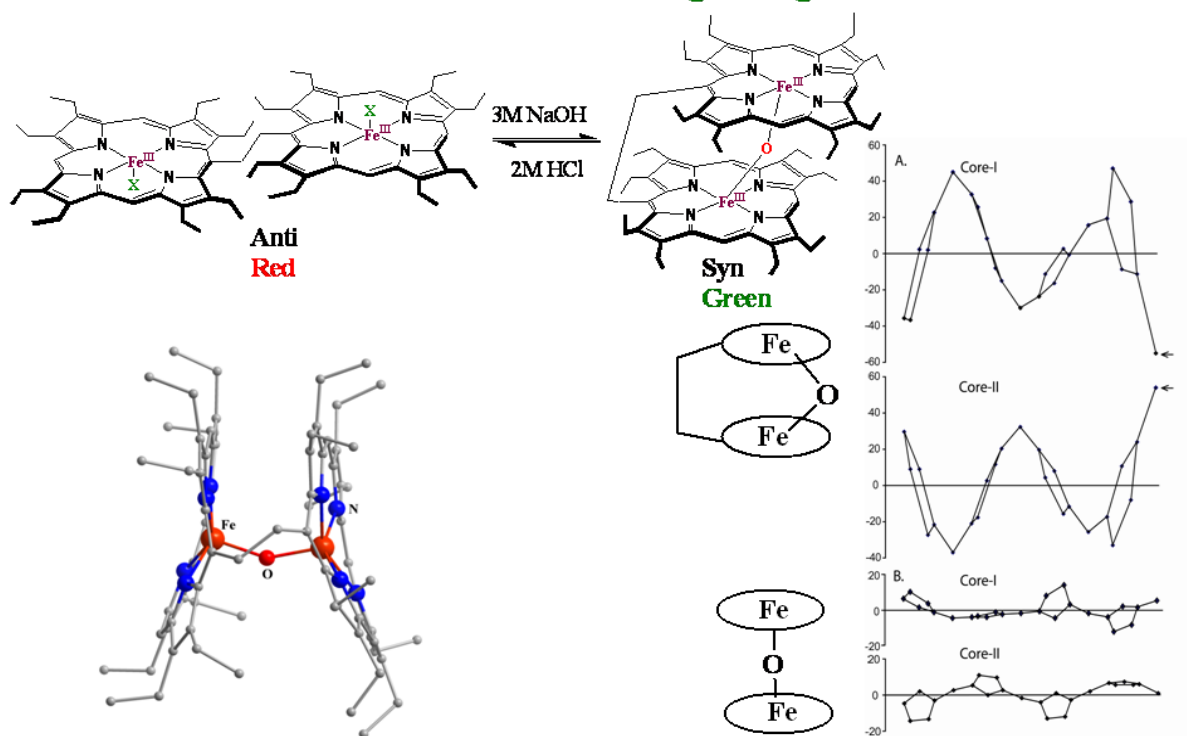


μ -Hydroxo Fe(III) Porphyrin Dimers: Modulation of Metal Spins by Counteranions

Oxo and hydroxo bridged diiron active centers are common structural motifs found in a variety of proteins in biology. The highly versatile oxo/hydroxo-bridged dimetallic centers, regulated by a simple protonation/deprotonation process, permits the enzyme a natural way to control the intermediates in the catalytic cycles. The chemical and electrochemical nature of the Fe-O-Fe/Fe-O(H)-Fe unit are suitably controlled by the intermacrocylic interaction between two heme centers and thereby influence the structure, property and reactivity of the molecule to a large extent. A close approach of the two rings in the ethene and ethane-bridged μ -hydroxo complex results in an unequal core deformations that leads to unusual stabilization of two different spin states of iron(III) in a single molecular framework. Also, spin states vary on the counter ion (X) used and are reversibly interconvertible although the counter anions are far away and not apparently involved in any kind of direct interactions with the metal ion. The small environmental perturbations coming out of the counter anion, H-bonding interaction, heme-heme interaction etc. can change the structure and properties of the individual heme centers drastically and it seems very likely that Nature uses some of these techniques to control the property of the biomolecules for a specific function.

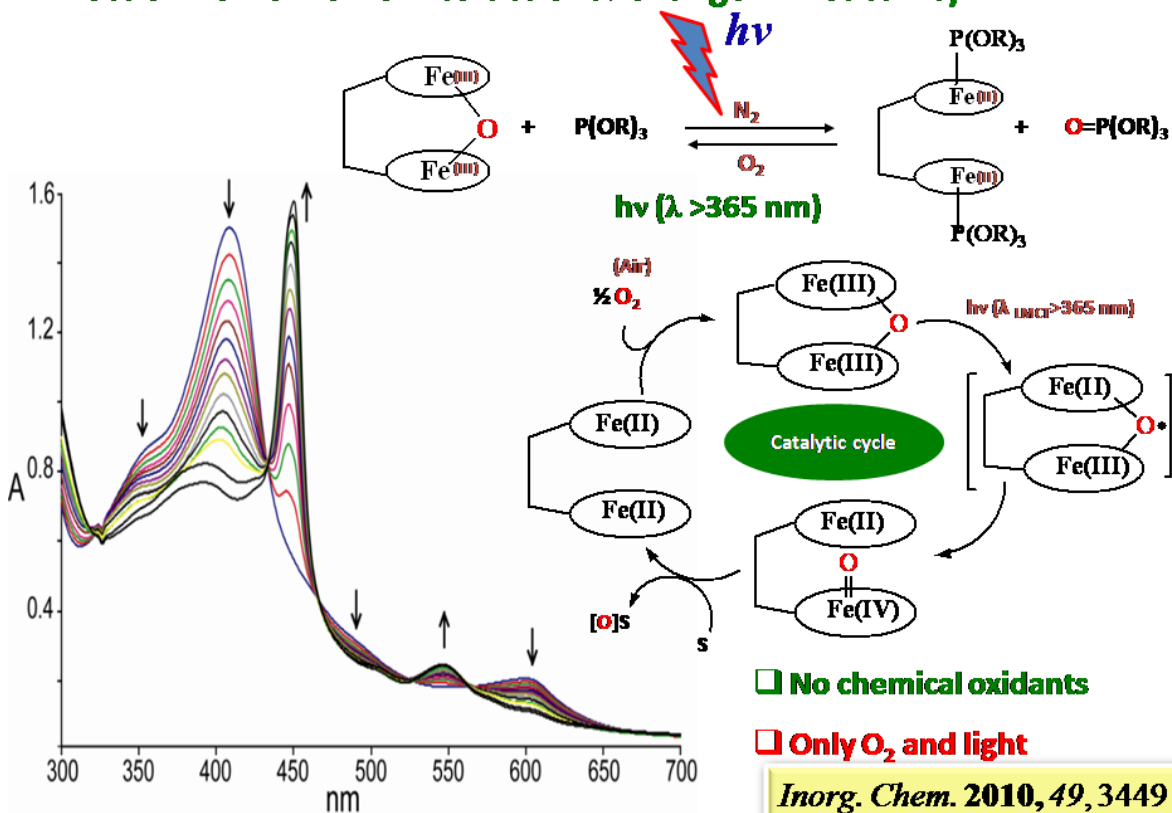
Effect of Heme-Heme Interactions: Large Ring Distortion



Smallest known Fe-O-Fe angle!

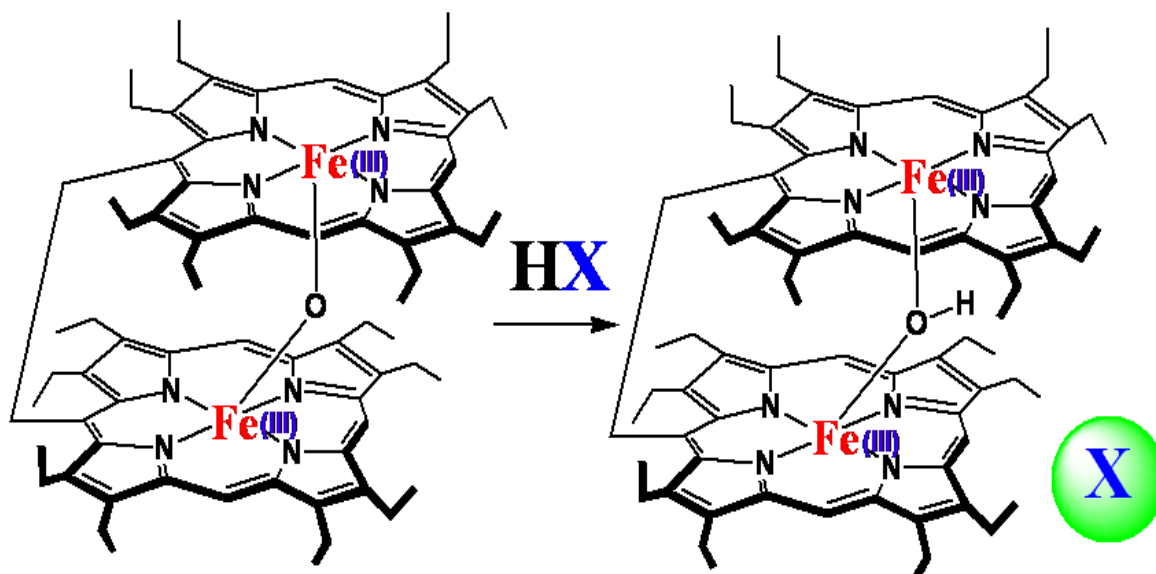
Inorg. Chem. **2010**, *49*, 3449
Inorg. Chem. **2008**, *47*, 10196

Effect of Heme-Heme Interactions: Change in Reactivity



Inorg. Chem. **2010**, *49*, 3449
Inorg. Chem. **2008**, *47*, 10196

Stabilization of Two Different Fe Spins



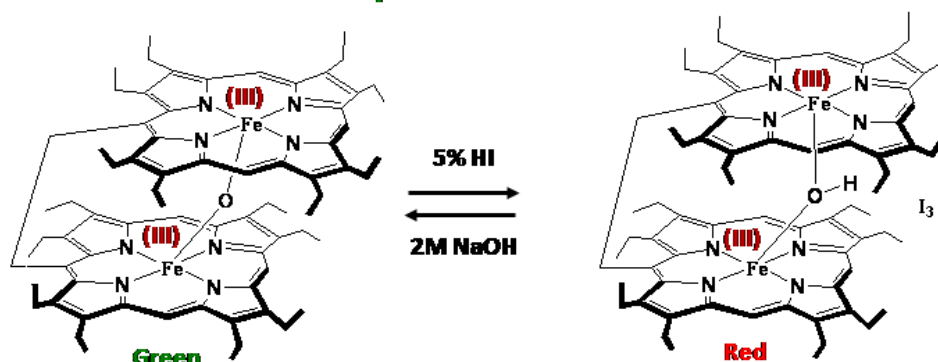
Counter anion is,

- ❖ Very far from the metal ion
- ❖ Still controls the iron spins

Two different spins
of Fe in a single
molecule!!

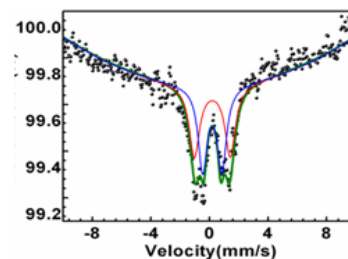
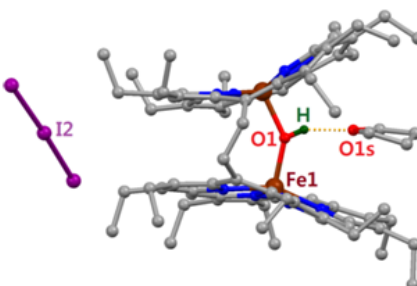
Dalton Trans. **2017**, 46, 1012. (Invited *Perspective article*)
Coord. Chem. Rev. **2017**, 337, 112.

Stabilization of Two Different Fe Spins: Effect of Heme-Heme Interaction



Smallest known Fe-O(H)-Fe angle!

	Core-I	Core-II
Fe-O [Å]	1.897(3)	1.934(3)
Fe-N ₄ [Å]	2.051(3)	2.007(3)
Fe-O-Fe [°]	142.5(2)	
$\Delta 24^{Fe}$ [Å]	0.55	0.48
$\Delta 24$ [Å]	0.21	0.30
Spin state	S = 5/2, 3/2	

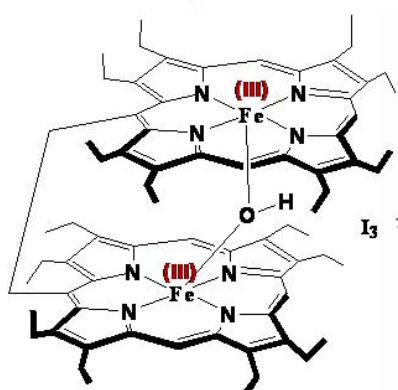


IS: 0.30 mm/s
QS: 2.12, 1.15 mm/s

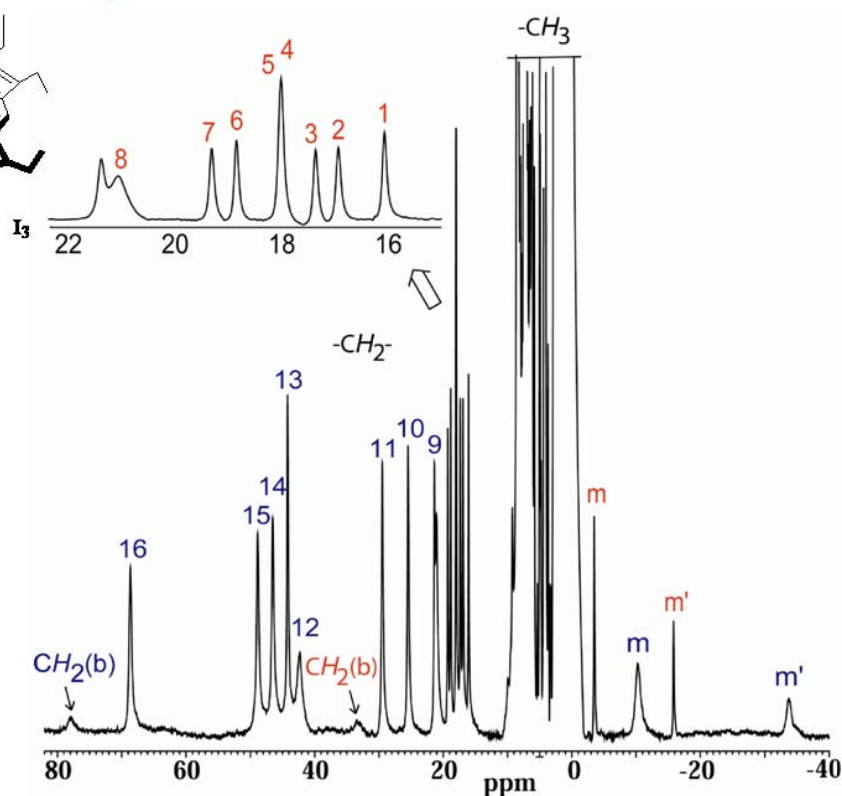
Two different spin states in a single molecule for the first time!

J. Am. Chem. Soc. (Communication) 2010, 132, 17983.

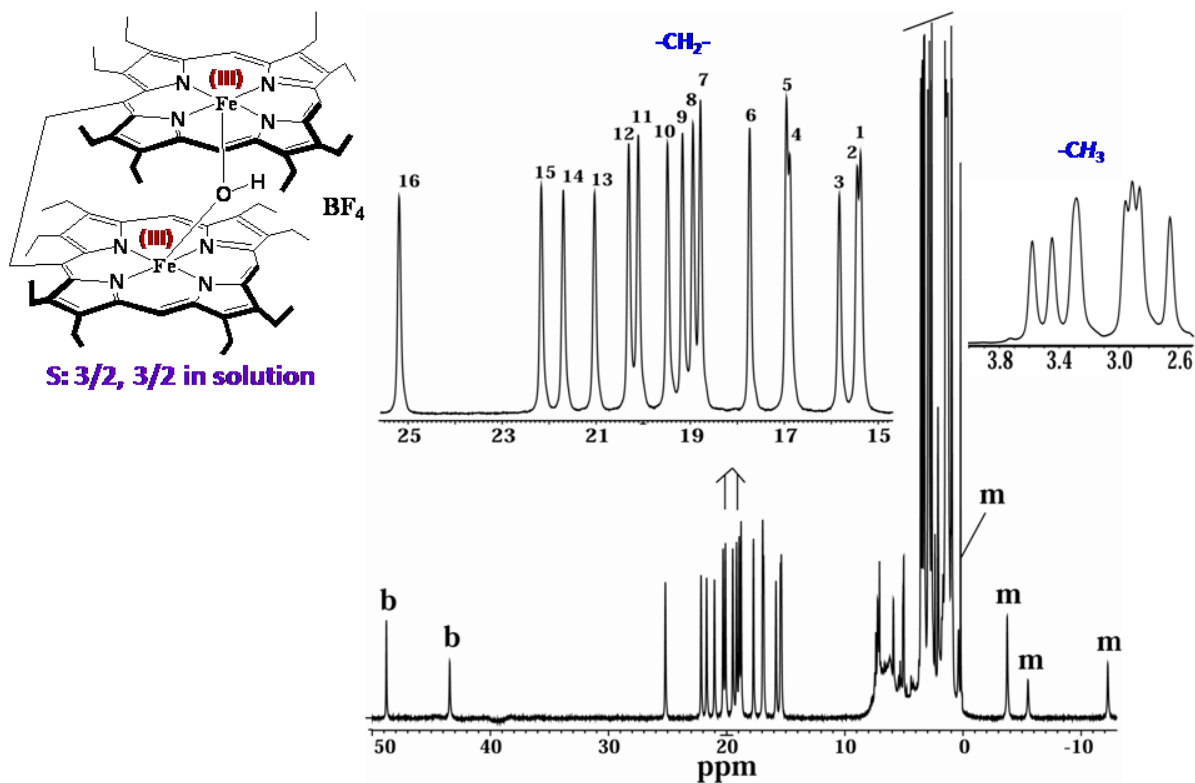
¹H NMR Spectrum in CDCl₃ at 289K



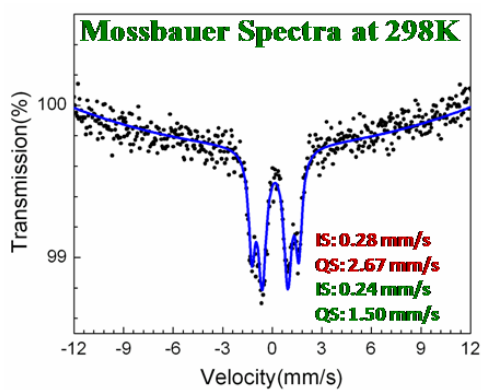
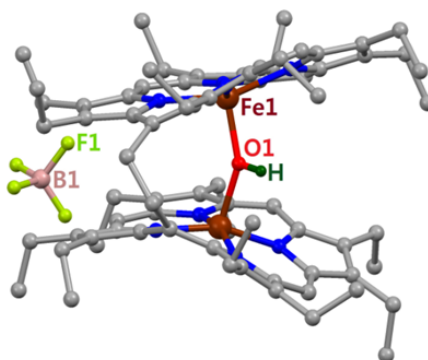
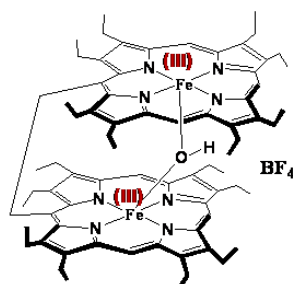
S: 5/2, 3/2 in solution



^1H NMR spectrum in CDCl_3 at 289K



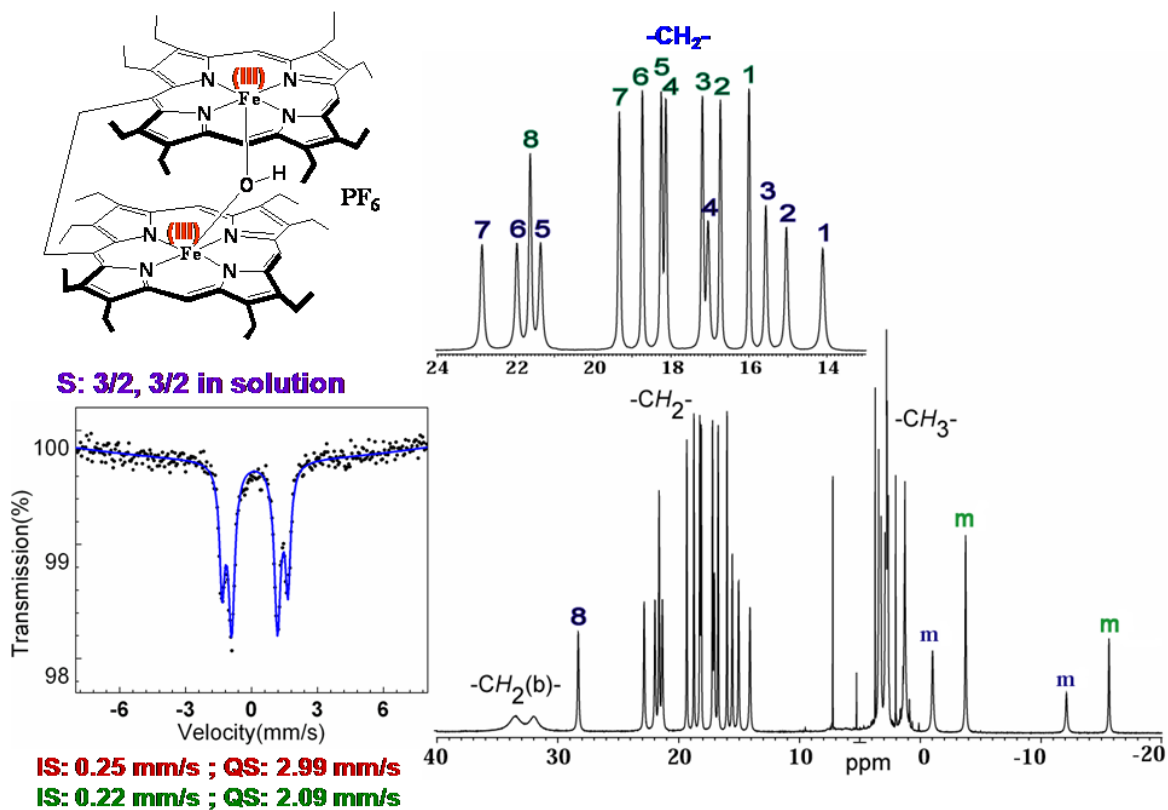
X-ray Structure



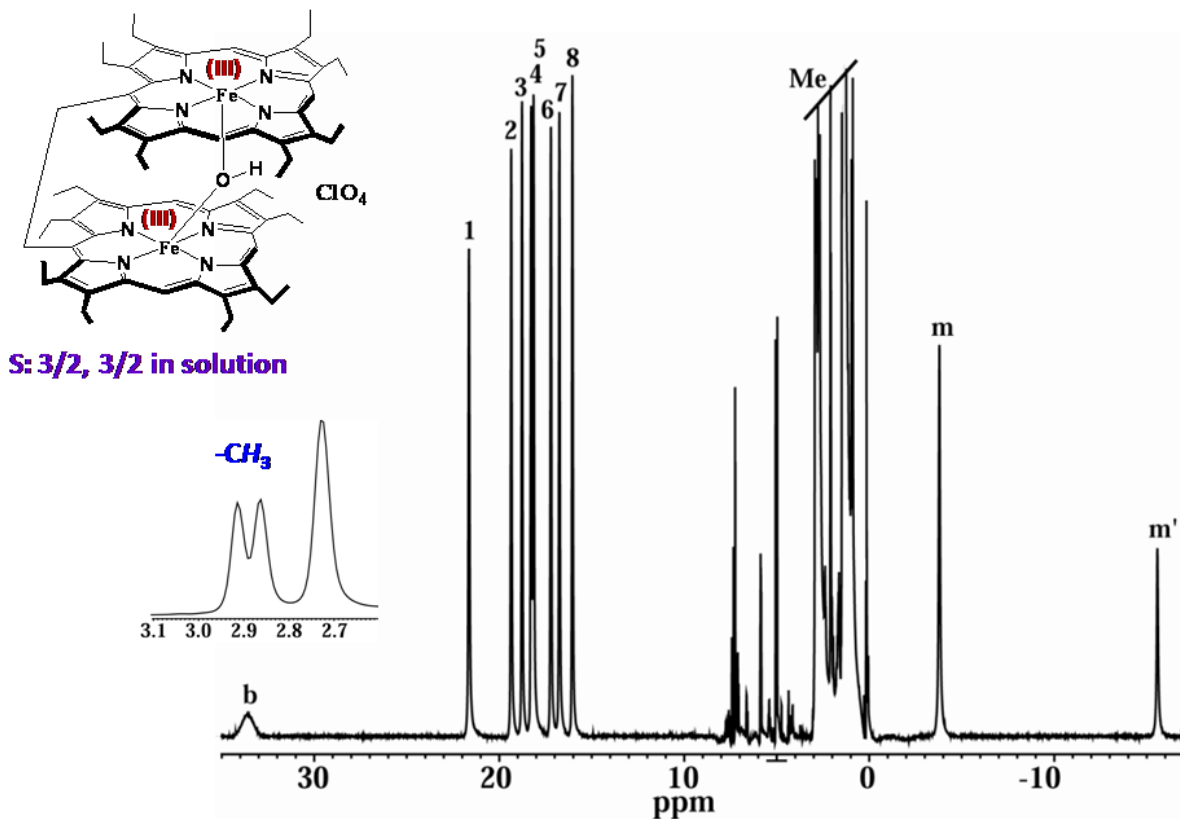
X-ray Structural Parameters at 100K:

	Core-I	Core-II
Fe-O[A]	1.926(3)	1.968(3)
Fe-N _p [A]	2.019(4)	1.967(3)
Fe-O-Fe [°]	148.46(16)	
$\Delta 24^{\text{Fe}}$ [A]	0.41	0.39
$\Delta 24$ [A]	0.22	0.31
Spin States	3/2, 3/2	

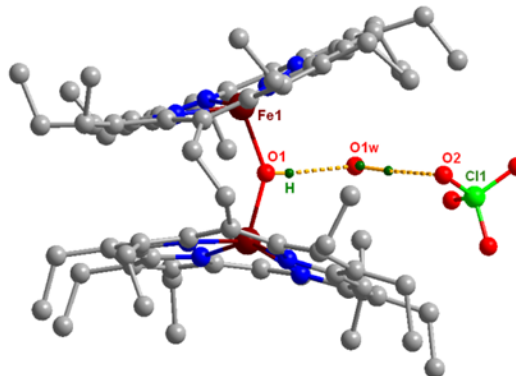
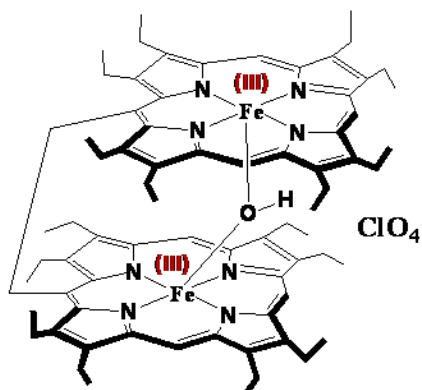
^1H NMR spectrum in CDCl_3 at 292K



^1H NMR Spectrum at 289K

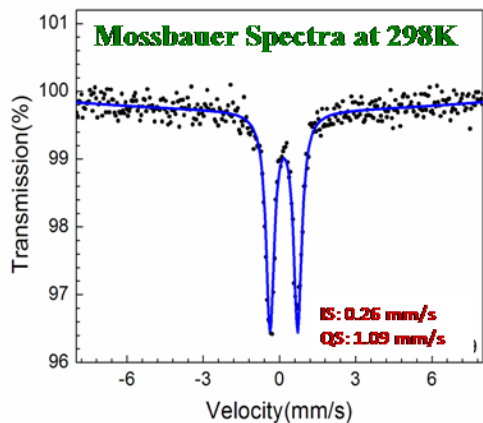


X-ray Structure

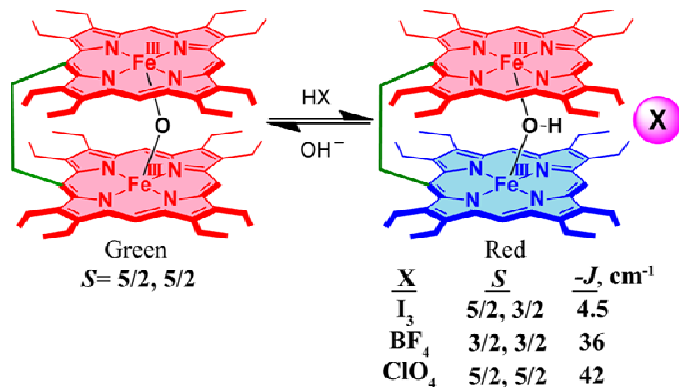


X-ray Structural Parameters at 100K:

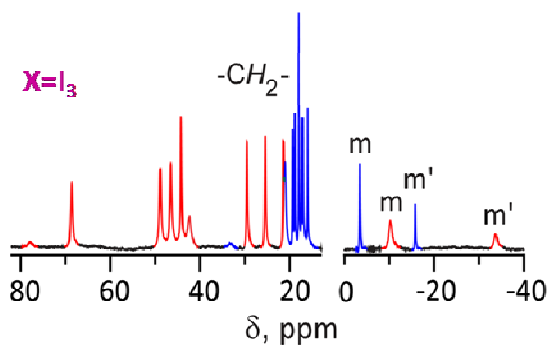
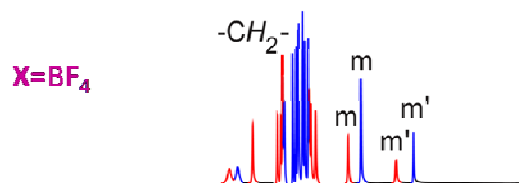
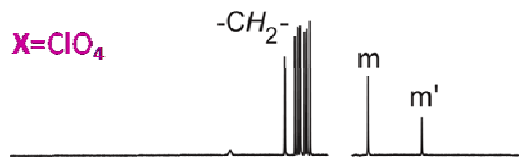
	Core-I	Core-II
Fe-O[A]	1.907(3)	1.921(3)
Fe-N _p [A]	2.062	2.055
Fe-O-Fe [°]	141.6(2)	
$\Delta 24^{\text{Fe}}$ [Å]	0.57	0.48
$\Delta 24$ [Å]	0.17	0.13
Spin States	5/2, 5/2	



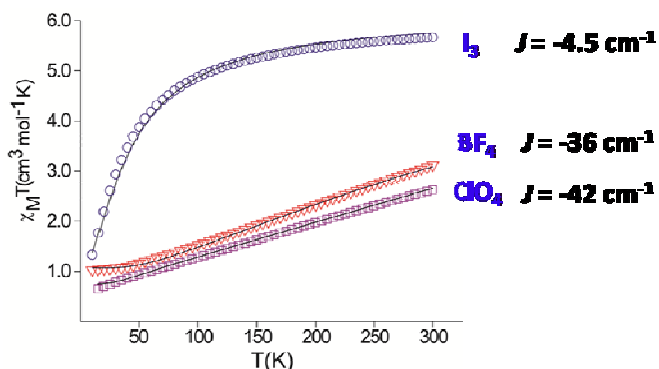
Stabilization of Two Different Fe Spins: Effect of Heme-Heme Interaction



¹H NMR (at 295 K):



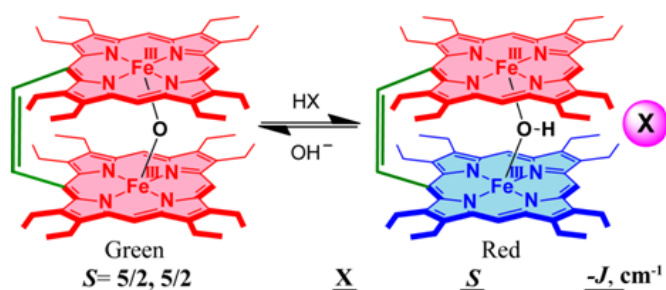
Variable temperature magnetic study



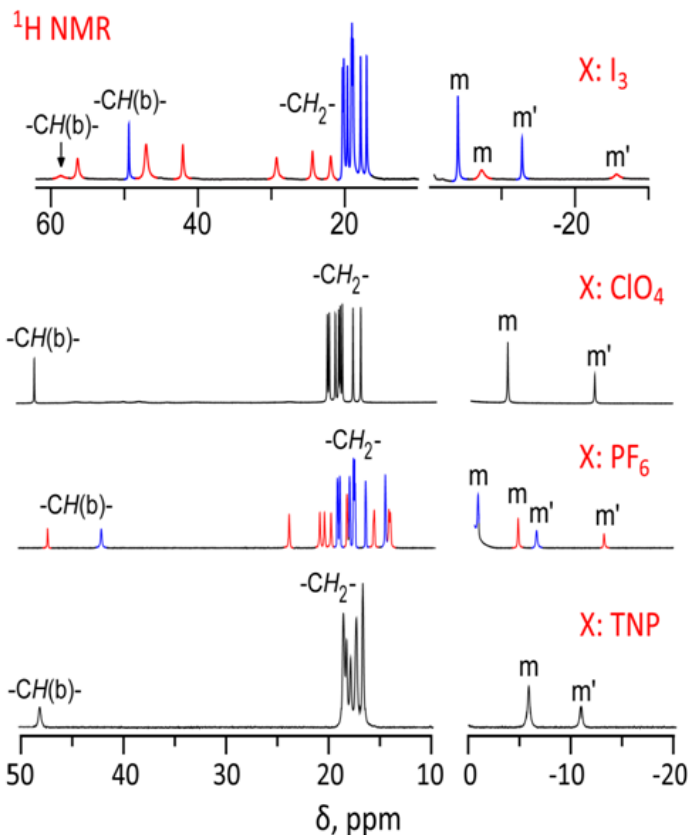
Counter Anion Specific Spin States!

J. Am. Chem. Soc. **2010**, *132*, 17983.
Chem. Eur. J. **2012**, *18*, 13025.
Chem. Eur. J. **2013**, *19*, 17846.

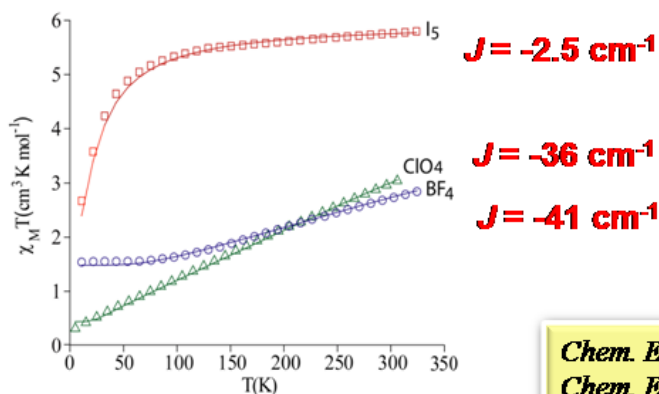
Counter Anion Specific Spin States



X	S	$-J, \text{cm}^{-1}$
I_5^-	5/2(3/2), 3/2(5/2)	2.4
BF_4^-	5/2(3/2), 3/2(5/2)	46.0
PF_6^-	5/2(3/2), 3/2(5/2)	32.6
SbF_6^-	5/2(3/2), 3/2(5/2)	33.5
ClO_4^-	5/2, 5/2	34.0

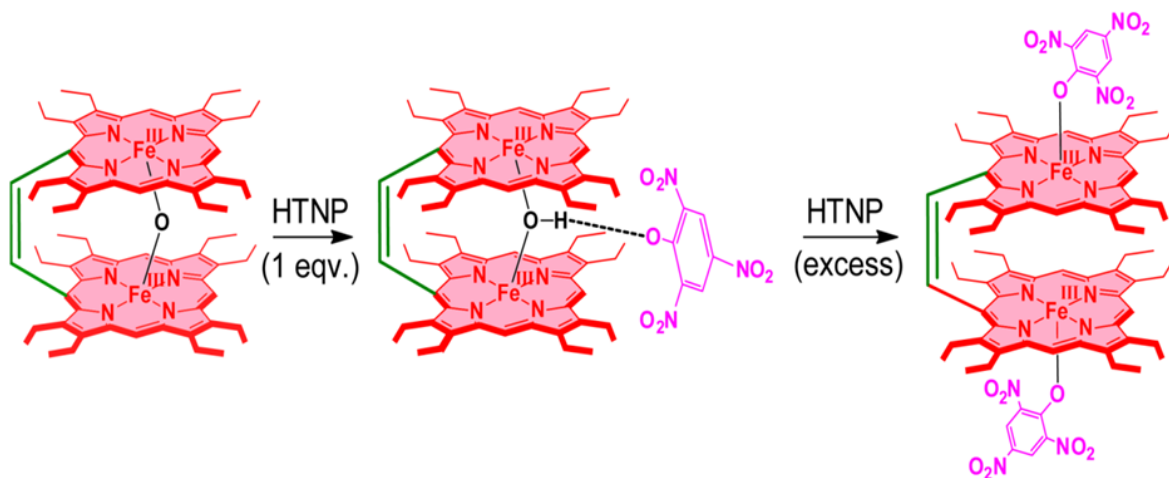


Variable temperature magnetic study



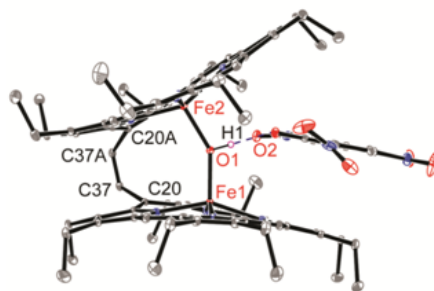
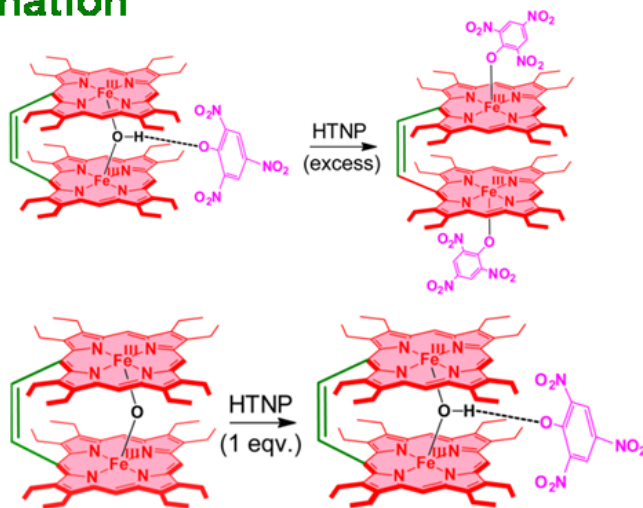
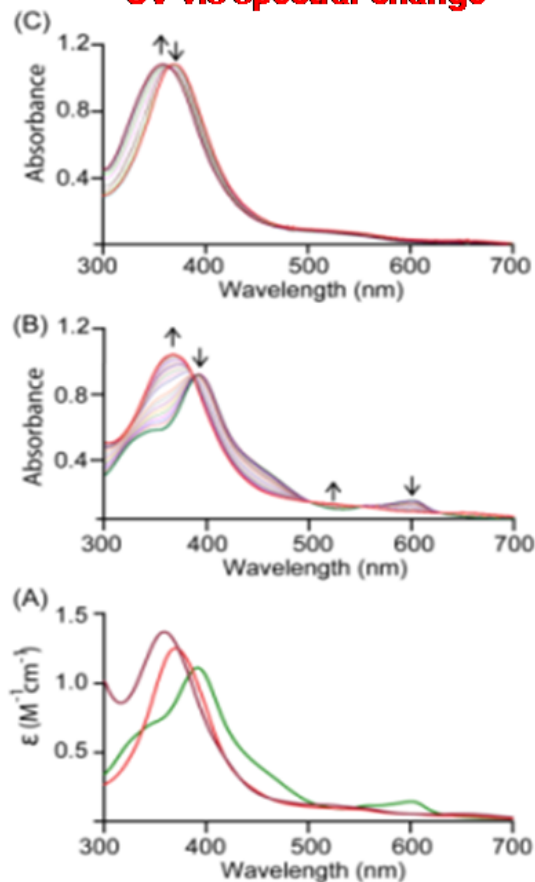
Chem. Eur. J. 2016, 22, 16124.; *Chem. Eur. J.* 2016, 22, 14585.
Chem. Eur. J. 2016, 22, 11214.; *Chem. Eur. J.* 2014, 19, 17846.

What Role Do Counter Ions Play?



Using Picric Acid for Protonation

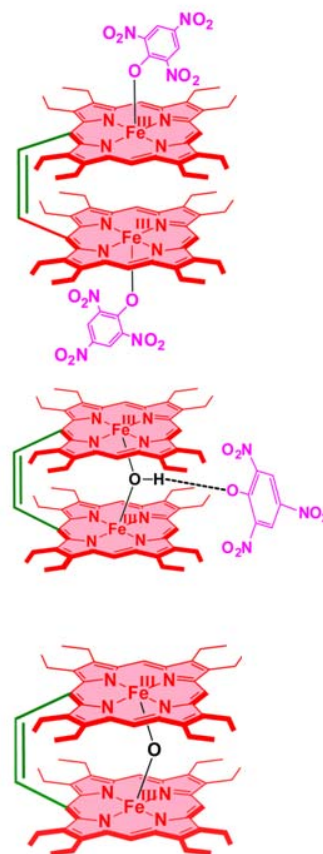
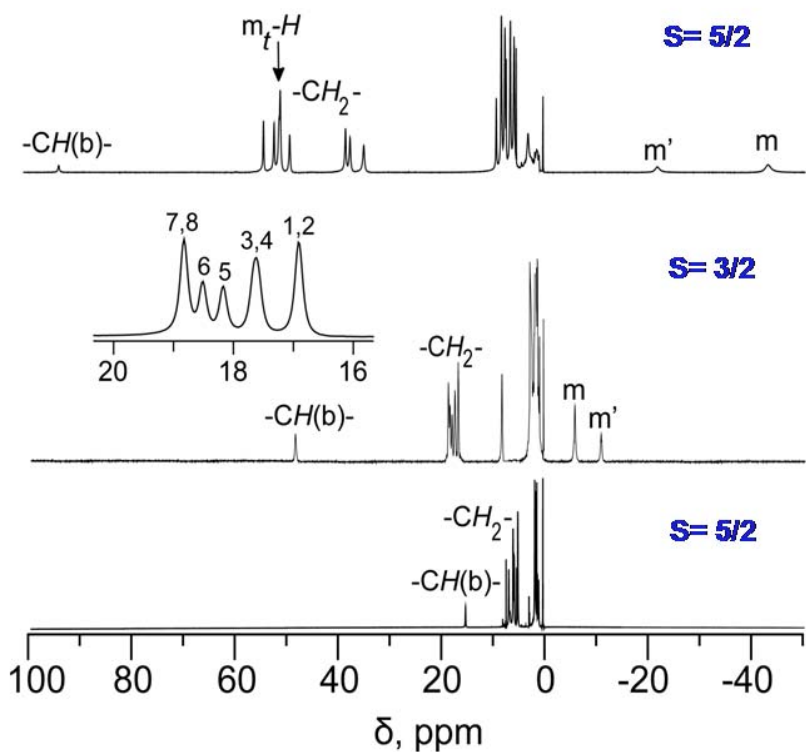
UV-vis spectral change



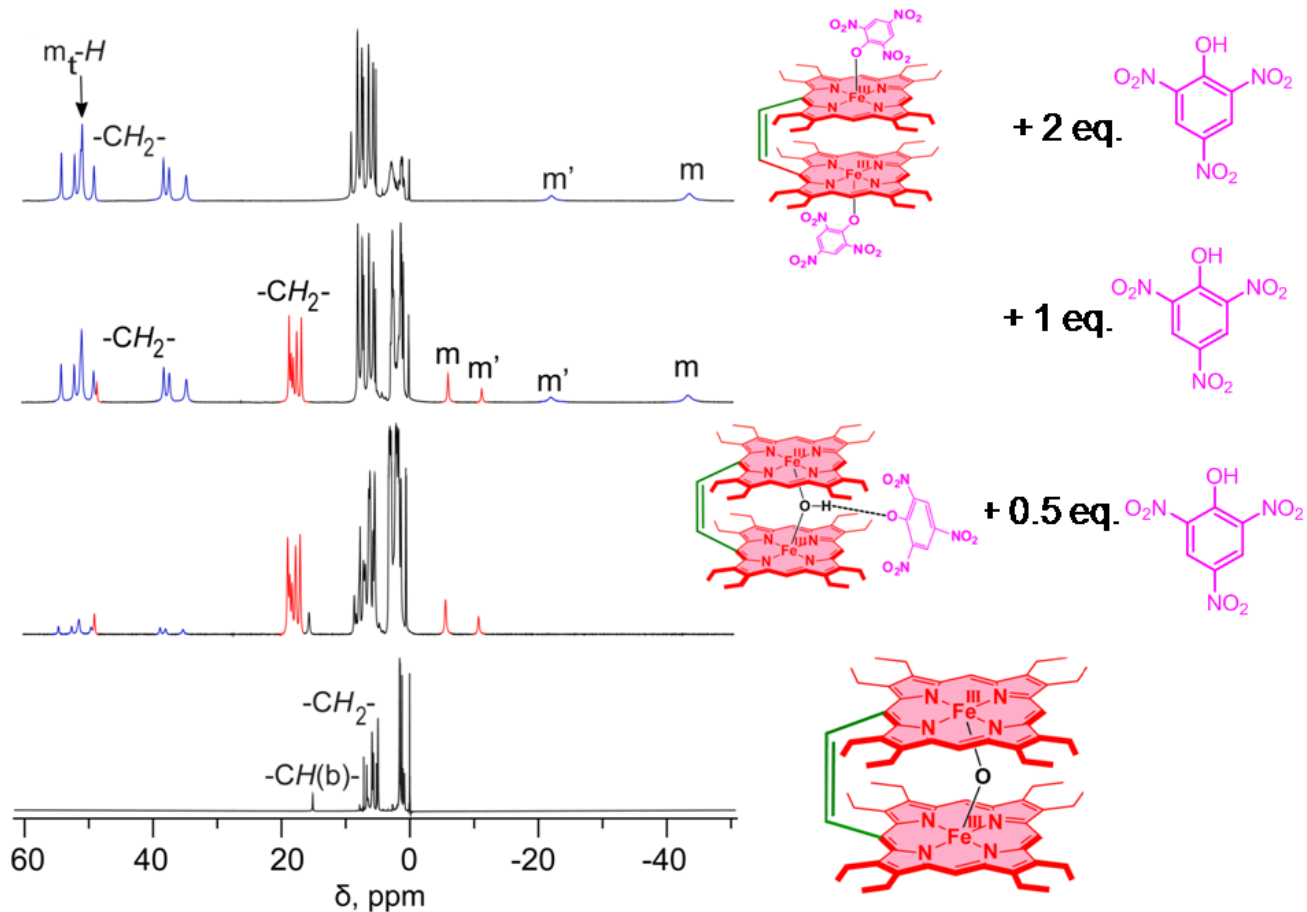
high-spin ($S=5/2$) state

Chem. Eur. J. 2016, 22, 16124.

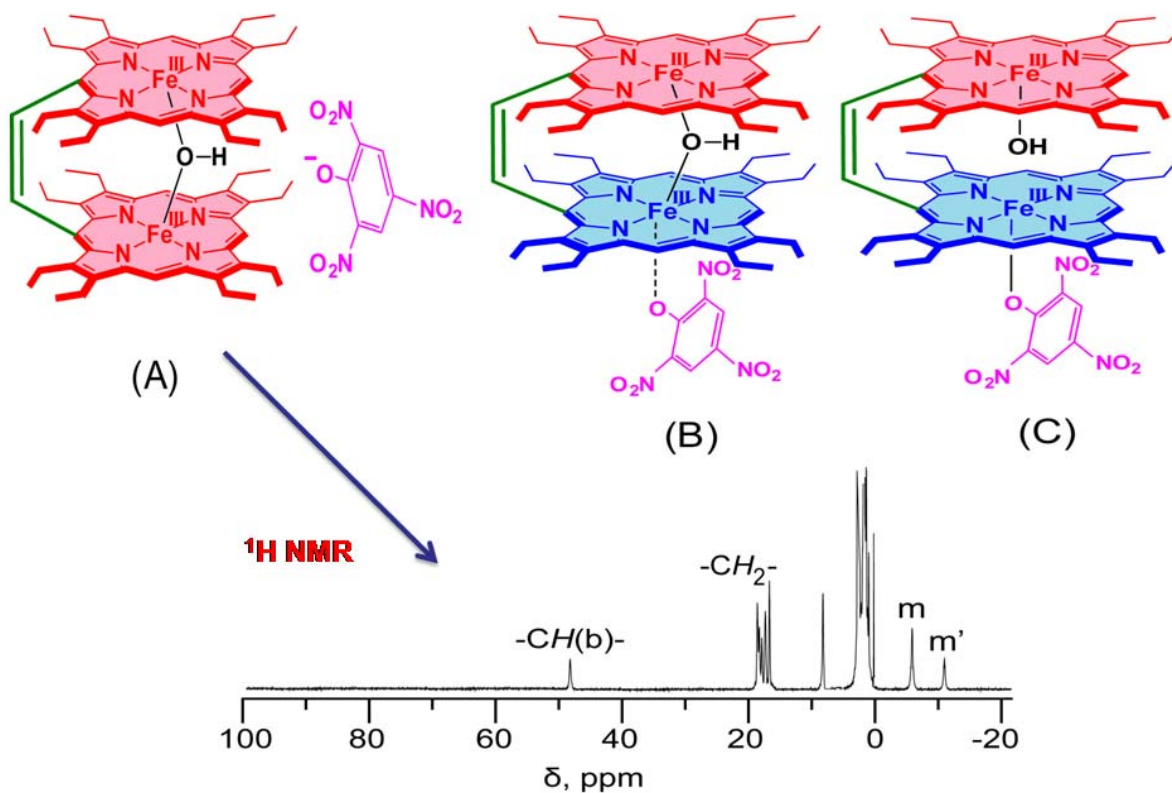
1H NMR in $CDCl_3$ at 295 K



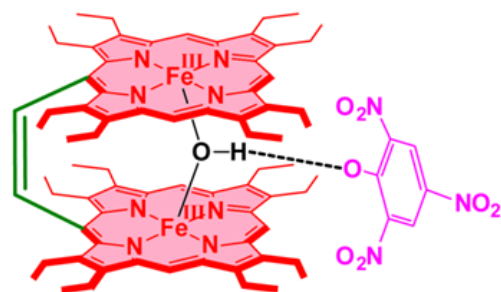
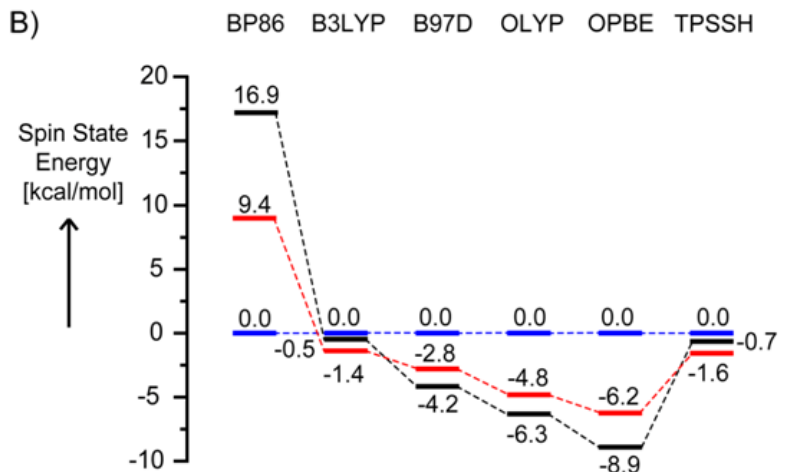
^1H NMR Titration in CDCl_3 at 295 K



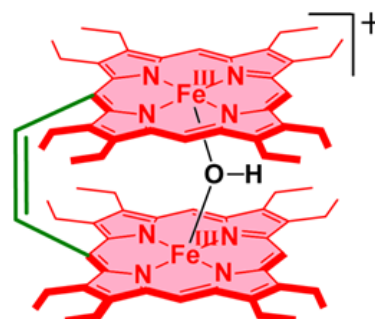
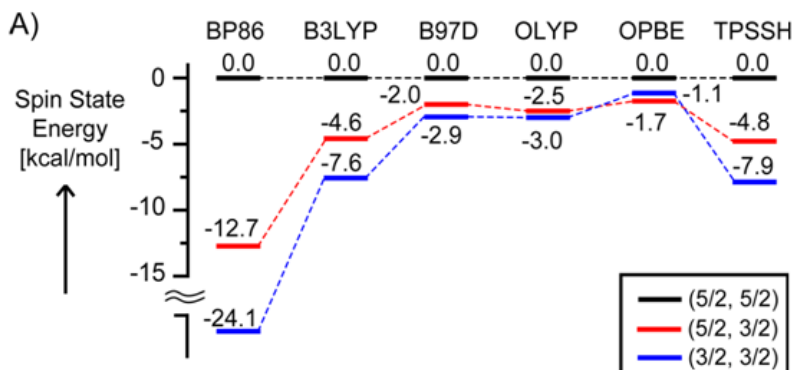
Possible Arrangements of the Counter Anion in Solution



Spin Flip between Solid and Solution

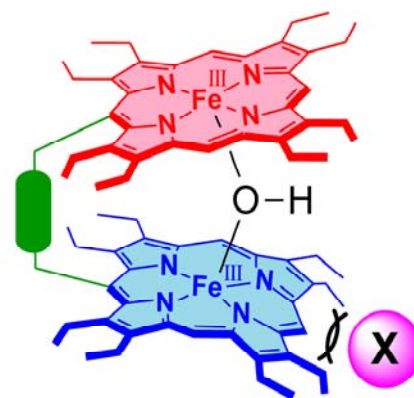
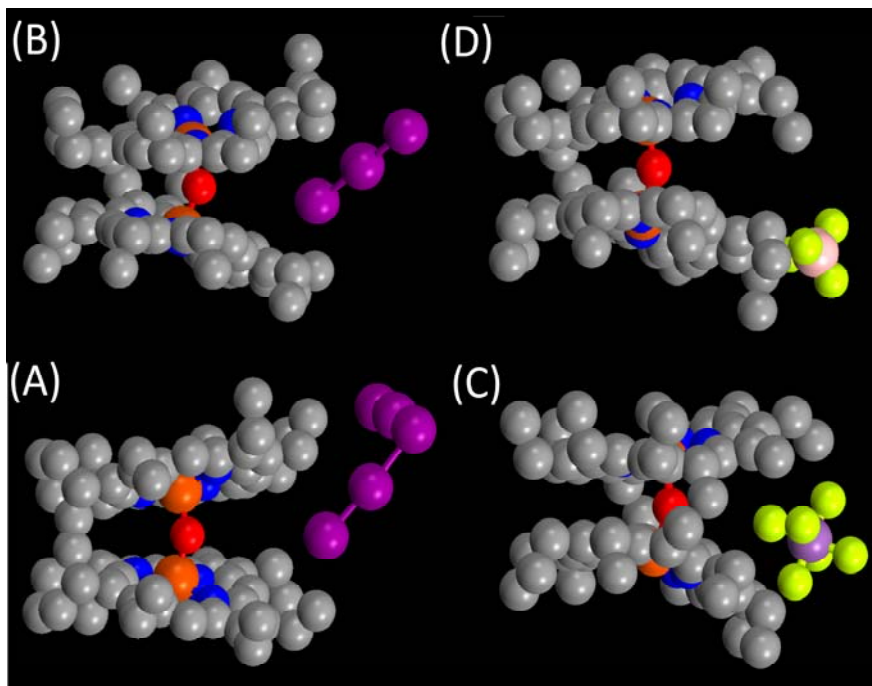


$S = 5/2$



$S = 3/2$

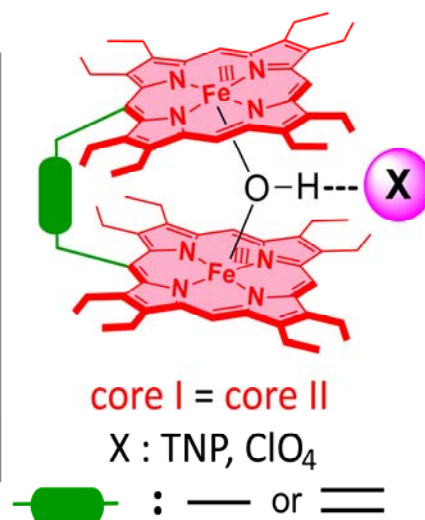
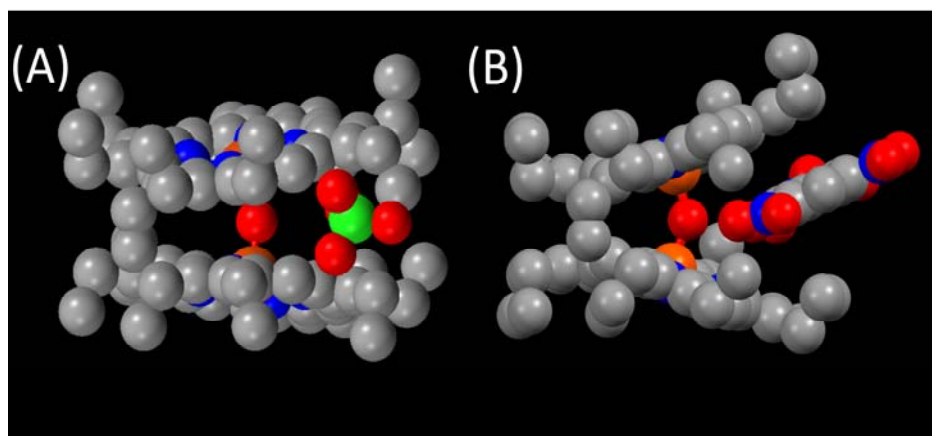
Chem. Eur. J. 2016, 22, 16124.



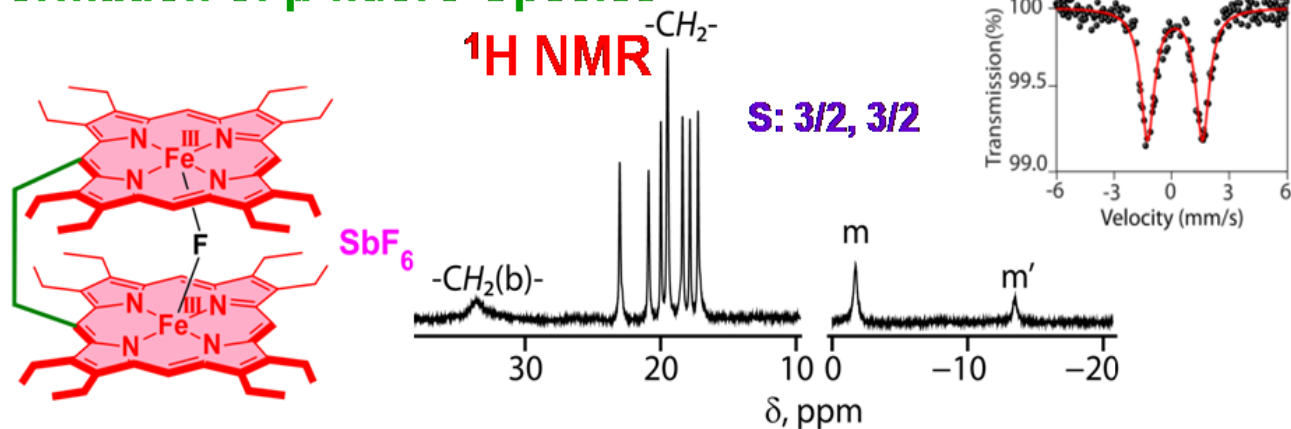
core I \neq core II

X : I₃/I₅, BF₄, PF₆, SbF₆

— : — or =

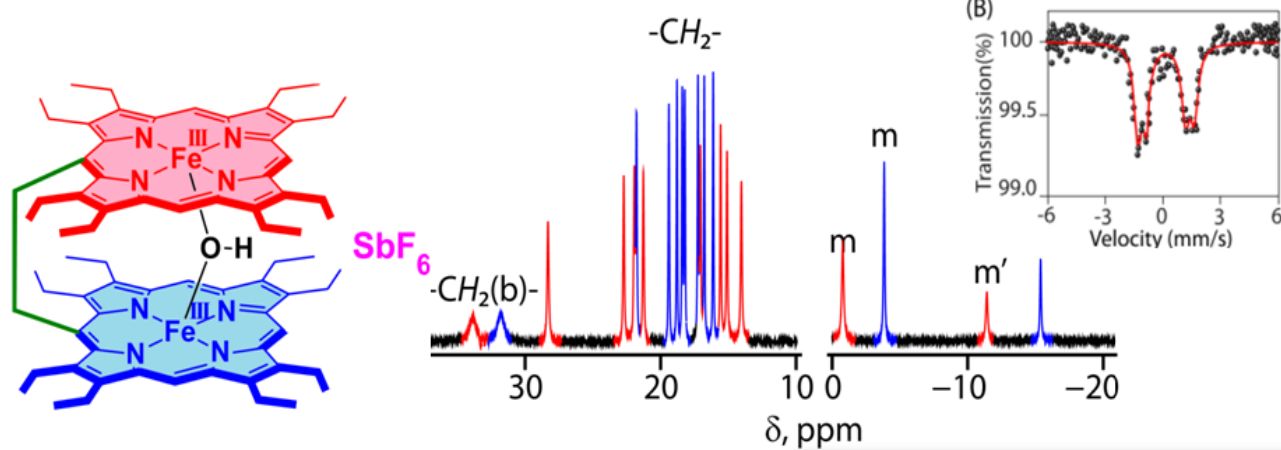


Formation of μ -fluoro Species



Iron centers are equivalent

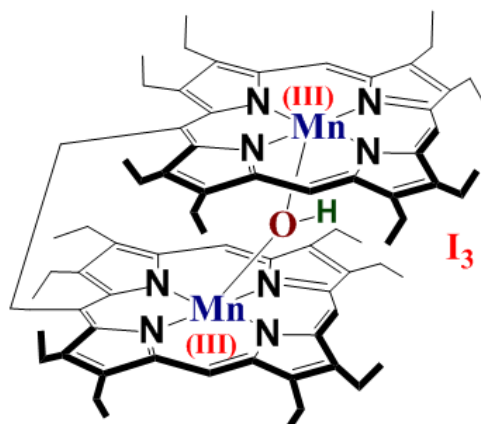
S: admixed state



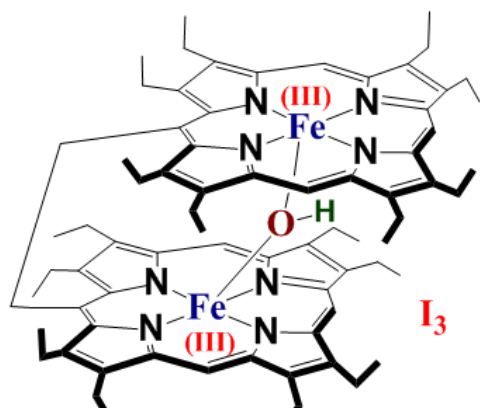
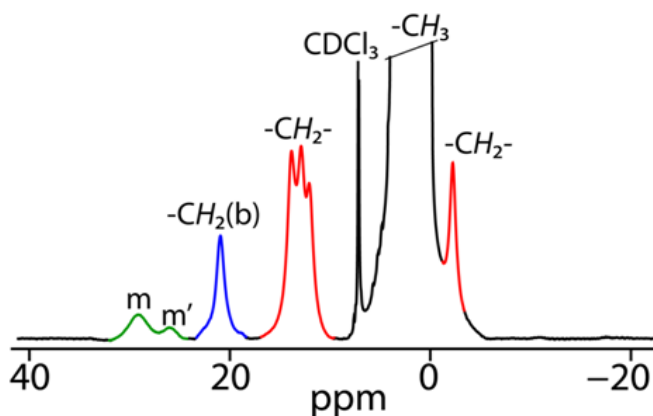
Iron centers are non-equivalent

Chem. Eur. J. 2016, 22, 11214.

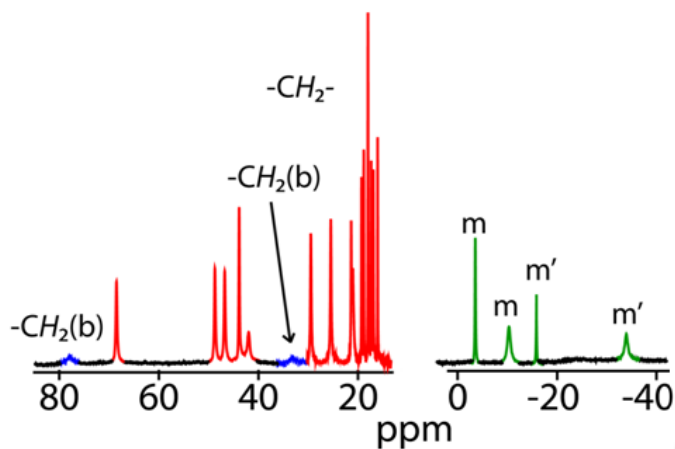
¹H NMR: Comparison between Fe(III) and Mn(III) Complexes



Mn•••Mn: 3.752(1)

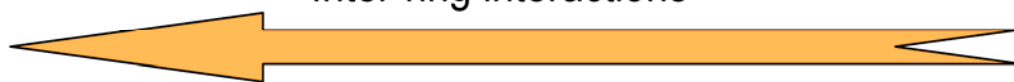


Fe•••Fe: 3.627(1)



Inorg. Chem. 2016, 55, 3239

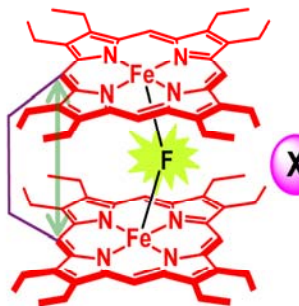
Inter-ring interactions



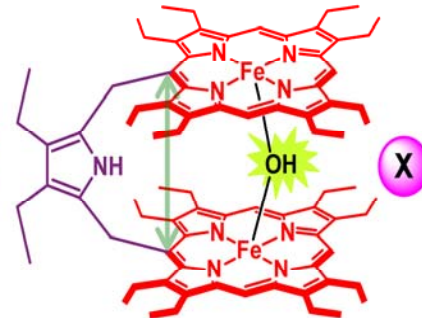
core I ≠ core II



core I ≠ core II



core I = core II



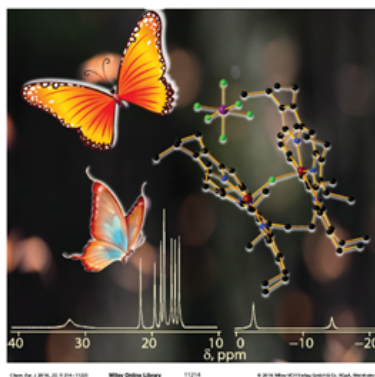
core I = core II



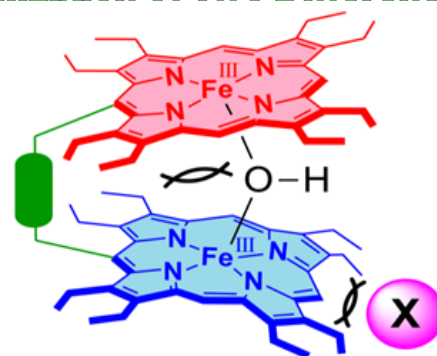
Inter-porphyrin distance



Electronic Structures [Hot Paper]
 Diiron(III)- μ -Fluoro Bisporphyrins: Effect of Bridging Ligand on the Metal Spin State
 Debangsu S1, Amit Kumar, and Sankar Prasad Rath^{1*}
 Dedicated to Professor Alan L. Balch on the occasion of his 75th birthday

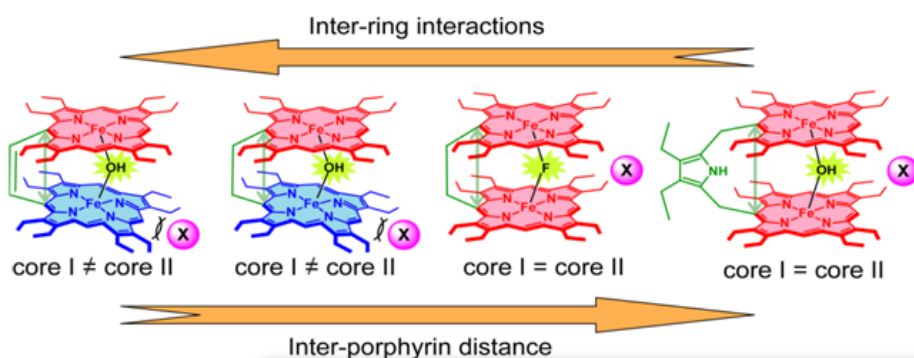
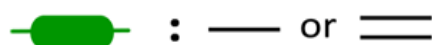


Stabilization of Two Different Fe Spins



core I \neq core II

X : I₃/I₅, BF₄, PF₆, SbF₆



Dalton Trans. **2017**, *46*, 1012. (*Perspective article*)
Coord. Chem. Rev. **2017**, *337*, 112.

Representative Publications:

- Oxo- and Hydroxo-bridged Diiron(III) Porphyrin Dimers: Inorganic and Bio-inorganic Perspectives and Effects of Intermacrocylic Interactions**

T. Guchhait, S. Sasmal, F. S. T. Khan, and S. P. Rath*

Coord. Chem. Rev. **2017**, *337*, 112-144.

- Hydroxo-Bridged Diiron(III) and Dimanganese(III) Bisporphyrins: Modulation of Metal Spins by Counter Anions**

F. S. T. Khan, T. Guchhait, S. Sasmal and S. P. Rath*

Dalton Trans. **2017**, *46*, 1012-1037 (*Invited Perspective and Cover page Article*)

3. **Remarkable Anion Dependent Spin state Switching in Diiron(III)- μ -Hydroxo Bisorphyrins: What role do Counter ions play?**
F. S. T. Khan and S. P. Rath*
Chem. Eur. J. **2016**, *22*, 16124-16137.
4. **Diiron(III)- μ -fluoro Bisorphyrins: Effect of Bridging Ligand on the Metal Spin State**
D. Sil, A. Kumar and S. P. Rath
Chem. Eur. J. **2016**, *22*, 11214-11223. [Highlighted as Frontispiece (*Hot Paper*)]
5. **Effect of Inter-porphyrin Distance on Spin-state in Diiron(III) μ -Hydroxo Bisorphyrins**
D. Sil and S. P. Rath*
Chem. Eur. J. **2016**, *22*, 14585-14597.
6. **Experimental and Theoretical Investigation on a Series of Novel Dimanganese(III)- μ -hydroxo Bisorphyrins: Magneto-Structural Correlation and Effect of Metal Spin on Porphyrin Core Deformation**
D. Sil, S. Bhowmik, F. Khan and S. P. Rath*
Inorg. Chem. **2016**, *55*, 3239-3251.
7. **Spin State Ordering in Hydroxo Bridged Diiron(III)bisorphyrin Complexes**
M. A. Sainna, D. Sil, D. Sahoo, B. Martin, S. P. Rath,* P. Comba* and S. P. de Visser*
Inorg. Chem. **2015**, *54*, 1919 - 1930.
8. **Ethane-bridged Porphyrin Dimer as Model of Di-heme Proteins: Inorganic and Bioinorganic Perspectives and Consequences of Heme-Heme Interactions**
D. Sil and S. P. Rath*
Dalton Trans. **2015**, *44*, 16195 - 16211. (*Invited Perspective Article*)

9. **Unusual Stabilization of an Intermediate Spin of Iron upon Axial Phenoxide Coordination on a Diiron(III)bisporphyrin: Effect of Heme-Heme Interactions**
S. Bhowmik, S. Dey, D. Sahoo and S. P. Rath*
Chem. Eur. J. **2013**, *19*, 13732 - 13744.
10. **Effect of Heme-Heme Interactions and Modulation of Metal Spins by Counter Anions in a Series of Diiron(III)- μ -hydroxo Bisporphyrins: Unusual Stabilization of Two Different Spins in a Single Molecular Framework**
S. K. Ghosh, S. Bhowmik, D. Sil and S. P. Rath*
Chem. Eur. J. **2013**, *19*, 17846 - 17859.
11. **Protonation of an oxo-Bridged Diiron Unit Makes Two Iron Centers Different: A New Class of Diiron(III)- μ -hydroxo Bisporphyrin and Control of Spins by Counter Anions**
S. Bhowmik, S. K. Ghosh, S. Layek, H. C. Verma and S. P. Rath*
Chem. Eur. J. **2012**, *18*, 13025 – 13037.
12. **Control of Spins by Ring Deformation in a Diiron(III)bisporphyrin: Reversal of ClO_4^- and CF_3SO_3^- Ligand Field Strength on the Magnetochemical Series**
S. Bhowmik, S. K. Ghosh and S. P. Rath*
Chem. Commun. **2011**, *47*, 4790 - 4792.
13. **A Remarkably Bent Diiron(III)- μ -Hydroxo Bisporphyrin: Unusual Stabilization of Two Spin States of Iron in a Single Molecular Framework**
S. K. Ghosh and S. P. Rath*
J. Am. Chem. Soc. **2010**, *132*, 17983 - 17985.
14. **Synthesis and Characterization of Anti-bisFe(III) Porphyrins, Syn-bisFe(III)- μ -oxo Porphyrin and Syn-bisFe(III)- μ -oxo Porphyrin Cation Radical**
S. K. Ghosh, R. Patra and S. P. Rath*
Inorg. Chem. **2010**, *49*, 3449 - 3460.
15. **Remarkably Bent, Ethane-Linked, Diiron(III) μ -Oxobisporphyrin: Synthesis, Structure, Conformational Switching, and Photocatalytic Oxidation**
S. K. Ghosh, R. Patra and S. P. Rath*
Inorg. Chem. **2008**, *47*, 10196 - 10198.