the more highly-charged iron centers of oxidized 1 and PF6–. This guest ejection via oxidative structural rearrangement thus provides a new mode of control over host-guest chemistry in metal–organic assemblies.

Intrigued by the ability of our ferrocene cores to dictate the mer stereochemistry of tris-pyridylmine metal vertices, we investigated the self-assembly of mono-functional ferrocene-aniline subcomponent B into mononuclear complexes (Fig. 4). The assembly of FeII ions, 2-formylpyridine and B produced mer-3 as the exclusive product (Fig. 4). ESI-MS showed the formation of a discrete FeII3L3 complex, while 1H and 13C NMR showed three distinct ligand environments for mer-3 (Fig. S36 and S37†), as well as confirming the low-spin character of the complex. No equilibration to the statistical mixture (1 : 3 fac : mer) was observed over the range 233–300 K.

Building on observations from other systems,19 we infer that this preference for mer stereochemistry results from steric clash between the ferrocene units in the fac complex in some of their rotational configurations, disfavoring its formation. In the mer structure, rotation of the ferrocene units is unhindered and steric repulsion is minimized, as seen in the MM3 molecular models presented in Fig. 4.

Conclusions

A bulky, axially-flexible ferrocene substituent can thus be used to design low-symmetry assemblies with meridional coordination stereochemistry. The new structure type of assembly 1 can be formed because of the ease of rotation of ferrocenes. Our strategy of using metallocenes of different symmetries may grant access to even larger and more complex assemblies in the future. The oxidation-driven reassembly and guest release demonstrated herein may also be put to use in larger systems, where the anions may be more complex and biologically relevant.

Conflicts of interest

There are no conflicts to declare.

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