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Molecular Assembly Line for Intramolecular Electron Transferring Bimetallic Fe and Mn Cyanometallate Clusters

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Molecular Assembly Line for Tuning Intramolecular Electron Transfer Within Cyanometallate Clusters

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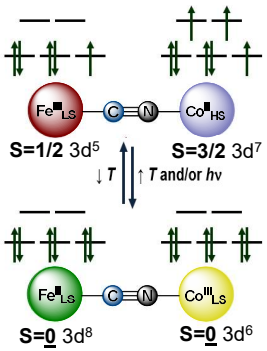
Introduction

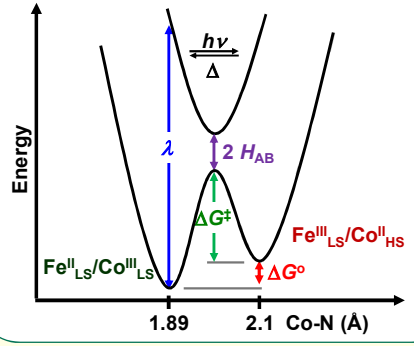
Future electronics demand smaller and more efficient materials, motivating a surge in molecule-based switchable materials research. In 1996, Hashimoto and coworkers reported that three dimensional cyanide networks known as Prussian blues show dramatic changes in their optical and magnetic properties upon light exposure or changing temperature. We are particularly interested in soluble molecular model complexes that mimic their behavior, so that we may better understand how to tune their properties.

Tuning Electron Transfer: Marcus-Hush Theory

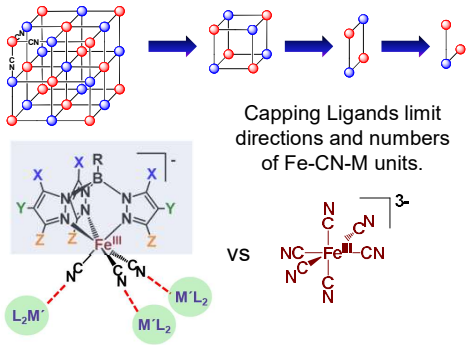
States energies and their electron transfer rates may be investigated *via* Marcus-Hush theory.



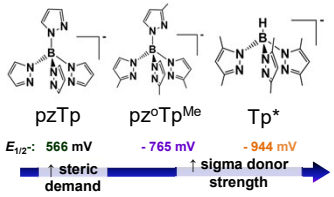
In iron/cobalt Prussian blue analogues, the metal centers undergo reversible one electron transfer.



Dimensional Reduction: Molecular Model Complexes

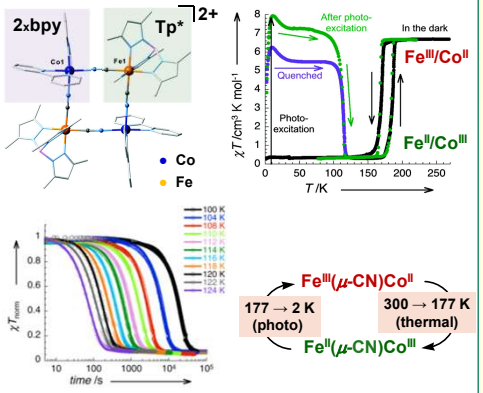


Molecular Toolbox: poly(pyrazolyl)borates Ligands



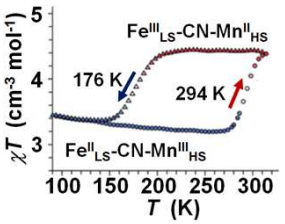
First Photo- and Thermochromic Model Complex

{[(Tp*)Fe^{III}(CN)$_3$]$_2$[Co^{II}(bpy)$_2$]$_2$}[Otf]$_2$·4DMF·2H2O



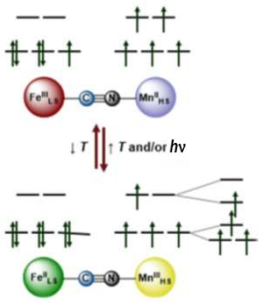
Zhang, Y.; Li, D.; Clerac, R.; Kalisz, M.; Mathoniere, C.; Holmes, S. *Angew. Chem., Int. Ed.* **2010**, *49*, 3752.

What About Photoactive Fe/Mn Clusters?

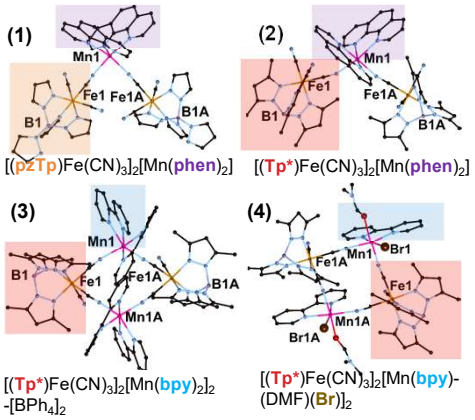


Electron transfer introduces Mn$^{III}_{HS}$ ions that undergo *Jahn-Teller* distortions. Mn-N bond elongation seen.

These distortion should increase reorganization energies and electron transfer energy barriers.



X-Ray Crystallography: Selected Structures

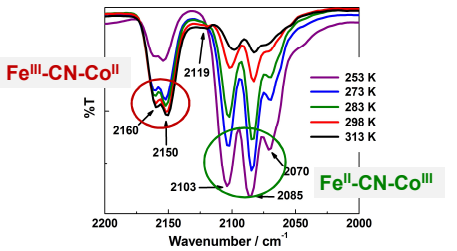


[(pzTp)Fe(CN)$_3$]$_2$[Mn(phen)$_2$] [(Tp*)Fe(CN)$_3$]$_2$[Mn(phen)$_2$]

[(Tp*)Fe(CN)$_3$]$_2$[Mn(bpy)$_2$]$_2$ -[BPh$_4$]$_2$ [(Tp*)Fe(CN)$_3$]$_2$[Mn(bpy)-(DMF)(Br)]$_2$

	(1)	(2)	(3)	(4)
color	Orange	Red	Red	Purple
Fe – C_{avg} (Å)	1.92	1.92	1.92	1.92
Mn – N_{avg} (Å)	2.20	2.18	2.14	2.19
N-Mn-N (°)	87.7°	98.0°	106°	97.2°

Infrared Spectroscopy: Diagnostic Tool



Compound	ν_{CN}	
1	2157, 2141, 2121	**2094, 2070**
[(pz^{0}Tp^{Me})Fe(CN)$_3$]$_2$ -[Mn(bpy)$_2$]	2141, 2131, 2123	**2093, 2076**
2	2154, 2149, 2137, 2119	**2089, 2070**

Electron transfer? Resembles [FeCo]$_n^{n+}$ clusters.

Conclusions

1. **X-Ray Crystallography** confirms both tri- and tetranuclear complexes containing Fe-CN-Mn units may be prepared. Mn-N bond lengths (ca. 2.2 Å) suggest Fe$^{III}_{LS}$-CN-Mn$^{II}_{HS}$ linkages are present.
1. **Infrared spectroscopy** indicates the Tp^R ligands act to tune the electron density within the Fe-CN-Mn units, and increase in the order of **Tp*, pz^{0}Tp^{Me}, pzTp** which is inversely proportional to their sigma donor strength.
1. **Overall** We hypothesize that for reversible electron transfer to be seen, the Fe/Mn clusters still require further work to modify their redox potentials. This will be explored through additional ligand substitution and electrophile addition work.

Funding

NSF