# An Acid–Base Controlled Molecular Switch. *syn–anti* Conformational Switching in a $\mu$-oxo Bis(Iron Porphyrin)

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It was found that **FeD** adopted a stable *syn* conformation as a result of the inclusion of atomic oxygen in a $\mu$-oxo fashion, but on exposure to acidic conditions converted into the extended *anti* form. When this was subsequently made basic the *syn* conformation was re-adopted, simply due to re-inclusion of atomic oxygen forming the $\mu$-oxo species. It was found that the combination of these affects allowed **FeD** to undergo repeated conformational switching cycles that were reproducible and robust.

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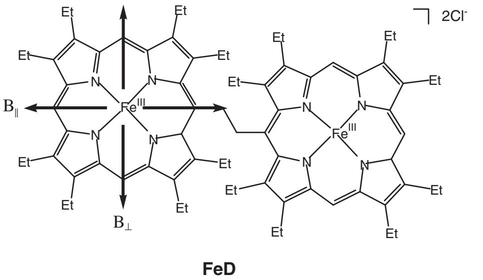
In recent times there has been great interest in the scientific and wider community regarding the progress being made towards the development of molecular devices,[1] in which the rational application of the physico–chemical properties of a molecular system allows tasks to be performed. To this end porphyrins have been widely investigated and applied, finding applications in areas such as: material and nano-science,[2] nonlinear optics,[3] supramolecular chemistry[4] and chirogenesis.[5] Iron porphyrins are an important class of molecule found both in nature, such as in the function of heme groups in haemoglobin and myoglobin,[6] and in the catalytic activity of cytochrome P-450[7] amongst others; and also in synthetic systems such as cytochrome P-450 mimics,[8] models for photosynthetic electron transfer[9] and in catalysis.[10] Recently, application of the properties of bis(iron porphyrin)s has been more increasingly realized, leading to the development of effective catalysts for the selective oxidation and photo-oxidation of organic compounds under mild conditions via the $\mu$-coordinated atomic oxygen.[11] The propensity for forming the $\mu$-oxo dimer has also been applied to the generation of novel structures such as chiral oligomers.[12] In light of the proven effectiveness of the functioning of such bis-porphyrin molecules, we undertook to evaluate the properties and function of the ethane linked bis(iron(III) octaethylporphyrin), **FeD** (Scheme 1).[13] It is hoped that the specific coordination and electrochemical characteristics of bis(iron porphyrin)s in comparison to other metalloporphyrin analogues will open up the ability to study and manipulate new classes of molecule, particularly oxygen and sulphur containing species.



**FeD**

**Scheme 1.** **FeD** dimer (for clarity the $B_{\parallel}$ and $B_{\perp}$ transitions are only shown on one porphyrin ring, and the Fe–Cl coordination bonds are not shown).

It was found that due to the propensity of ferric porphyrins to form oxo-bridged species, and the favourable distance between the porphyrin rings,[14] **FeD** incorporated a single atomic oxygen in a $\mu$-oxo Fe-O-Fe fashion, and existed as *syn* $\mu$-oxo **FeD**. The stability of this species was such that in the electrospray ionization mass spectrum no trace of **FeD** was found, with only the signals corresponding to [$\mu$-oxo **FeD**]$^+$ observed at 1218.5 and 1219.7. Further, it was also electrochemically stable on exposure to potentials of up to $-1000$ mV applied in an attempt to reduce the Fe(III) to Fe(II). Whilst $^1$H NMR spectroscopy was not an appropriate technique for characterizing *syn* $\mu$-oxo **FeD** due to the paramagnetic nature of the Fe ions, UV–vis spectroscopy fully supported the face-to-face orientation of the porphyrin macrocycles. The maximum of the B (Soret) band (407 nm) was blue-shifted in comparison to that of the hetero Fe-2H bis-porphyrin (417 nm)[13] which could not form the $\mu$-oxo dimer due to the absence of a second iron porphyrin, and was thus in an *anti* conformation. However, it was red-shifted in comparison to that of bis(zinc porphyrin) in the *syn* conformation without external ligands (398 nm) due to the atomic oxygen coordination effect, thus clearly revealing the *syn* conformation of $\mu$-oxo **FeD**. These observations are also in good agreement with Kasha's exciton coupling theory.[15] Furthermore, it was recently found that the major B transition of the tweezer conformation of bis(zinc porphyrin) in which 1,2-diamines located between the two porphyrin planes,[16] and the B transition of $\mu$-oxo **FeD** occured at almost the same position (411 and 407 nm, respectively) indicating that the porphyrin rings in the two systems had similar spatial arrangements. To remove the atomic oxygen to thus allow ligand access to the two iron centers a dichloromethane solution of *syn* $\mu$-oxo **FeD** (ca. $1 \times 10^{-6}$ M) was simply treated with a 3 M solution of HCl, resulting in the oxygen free **Fe$^{III}$D** species. Unexpectedly, on examining the UV–vis spectra of this compound it was observed that the spectrum underwent dramatic changes (Figure 1).

The Soret band, previously at 407 nm, had split into two well resolved $B_{\perp}$ and $B_{\parallel}$ transitions (which are in a perpendicular and parallel orientation relative to the axis connecting the two porphyrins, respectively, see Scheme 1), with a blue-shifted maximum at 391 nm and a red-shifted maximum at 422 nm; further, the Q band at 576 nm disappeared with the corresponding appearance of two new Q bands with maxima at 520 nm and 650 nm. These spectral changes reveal that *syn* $\mu$-oxo **FeD** has undergone *syn–anti* conformational switching to form *anti* **FeD** (Figure 2), agreeing well with those predicted by Kasha's exciton coupling theory[15] to be associated with such an event.

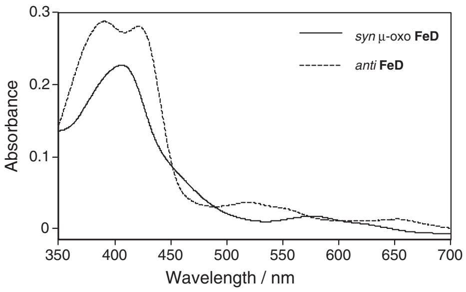


**Figure 1.** The UV–vis spectra of *syn* $\mu$-oxo **FeD** and *anti* **FeD** in dichloromethane.

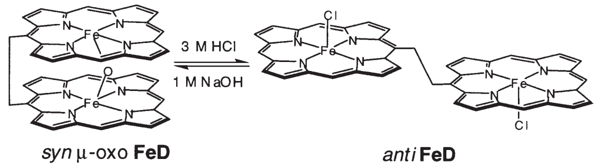


**Figure 2.** Schematic representation of the acid/base mediated molecular switching. The peripheral ethyl groups are omitted for clarity.

Whilst the two pairs of porphyrin electronic transitions ($B_{\parallel}$ and $B_{\perp}$) in *syn* $\mu$-oxo **FeD** are orientated in a parallel fashion, allowing the transitions to the highest level of the $B_{\parallel}$ and $B_{\perp}$ states,[17] the same pairs of electronic transitions in *anti* **FeD** are spatially orientated in a parallel ($B_{\perp}$) and in-line ($B_{\parallel}$) fashion, allowing the transition to the highest level of the $B_{\perp}$ states and to the lowest level of the $B_{\parallel}$ states, this corresponds to the split of the Soret band (Davydov splitting) into the blue-shifted $B_{\perp}$ component and a red-shifted $B_{\parallel}$ component. This phenomenon is often observed for various porphyrin dimers and trimers in linear spatial orientations.[18] Furthermore, the same split is found for the *anti* conformation of bis(zinc porphyrins) in the presence of external ligands[5b,19] as a result of coordination to the zinc ions. To show the reversibility of the switching the acidic solution was treated with 1 M NaOH, resulting in the reappearance of the original UV–vis spectrum, revealing the reverse, *anti–syn*, conformational change (Figure 2).

Subsequent cycles of exposing **FeD** to acidic and basic conditions showed that these *syn* $\mu$-oxo **FeD** to *anti* **FeD** switching cycles were reproducible and robust (Figure 3). Thus, here we have been able to take two known affects ($\mu$-oxo formation in ferric porphyrins, and the destruction of the Fe–O–Fe bond by acid treatment) and combine them in a single molecule to allow this conformational activity. In effect, this cycle has shown that the **FeD** system has acted as an acid/base mediated molecular switch. Thus in this system we are able to make use of the facile formation of the $\mu$-oxo species that in other areas, such as electrochemistry and catalysis, renders the molecule inert, to produce the driving force for these conformational changes. Of note is that the Soret band maximum in the initial *syn* conformation is ca. 3.5 nm more red-shifted in comparison to that when **FeD** is in subsequent *syn* conformations. The rationale for this is likely to be the presence of different counter anions in the initial *syn* $\mu$-oxo **FeD** ($Cl^-$) arising from the synthesis of **FeD**, and that in *syn* $\mu$-oxo **FeD** during the switching cycles ($OH^-$) arising from the NaOH treatment used to increase the basicity. In summary, this work has shown how the inclusion of the phenomena of $\mu$-oxo bond formation in ferric porphyrins, and its destruction by acid treatment into a single molecule enables **FeD** to function as a simple molecular switch that shows robust *syn–anti* conformational switching cycles, achieved by manipulating the acidity/basicity of the solution. In light of the proven functional effectiveness of similar bis-porphyrins elsewhere it is hoped, and intended, that we may further apply these preliminary results, particularly in the area of catalysis.

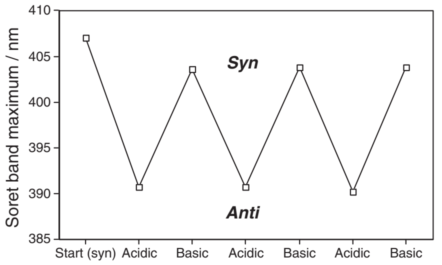


**Figure 3.** Switching cycle showing the position of the Soret band maximum in *syn* $\mu$-oxo **FeD** and the higher energy ($B_{\perp}$) transition in *anti* **FeD**.

### References and Notes

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