Fe(II) Spin Crossover Complexes with Novel Ligand Types

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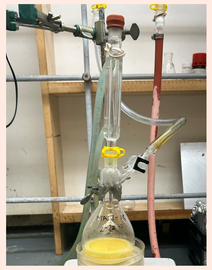
Background

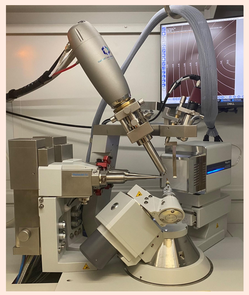
Transition metal complexes that exhibit spin crossover (SCO) are promising materials for application in next-generation stimuli responsive materials. SCO is the switching from high-spin (HS) and low-spin (LS) electronic configurations triggered by changes in temperature, pressure or light radiation. Previous research from our labs has explored the SCO behavior of the Fe^{II} complex with naphthalene functionalized 2,2′-biimidazol (xnap-bim). $[Fe(tpma)(xnap\text{-}bim)](ClO_4)_2$ showed an abrupt and hysteric thermally driven spin transition as well as a light induced excited spin state trapping (LIESST) at lower temperatures. Current research extends these studies to a new ligand, anthra-bim, obtained by *N*-alkylation of 2,2′-biimidazol with 2,3-dimethylanthracene. We examine how the change in ligand structure impacts the crystal packing of the new Fe^{II} complex, $[Fe(tpma)(anthra\text{-}bim)](BF_4)_2$, and it's structural, magnetic properties and photophysical behavior.

Method

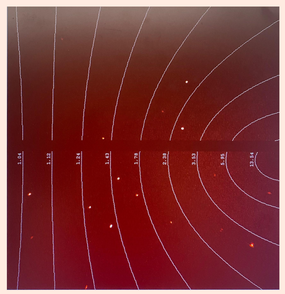


All ligands and complexes are synthesized under anaerobic conditions using schlenk techniques

Reagent-grade solvents are dried and deoxygenated by passing through a double-stage drying column system

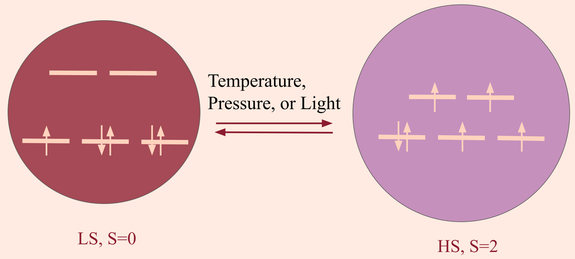


Crystal X-Ray diffractometer is used to investigate a single crystal



The X-ray diffraction images are processed and analyzed to determine atomic arrangements in the crystals

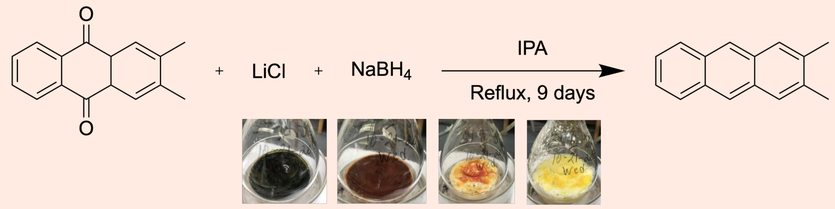
Spin Crossover



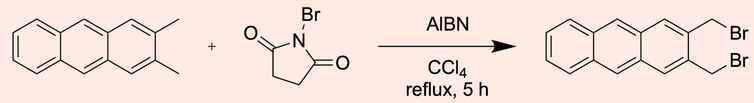
The LS ↔ HS change in the electronic configuration during SCO drastically alters structural, magnetic, and optical properties of a material.

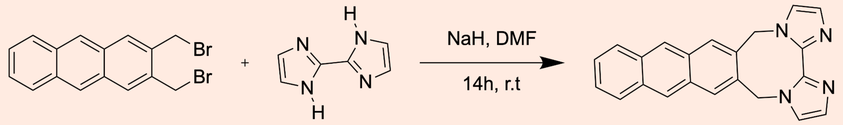
In LS, the orbital splitting is larger and the electrons will complete the lower orbital first. In HS, the splitting decreases and the number of unpaired electrons is maximized.

Ligand Synthesis

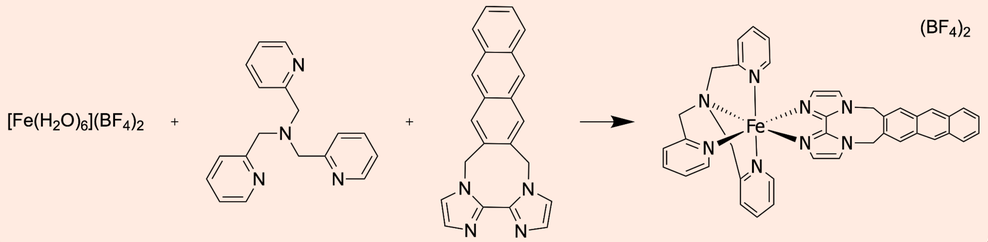


Observed color change during reflux



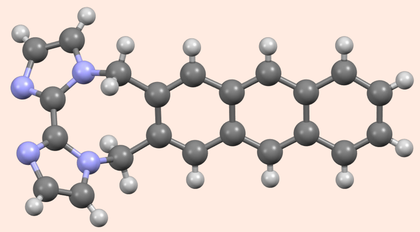


Complex Synthesis



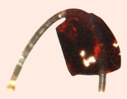
Crystal Structures

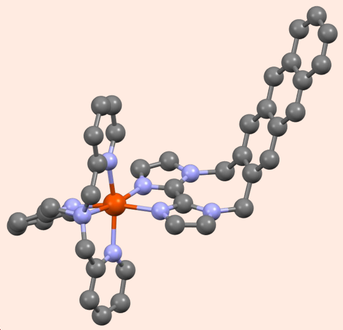
Anthra-bim



Unit Cell	230 K
a (Å)	12.280(2)
b (Å)	13.224(1)
c (Å)	13.215(2)
β (deg)	108.75(2)
V_{UC} (Å^3)	2032.02
Space group	$P2_1/c$

$[Fe(tpma)(anthra\text{-}bim)](BF_4)_2$





Parameter	100 K	230 K
d(Fe-N), Å	1.993(3)	2.103(3)
V_{UC}, Å^3	2391.01(1)	2511.3(2)
Σ_{90}(N-Fe-N)	83.3(1)	119.8(1)
Spin State	LS	~56% HS

References

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2. Gütlich, P.; et. al. Spin state switching in iron coordination compounds. *Beilstein Journal of Organic Chemistry* **2013**, *9*, 342-391.
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