Electron Transfer in molecule-based magnetic materials

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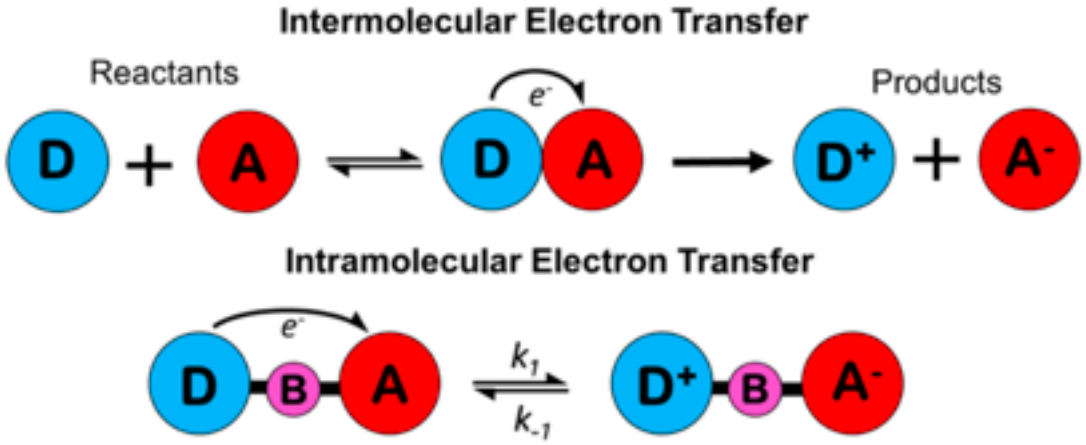
What is an electron transfer (ET) ?

✓ A simple definition : when one or more electrons move from one entity (molecule, ion or atom or a donor) to another entity (ie an acceptor)

✓ In Coordination Chemistry : Redox reaction between *complex* entities



Well studied in the 60-80's by Marcus and Hush

Marcus R. A. *J. Chem. Phys.* **1956** 24 966; *J. Chem. Phys.*1965, 43, 67

Piechota E. J. et al J. Chem. Educ., **2019**, 96, 2450

Hush N. et al J. Chem. Phys., **1958**, 28, 962

Thermodynamics: Nernst Law

$$\Delta G^{o} = -RT\ln(K_{eq}) = -F\Delta E^{\circ} = -nF[E^{\circ}(D) - E^{\circ}(A)]$$

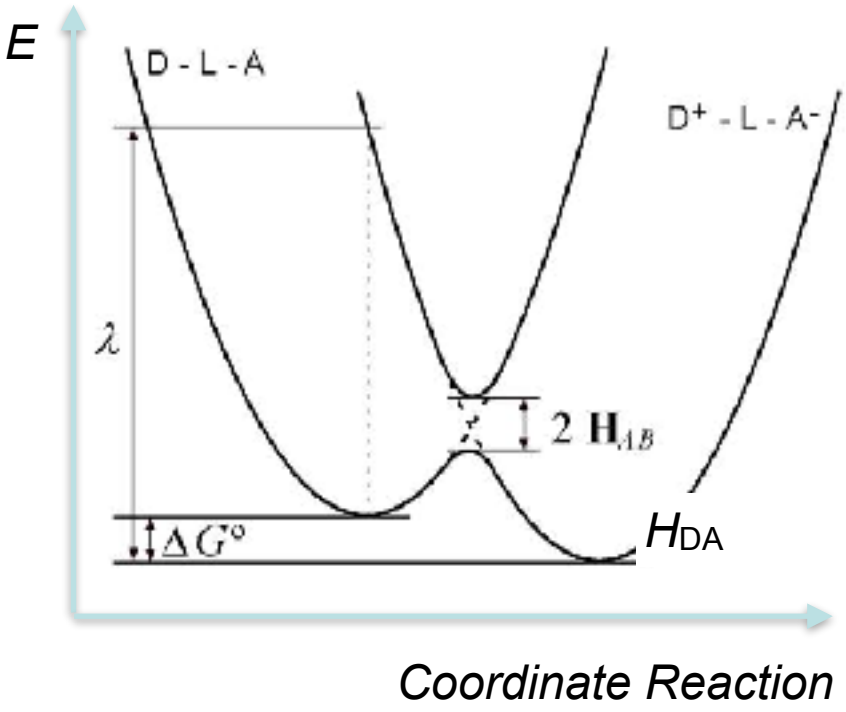
Kinetics (Marcus theory)

Electronic coupling

Rate constant

$$k_{ET} = \frac{2\pi}{\hbar}\frac{H_{DA}^{\ 2}}{\sqrt{4\pi\lambda k_b T}}\exp\left(-\frac{(\Delta G^{\circ} + \lambda)^2}{4\lambda k_b T}\right)$$

Reorganisation energy

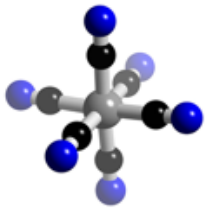


Marcus R. A. *J. Chem. Phys.* **1956** 24 966; *J. Chem. Phys.***1965** 43 67

Hush N. et al *J. Chem. Phys.*, **1958** 28 962

Interplay between thermodynamics, kinetics and structure

A textbook case : the real Prussian blue

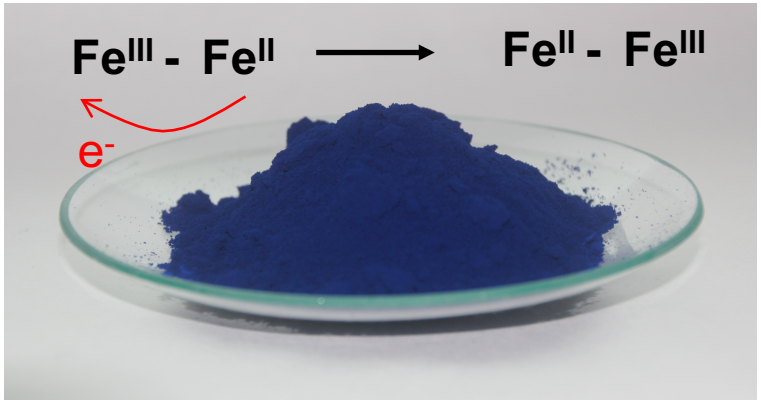


$[Fe^{II}(CN)_6]^{4-}$
yellow

\+ Fe^{3+}

Diesbach (Berlin)

≃ 1706

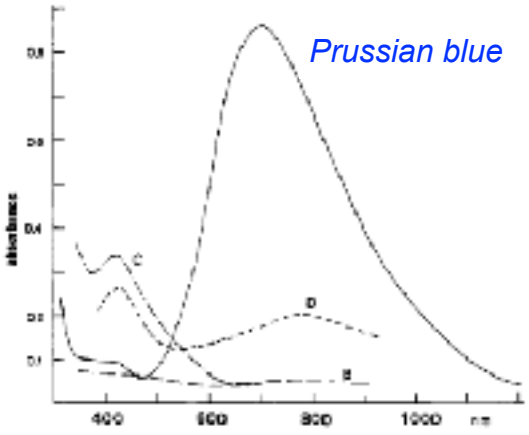


$Fe^{III}_4[Fe^{II}(CN)_6]_3 \cdot nH_2O$

Fe(II)-C = 1.92 Å , C-N = 1.13 Å and Fe(III)-N = 2.03 Å

[Optical studies in thin films and electrochromism]

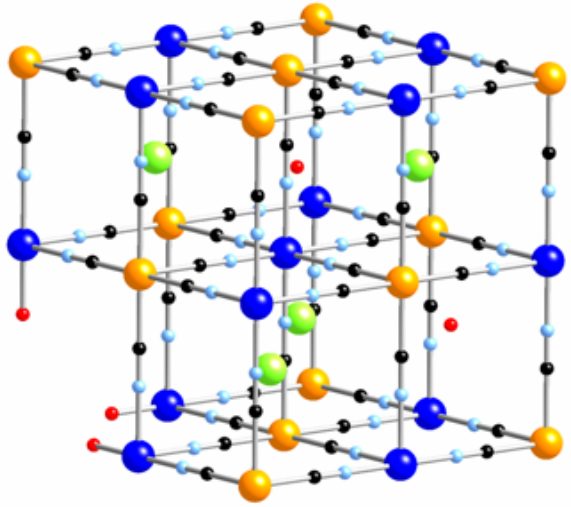
Metal-to-Metal Charge Transfer (MMCT)



[Spectroelectrochemistry]

(B) -0.2 V reduced form
Everitt

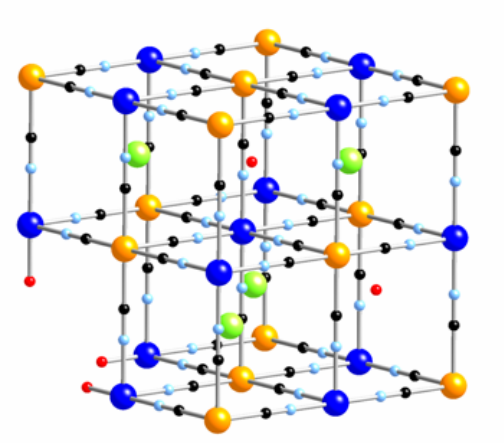
(D) +1.1 V oxidized form
Berlin green



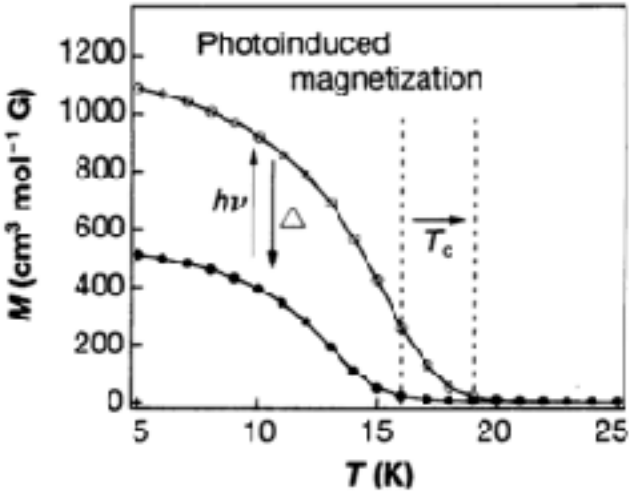
Itaya K. *Acc. Chem. Res.* ***1986*** 19 162

Buser H. J. et al. *J. Inorg Chem.* **1977** 16 2704

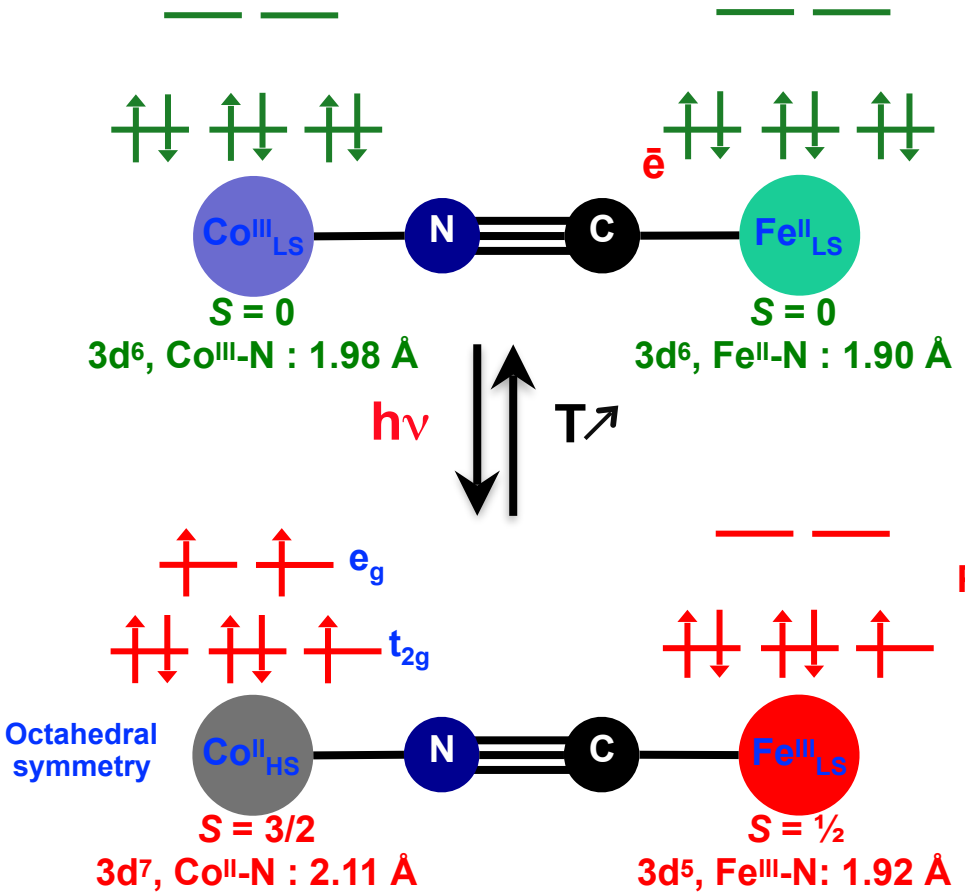
ET add a new functionality : Photomagnetism in Prussian Blue Analogs

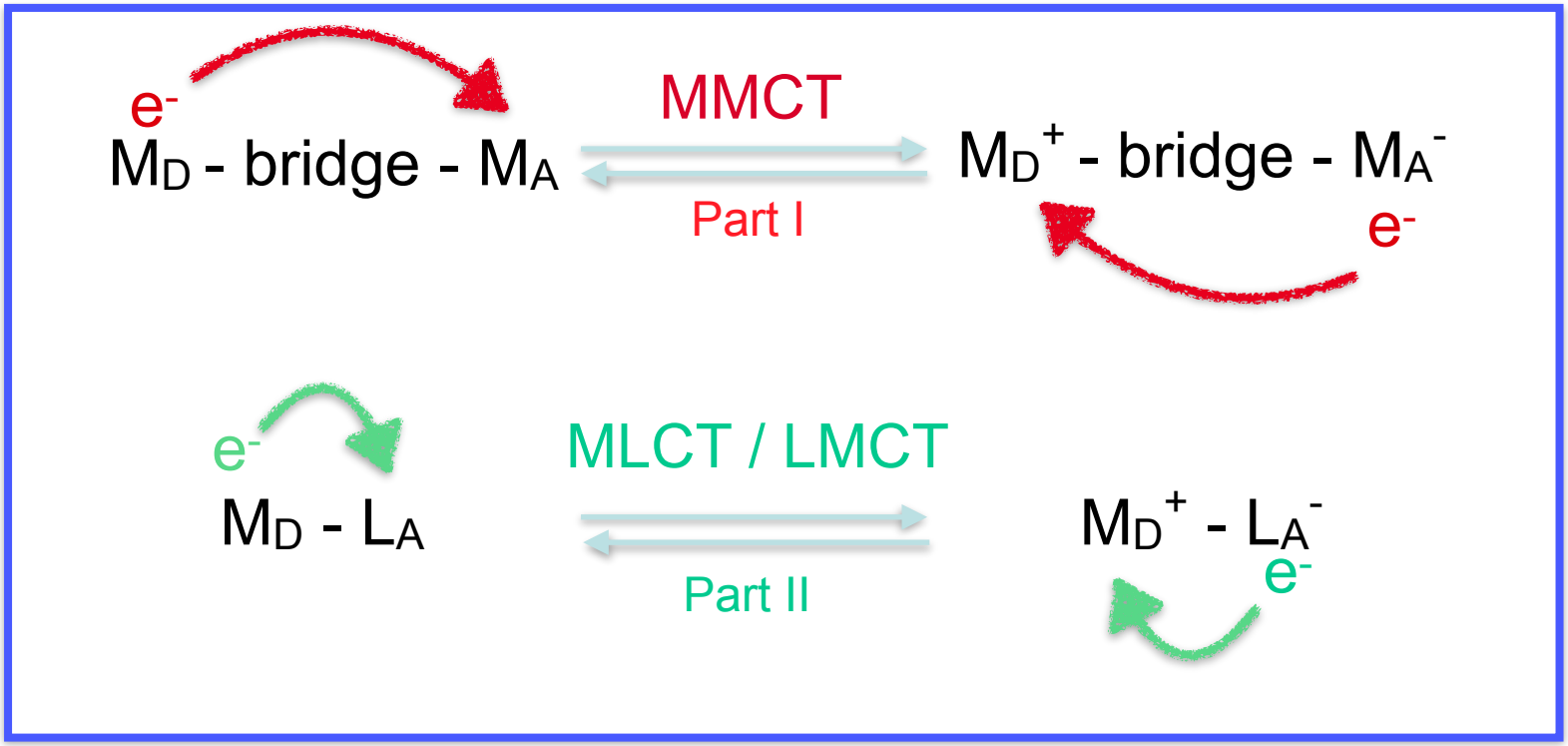


$K_{0.2}Co_{1.4}[Fe(CN)_6]\bullet 7H_2O$



Sato O. et al. *J. Science* **1996**, 272, 3752



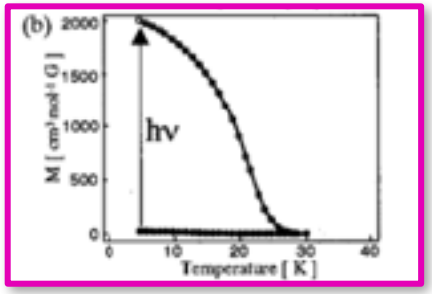


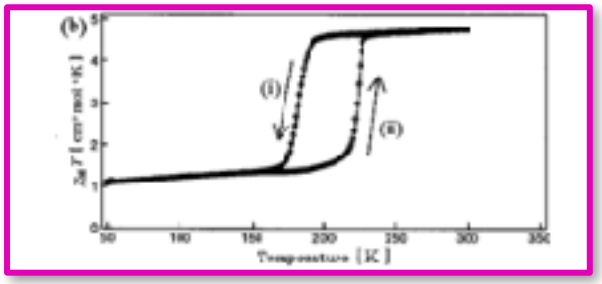
Part I : redox activity of metal ions

Part II : redox activity of metal ions and ligands

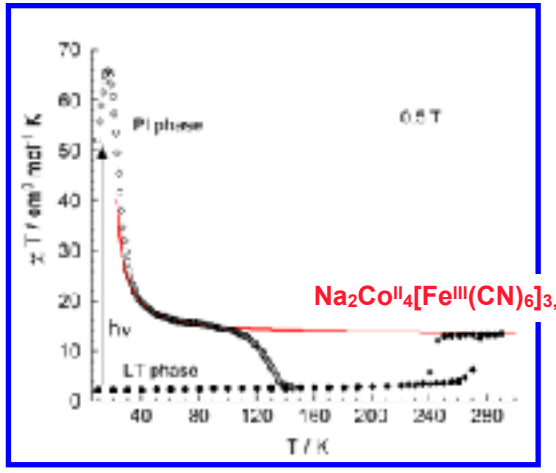
Photomagnetism in Prussian Blue Analogs

$Na_{0.37}Co_{1.37}[Fe(CN)_6]\bullet 5H_2O$



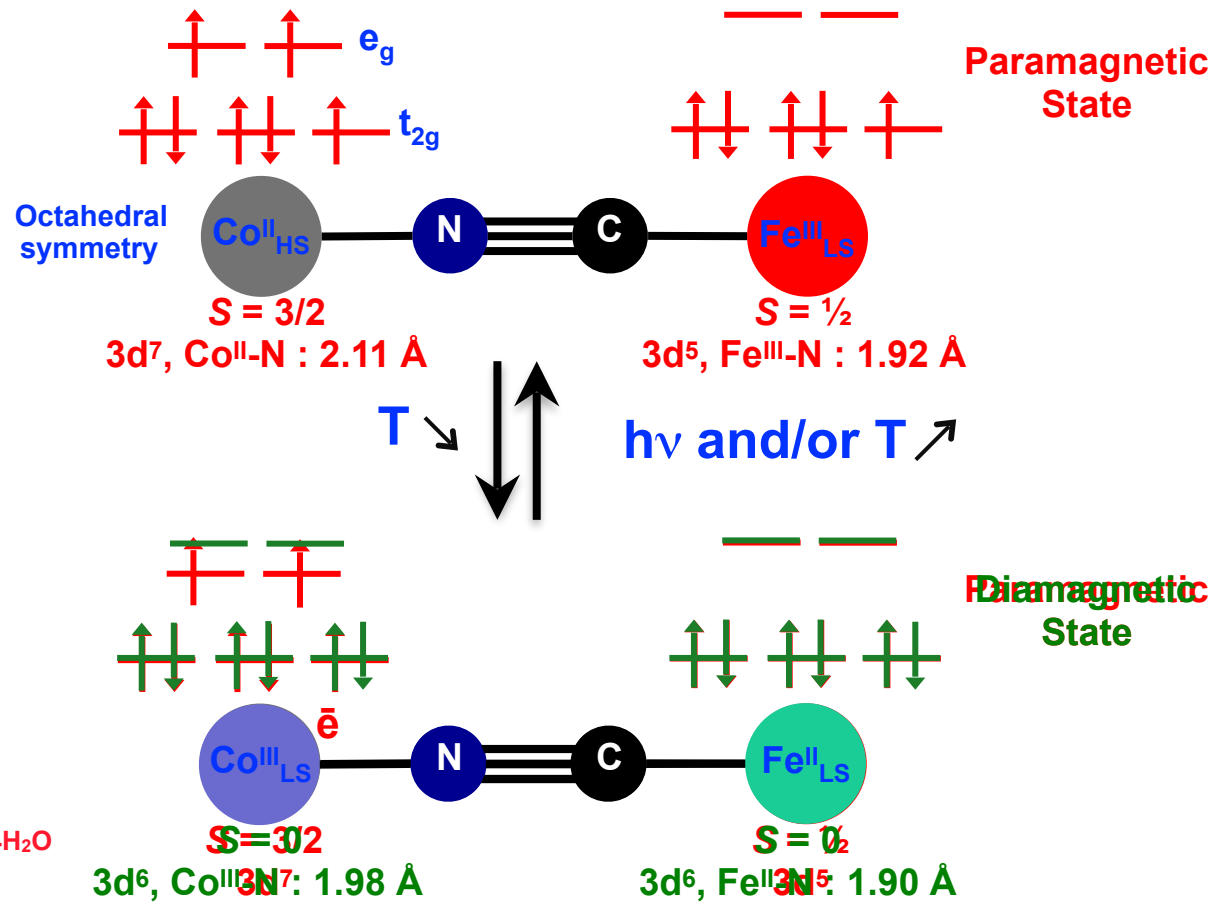


$Na_2Co_4[Fe(CN)_6]_{3,3}\bullet 14H_2O$

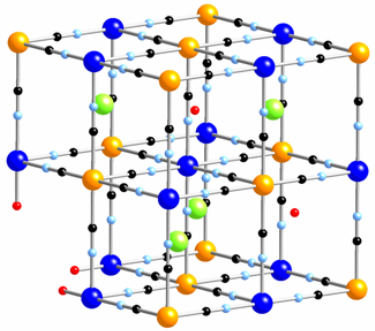


$Na_2Co^{II}_{0,77}Co^{III}_{3,33}[Fe^{II}(CN)_6]_{3,3}\bullet 14H_2O$

Ohkoshi O. et al. *Inorg Chem.* **1999** 38 4405; Shimamoto N. et al. *Inorg Chem.* **2002**, 41, 678; Bleuzen A.et al. *J. Am. Chem. Soc.* **2000** 122 6648; Bleuzen A.et al. *J. Am. Chem. Soc.* **2000** 122 6653; Escax V.et al. *J. Am. Chem. Soc.* **2001** 123 12536. Le Bris et al. *New J Chem.* **2009** 33 1255.



Photomagnetism in Prussian Blue Analogs



Ohkoshi O. et al. *Inorg Chem.* **1999** 38 4405; Shimamoto N. et al. *Inorg Chem.* **2002**, 41, 678; Bleuzen A.et al. *J. Am. Chem. Soc.* **2000** 122 6648; Bleuzen A.et al. *J. Am. Chem. Soc.* **2000** 122 6653; Escax V.et al. *J. Am. Chem. Soc.* **2001** 123 12536. Le Bris et al. *New J Chem.* **2009** 33 1255.

Conditions to observe the photomagnetism in FeCo PBA

→ **$Rb_{0.54}Co_{1.21}[Fe(CN)_6].17H_2O$ PHOTOMAGNET**

80 % diamagnetic pairs Co^{III}-NC-Fe^{II} + paramagnetic pairs Co^{II}-NC-Fe^{III} + 17 % vacancies Fe

Co^{III} ion in an average environment $Co(NC)_5(H_2O)$

→ **$CsCo[Fe(CN)_6].3.3H_2O$ NO LIGHT EFFECT**

100 % diamagnetic pairs Co^{III}-NC-Fe^{II}

No vacancies

Co^{III} ion in an average environment $Co(NC)_6$

→ **$K_{0.04}Co_{1.48}[Fe(CN)_6].6.8H_2O$ NO LIGHT EFFECT**

67 % paramagnetic pairs Co^{II}-NC-Fe^{III} + 33 % vacancies Fe

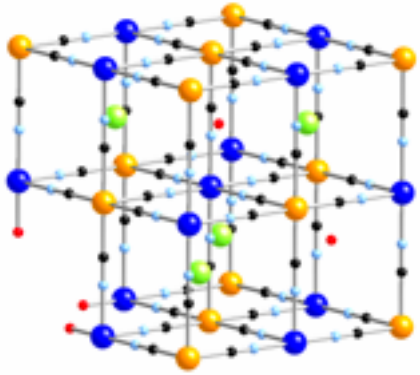
Co^{II} ion in an average environment $Co(NC)_4(H_2O)_2$

Presence of the photosensitive $Co^{III}Fe^{II}$ pairs
but also role of the network (redox potential and deformation around the Co ion)

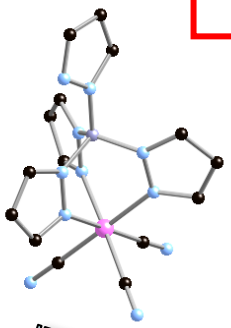
Rational building block approach: **molecular analogs**

S. M. Holmes

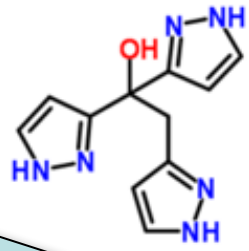
✓ The functional network



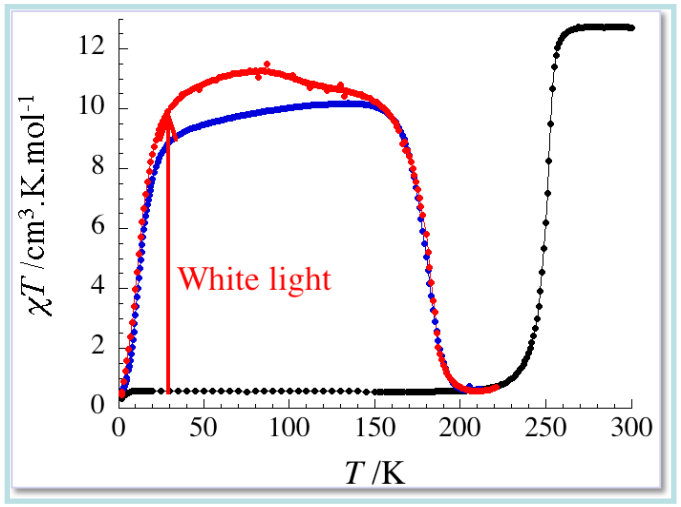
Selection of the Fe^{3+} and Co^{2+} precursors:
Fe anionic precursor with **tridentate** and CN ligands
Co cationic precursor with **tridentate** ligands



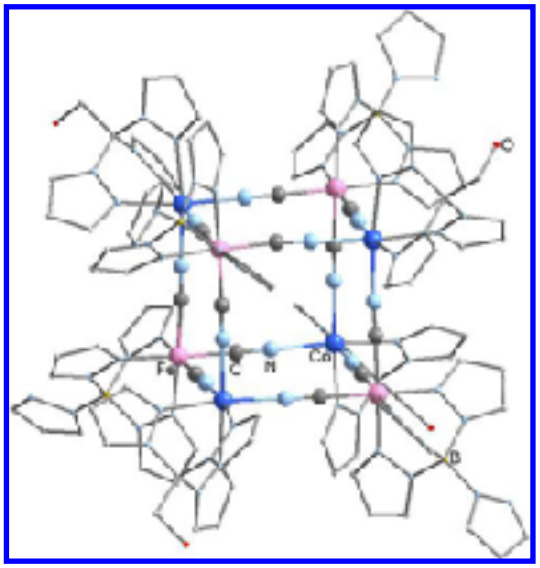
Li D. et al. *J. Am. Chem. Soc.* **2008** 130 252; Chen Z.-Y. et al. *Angew. Chem. Int Ed.* **2023**, *62*, e202301124



Co^{2+}

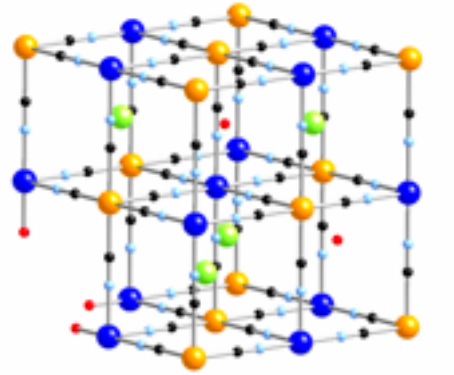


$P2_1/c$	260 K	90 K
$(Fe\text{-}C)_{average}$	1.93 Å	1.90 Å
$(Co\text{-}N)_{average}$	2.10 Å	1.98 Å
	$[Co^{II}Fe^{III}]_4$	$[Co^{III}Fe^{II}]_4$

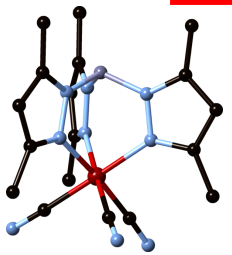


S. M. Holmes

✓ The functional network



Selection of the Fe^{3+} and Co^{2+} precursors:
Fe anionic precursor with **tridentate** and CN ligands
Co cationic precursor with **bidentate** ligands



Zhang. Y. et al. *Angew. Chem.* Int. Ed. **2010**, 49 3752; Nihei M. et al. *J. Am. Chem. Soc.* **2011,** 133, 3592; Mondal A. et al. *J. Am. Chem. Soc.* **2013,** 135, 1653…

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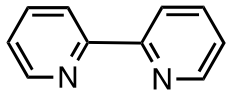
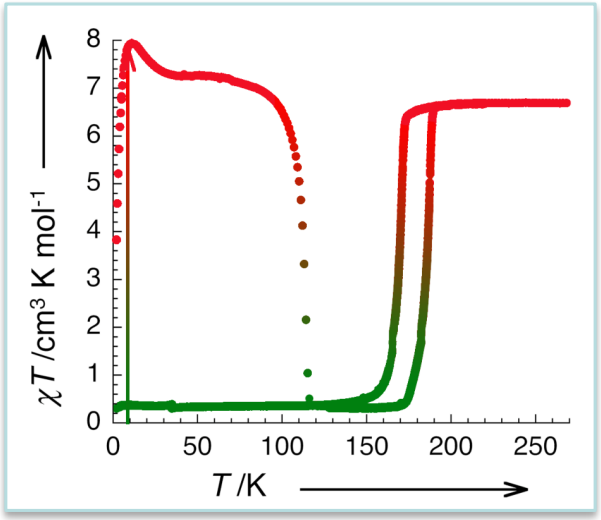
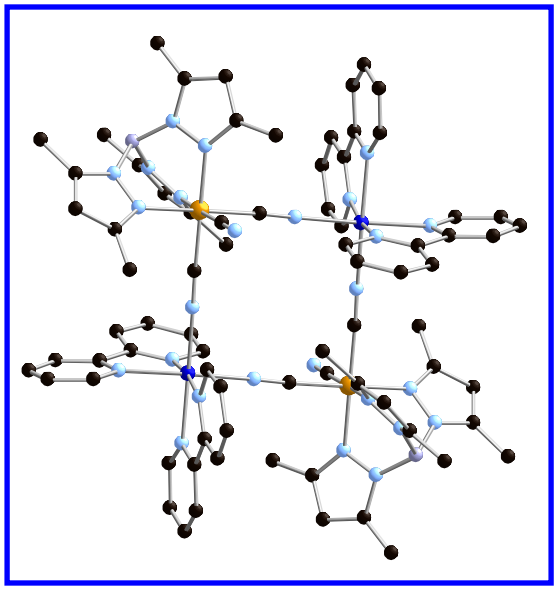


Co^{2+}



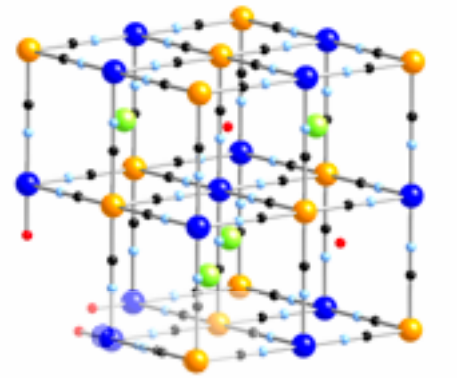
P-1	230 K	120 K
$(Fe\text{-}C)_{average}$	1.96 Å	1.97 Å
$(Co\text{-}N)_{average}$	2.11 Å	2.01 Å
	$[Co^{II}Fe^{III}]_2$	$[Co^{III}Fe^{II}]_2$

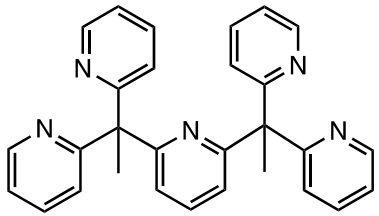


S. Calancea, PhD Thesis (2010-13)

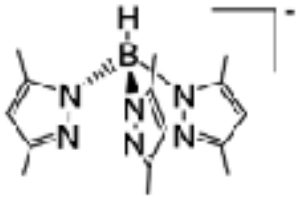
✓ The functional network

Selection of the Fe^{3+} and Co^{2+} precursors:
Fe anionic precursor with **tridentate** and CN ligands
Co cationic precursor with **pentadente** ligands

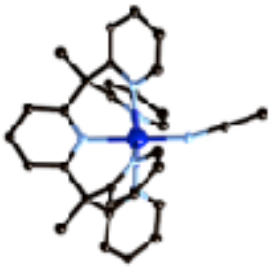




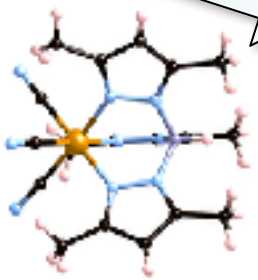
= $PY5Me_2$



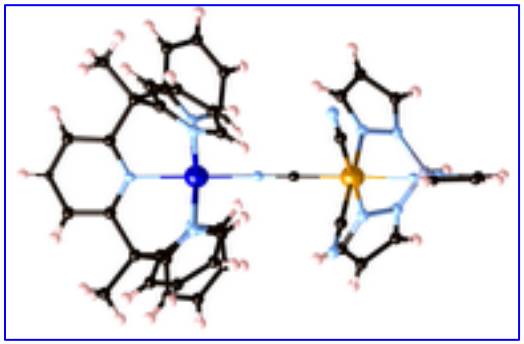
= Tp*



$[Co^{II}(PY5Me_2)(CH_3CN)](OTf)_2$

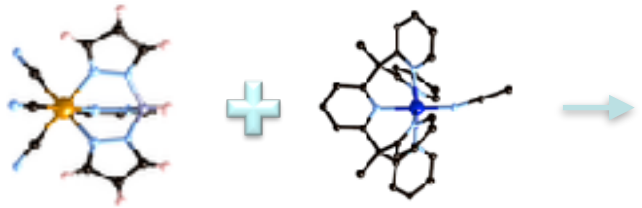


$(Et_4N)[Tp^*Fe^{III}(CN)_3]$



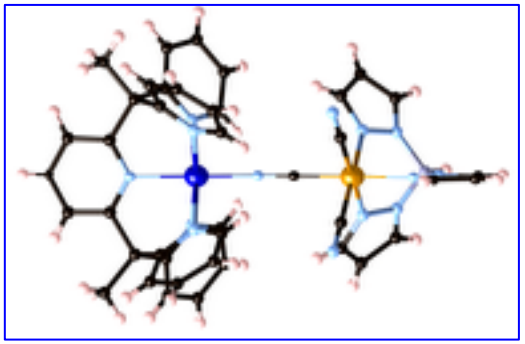
PY5Me$_2$ (2,6-bis(1,1-bis(2-pyridyl)ethyl)pyridine); Tp* = tris(3,5-dimethyl)pyrazolyl borate

More Electron-transfer Co/Fe pairs

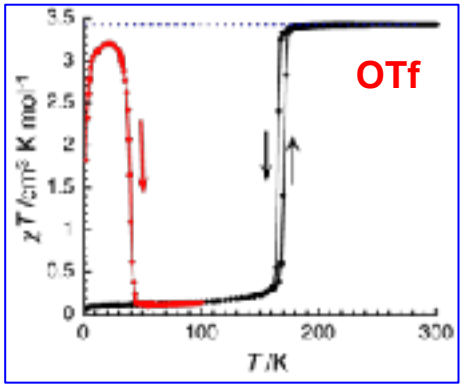


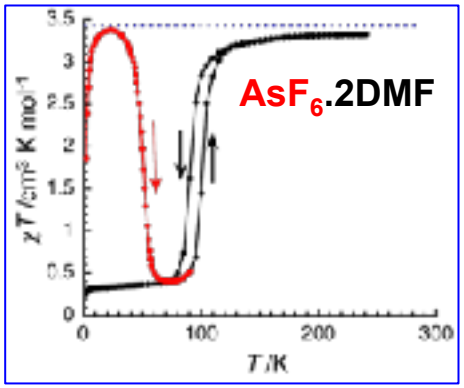
$(Bu_4N)[TpFe^{III}(CN)_3]$ $[Co^{II}(PY5Me_2)(CH_3CN)](X)_2$

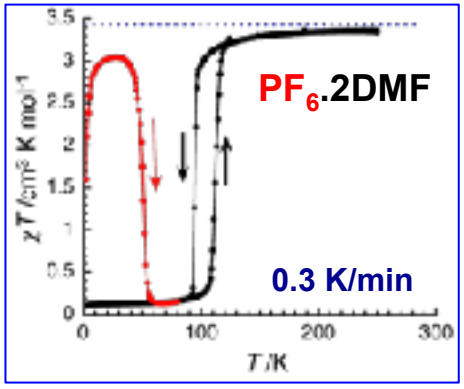
Modifying the counter-anions:

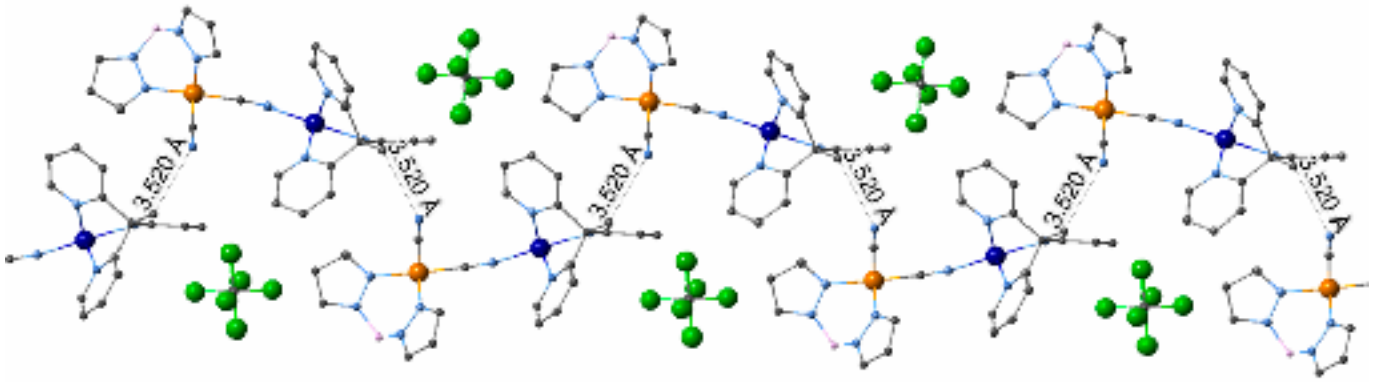


$[Co(PY5Me_2)Fe(Tp)(CN)_3][X]$









Short interpair CH…N contacts through H bonding !!!

$[Co(PY5Me_2)Fe(Tp)(CN)_3][OTf]$ 3.56 Å
$[Co(PY5Me_2)Fe(Tp)(CN)_3][AsF_6].2DMF$
$[Co(PY5Me_2)Fe(Tp)(CN)_3][PF_6].2DMF$ 3.52 Å

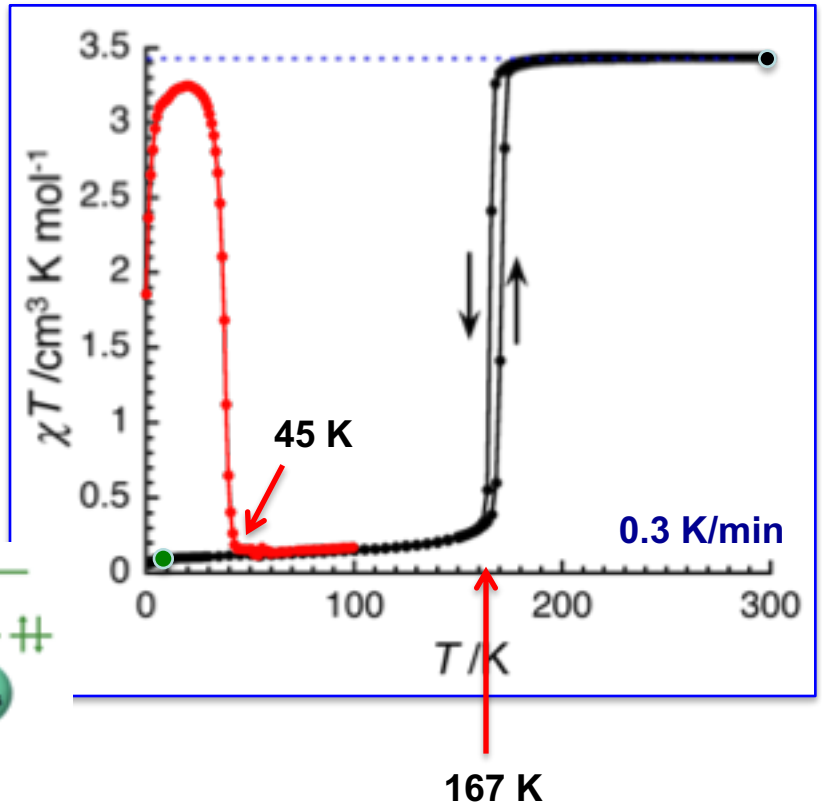
Koumousi E. et al. *J. Am. Chem. Soc.* **2014** 135 15461

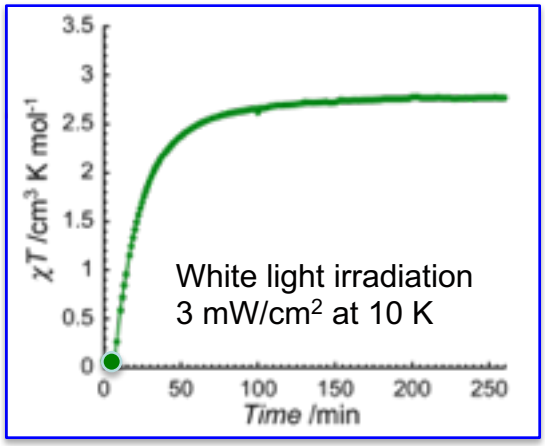
Tp: trispyrazolylborate; $PY5Me_2$ (2,6-bis(1,1-bis(2-pyridyl)ethyl)pyridine);
OTf-: trifluoromethanesulfonate

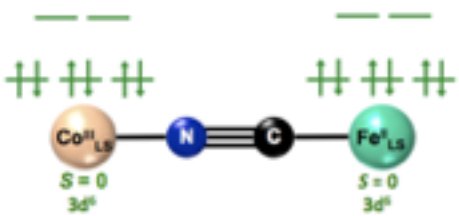
{[(Tp)Fe(CN)$_3$]$_2$[Co(Py5Me$_2$)]}[OTf]

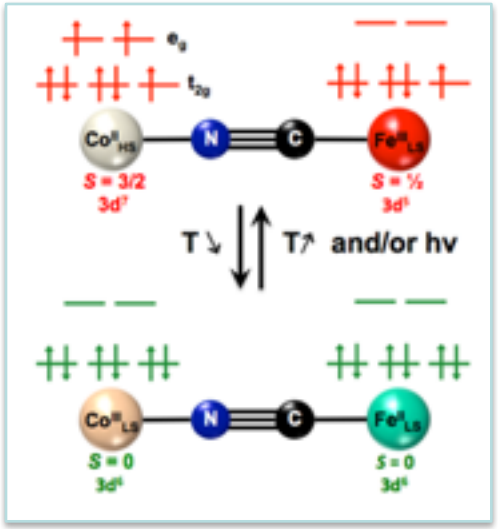
Koumousi E. et al., JACS, 2014 *135*, 15461

Magnetic properties under 1 T









Thermal and Light-induced Electron Transfer in solid state for a pair …

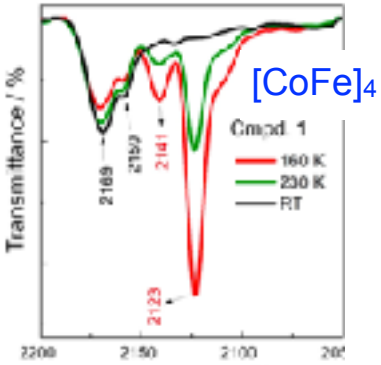
How to probe electron transfer?

In solid state : bulk characterizations

✓ Single Crystal diffraction : structures of the paramagnetic $[Co_{HS}^{II}Fe_{LS}^{III}]_n$ and diamagnetic $[Co_{LS}^{II}Fe_{LS}^{II}]_n$ states

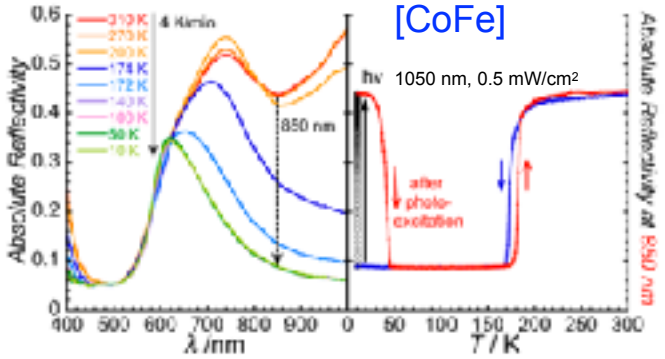
✓ IR spectroscopy : temperature studies

CN stretching regions

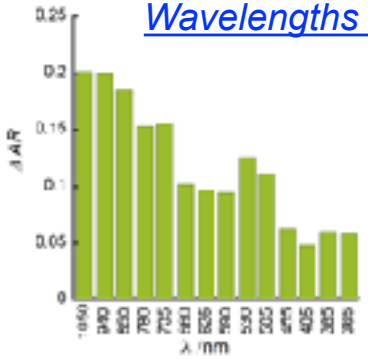


Chen Z.-Y. et al. *Angew. Chem. Int Ed.* **2023** *62* e202301124

✓ Optical reflectivity spectroscopy : temperature and excitation studies

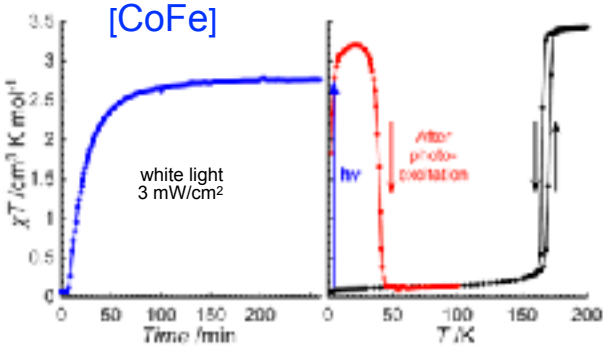


Wavelengths studies

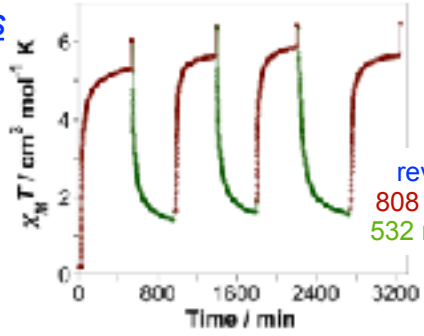


Koumousi E. et al. *J. Am. Chem. Soc.* **2014** 136 15461

✓ Magnetometry



Cycle studies



reversible excitations:
808 nm, 10 K, 6 mW/cm²
532 nm, 10 K, 10 mW/cm²

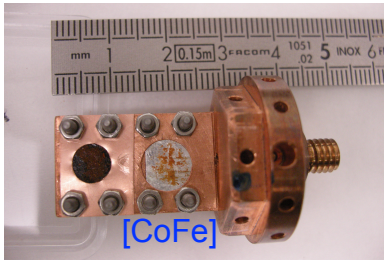
Mondal A. et al. *J. Am. Chem. Soc.* **2013** 135 1653

How to probe electron transfer?

In solid state : X-ray absorption spectroscopies (XAS)

✓ Soft X rays L edges: 2p to 3d levels ~10^{-10} mbar (robust compounds) surface sensitive (~ 5 nm)

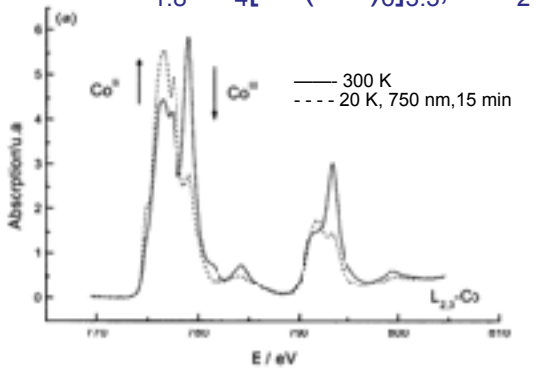
SOLEIL SYNCHROTRON DEIMOS



Cartier dit Moulin C. et al. *J. Am. Chem. Soc.* **2000** 122 6653

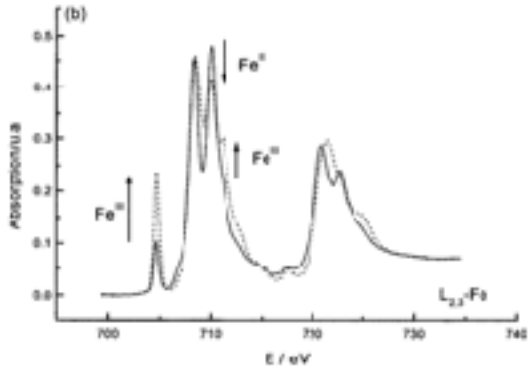
Jafri S. F. et al. *J. Am. Chem. Soc.* **2019** 141 3470

$Rb_{1.8}Co_4[Fe(CN)_6]_{3.3},13H_2O$



✓ Hard X rays K edges: 1s to 4p(3d) levels ~10^{-5} mbar and bulk sensitive

Possibility to study solutions or crystals immersed in solution



ESRF The European Synchrotron

ID12

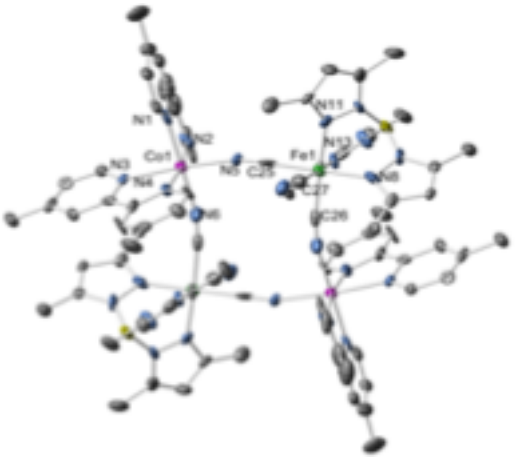
Oxidation states of both metal ions
Local geometries around both metal ions
X-ray Magnetic Circular Dichroism

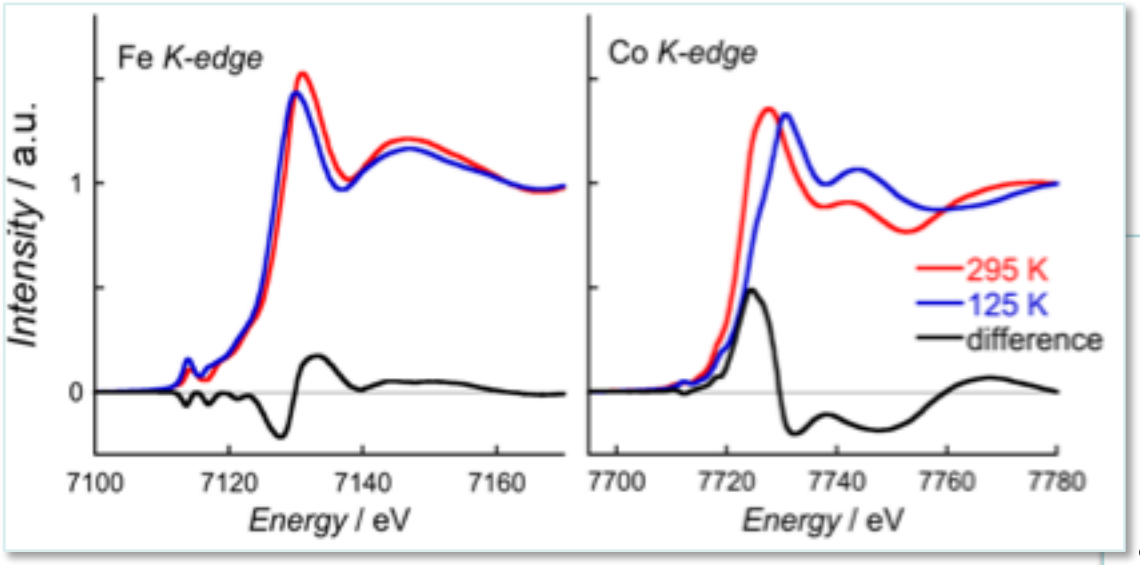
How to probe electron transfer?

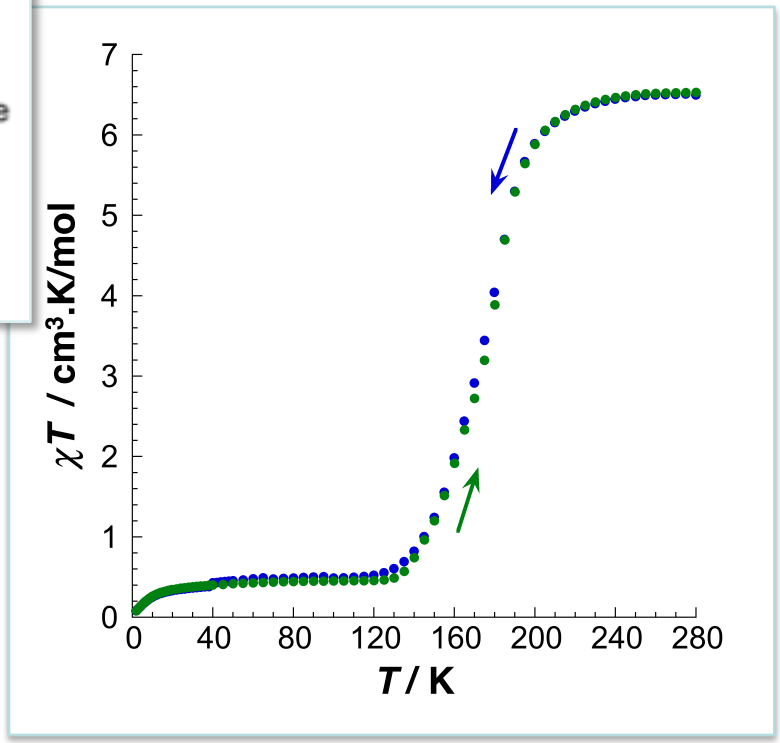
✓ Hard X rays K edges:

Study of a solvated ET compound as crystals immersed in solution
$\{[(Tp^*)Fe(CN)_3]_2[Co(Me_2bpy)_2]_2\}(ClO_4)_2 \cdot 2DMF$

Siretanu D., Holmes S., Mathonière C., Clérac R. et al., Chem. Eur. J., 2011 *17*, 11704





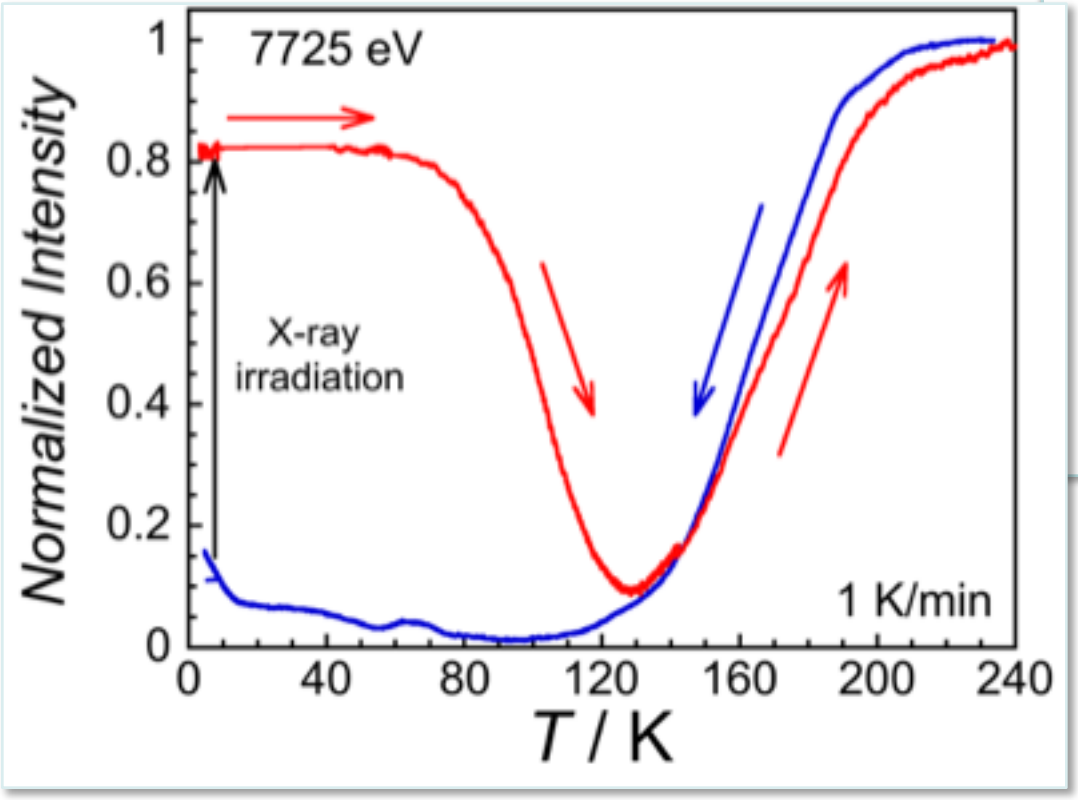


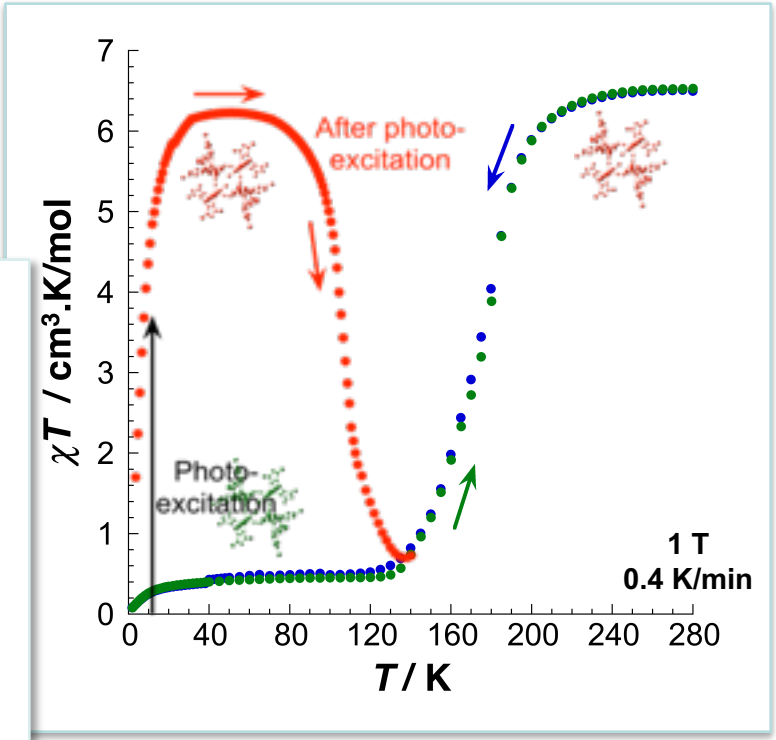
Thermal-induced ET by K-edges XAS in a solvated compound

Mathonière C. et al. Chem. Comm. 2022, 58, 12098

{[(Tp*)Fe(CN)$_3$]$_2$[Co(Me$_2$bpy)$_2$]$_2$}(ClO$_4$)$_2$·2DMF

Mathonière C. et al. Chem. Comm. 2022, 58, 12098





Relaxation and reversibility of the ET process by *K*-edges XAS

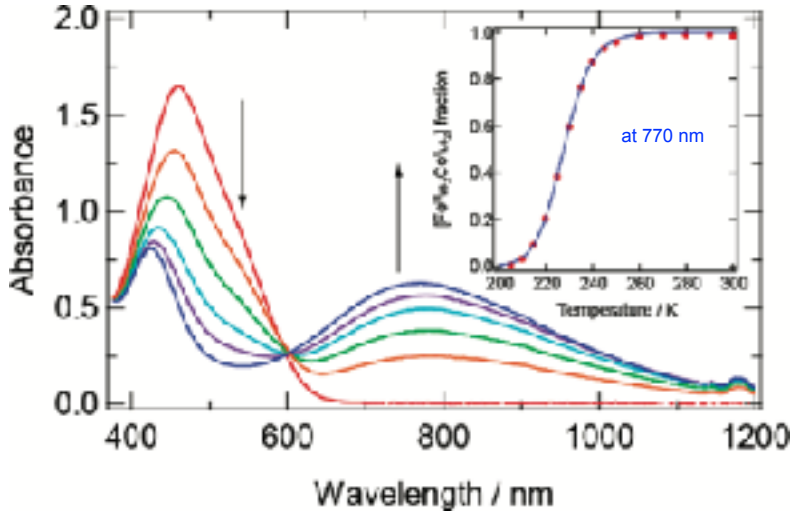
How to probe electron transfer?

In solutions :

✓ Absorption spectroscopy [CoFe]$_2$ dissolved in solvents : gradual ET

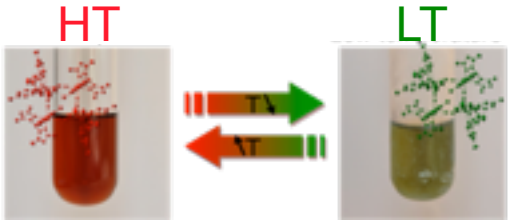
Nihei M. et al. *J. Am. Chem. Soc.* **2011** 133 3592

Siretanu D. et al. *Chem. Eur. J.* **2011** 17 11704



Ideal solution model $X = X_{LT} + \frac{X_{HT} - X_{LT}}{1 + \exp\left(\frac{\Delta H}{R}\left(\frac{1}{T} - \frac{1}{T_{1/2}}\right)\right)}$ $\Delta S = \frac{\Delta H}{T_{1/2}}$

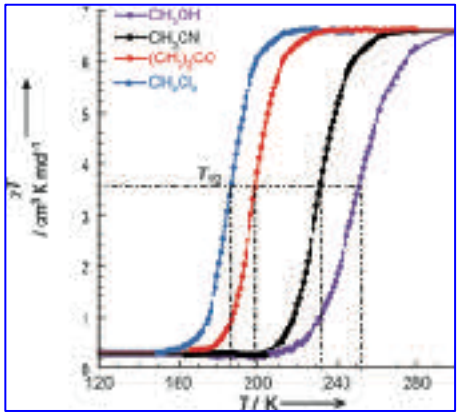
ΔH = 68 kJ mol^{-1}, $T_{1/2}$ = 227 K and ΔS = 299 J mol^{-1} K^{-1}

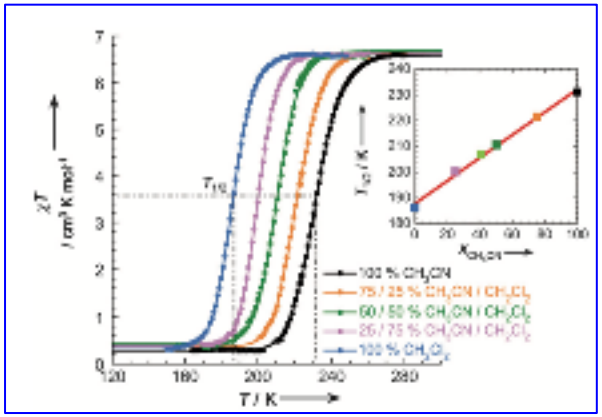


✓ Magnetometry [CoFe]$_2$ dissolved in different solvents

ΔH = 52-65 kJ mol^{-1} and ΔS = 208-274 J mol^{-1} K

ET Tuning with a mixture of solvents

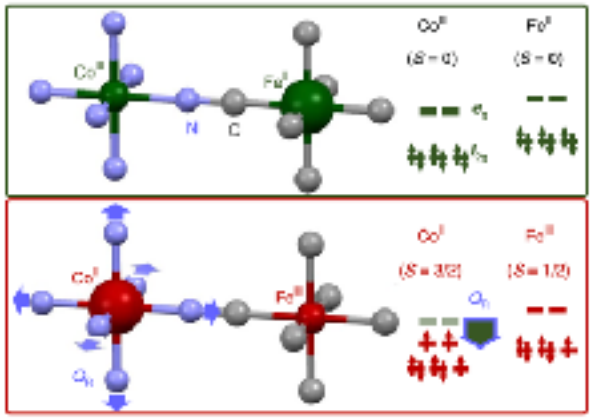




How to probe electron transfer?

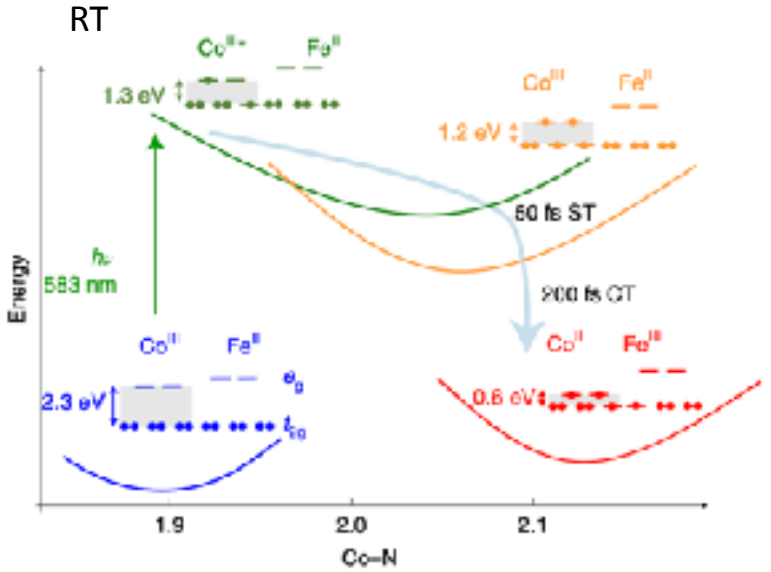
Transient spectroscopies (UV/Vis, IR and XAS)

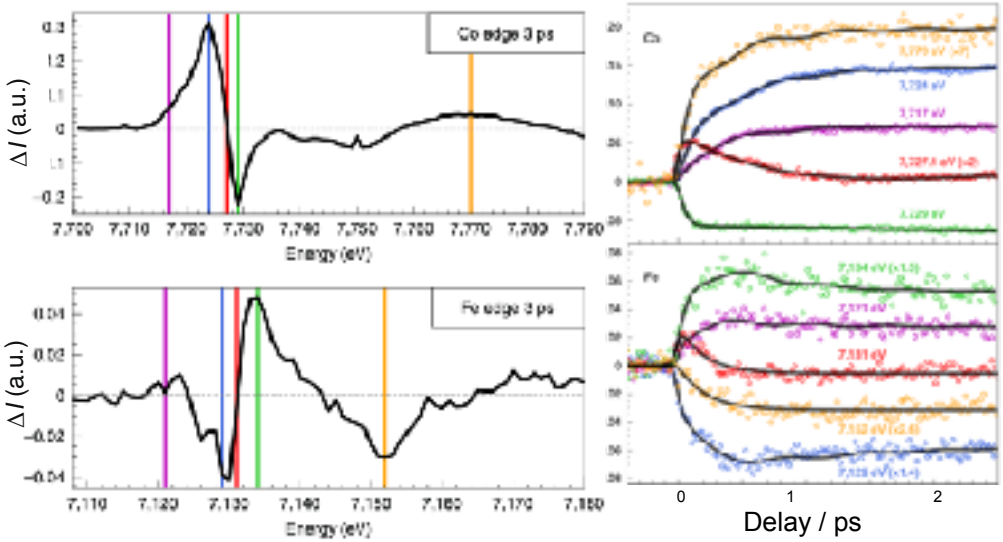
in literature: Charge Transfer Induced Spin Transition
Electron Transfer Coupled Spin Transition



Colloidal solution of CsCoFe (mainly $Co^{III}Fe^{II}$) PBA nanoparticles

XAS at femtosecond time scale (excitation in Co^{III} d-d transitions)



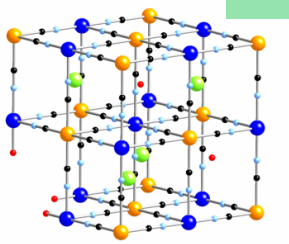


Cammarata M. et al. *Nat. Chem.* **2021** 13 14

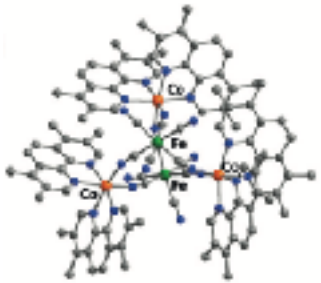
Barlow K. et al. *Phys. Chem. Chem. Phys.* **2021** 23 8118

CTIST Charge Transfer Induced Spin Transition; ETCST Electron Transfer Coupled Spin Transition

3D

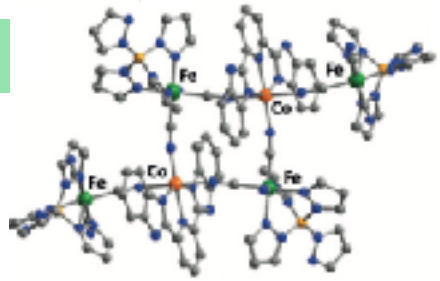


0D



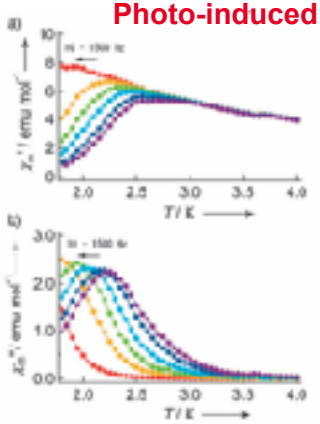
Dunbar K. group
J. Am. Chem. Soc. **2005** 127 6766.

0D

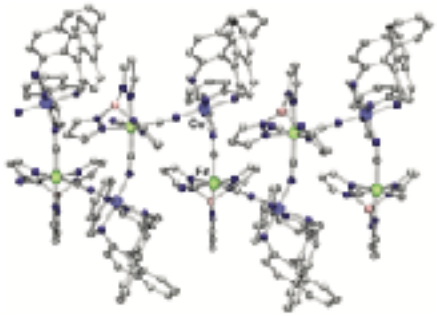


Oshio H. group *Angew. Chem. Int. Ed.* **2012** 51 6361

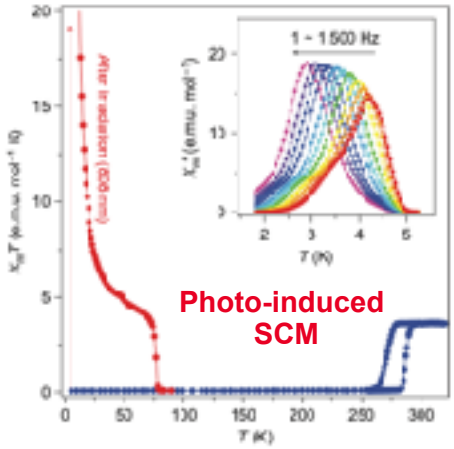
Photo-induced SMM

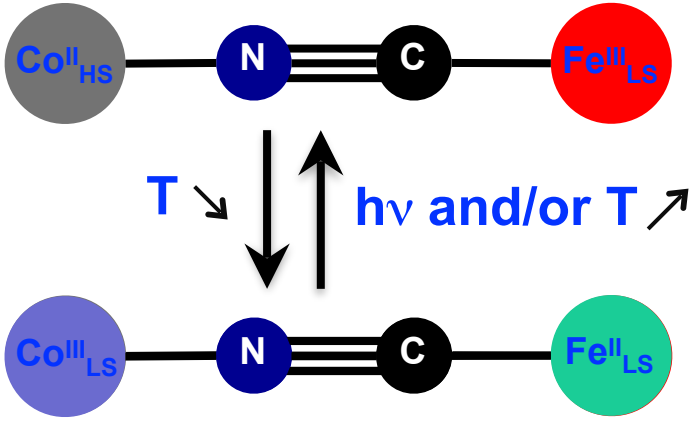


1D



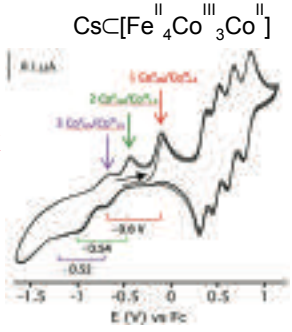
Sato O. group *Angew. Chem., Int. Ed.* **2012** 51 5119
Oshio H. group *Nat. Chem.* **2012** 4 921

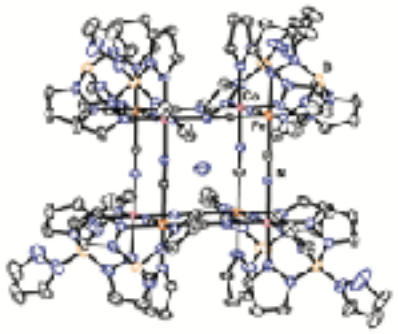




0D

Rich redox properties



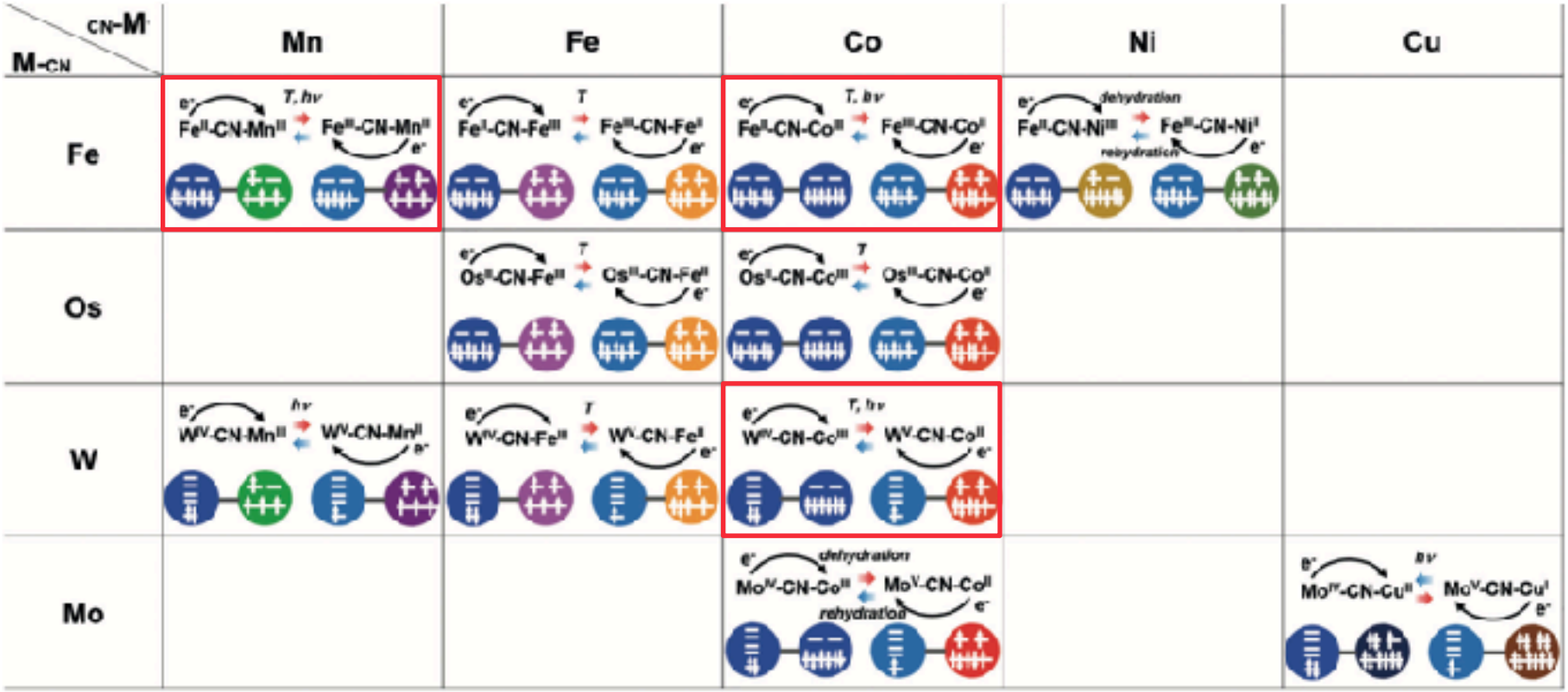


Lescouezec R. group *Dalton Trans.* **2017** 46 15549.

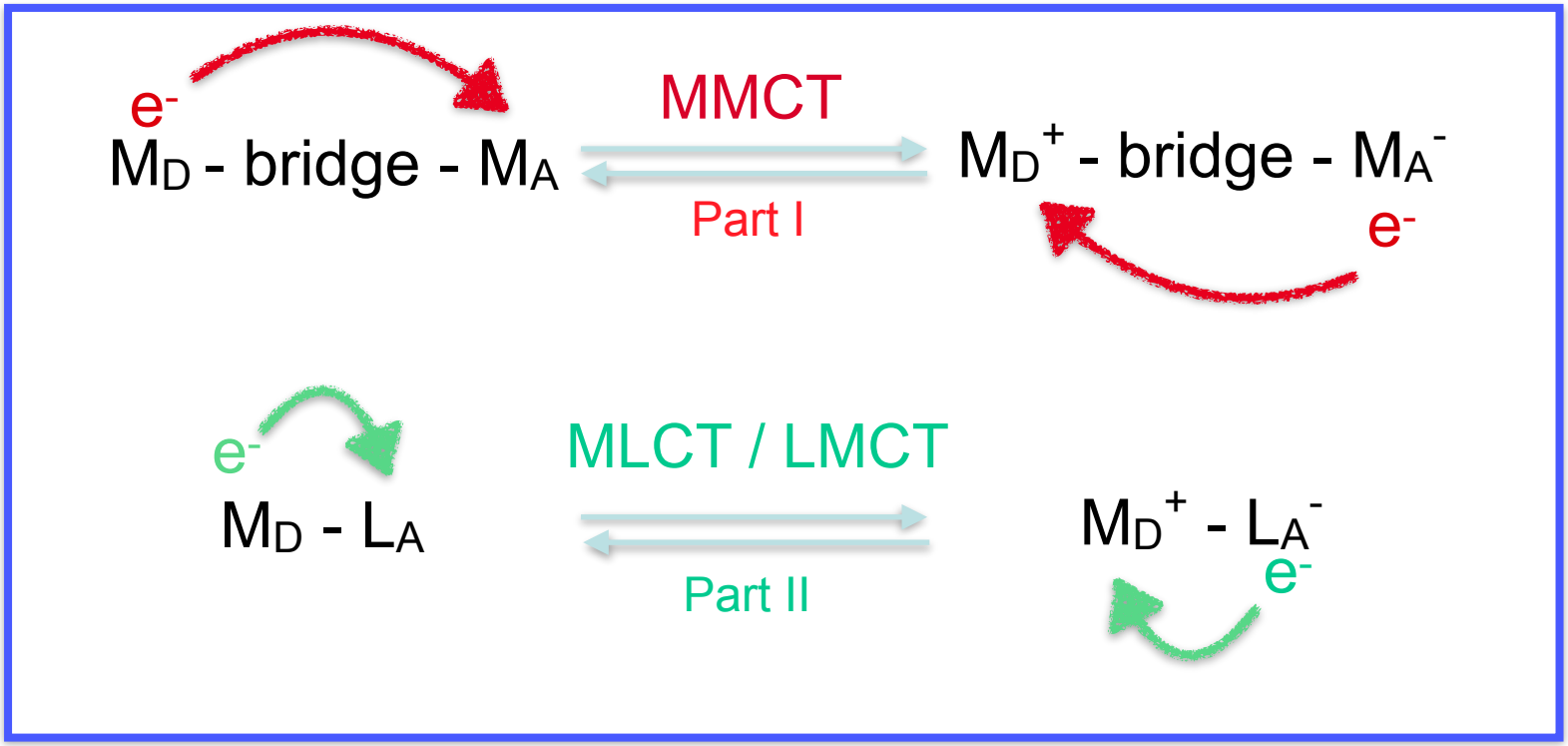
Manipulating Metal-to-Metal Charge Transfer for Materials with Switchable Functionality

Meng Y.-S.. et al. *Angew. Chem. Int. Ed.* **2018** 57 12216.

Tunable magnetic properties, optical properties, dielectric properties, thermal expansion behavior



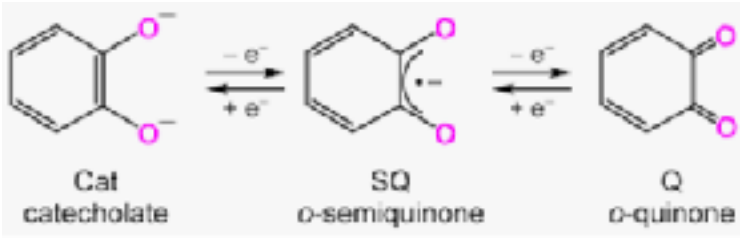
Other Reviews: Ohkoshi S-i. *Acc. Res.* **2012** 45 1749; Sato O. et al. *Angew. Chem. Int. Ed*. **2007** 46 2152; Aguila et al. *Chem. Soc. Rev.* **2016** 45 203; Zakrzewski J. et al *Chem. Rev.* **2024** 124 5930.



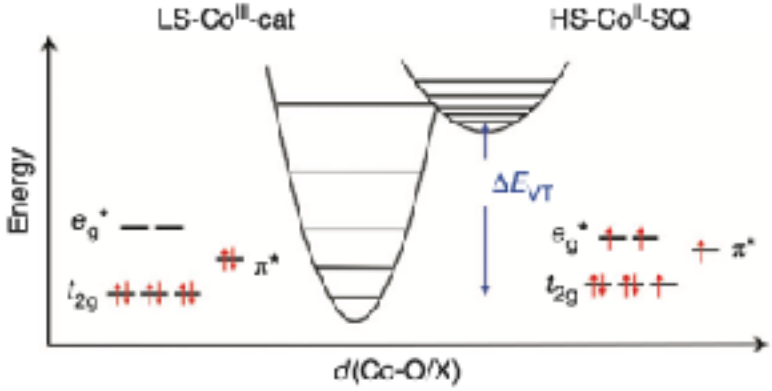
Part I : redox activity of metal ions

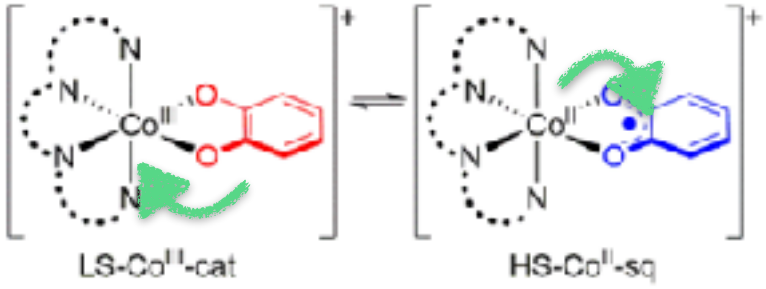
Part II : redox activity of metal ions and ligands

Co^{III}(catecholate)/Co^{II}(semiquinonate) compounds



Buchanan R. M. et al. *J. Am. Chem. Soc.* **1980** 102 4951





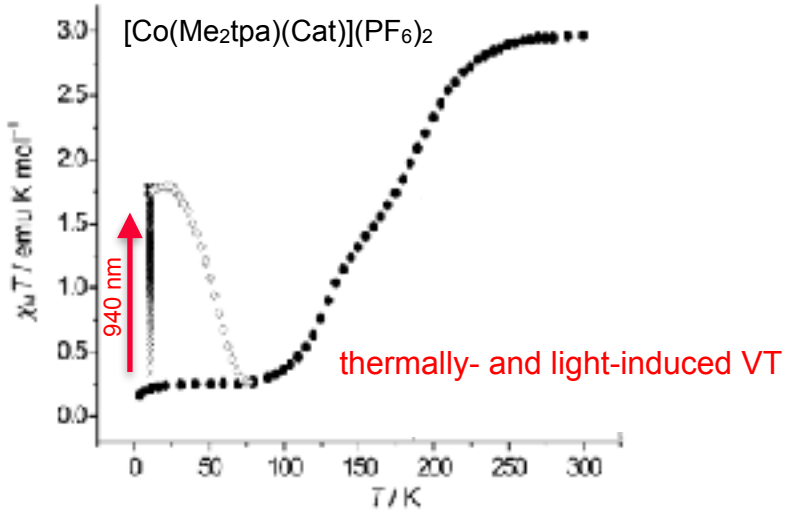
$S_{Co^{III}}=0$ $S_{rad}^{Cat}=0$

LT state

$S_{Co^{II}}=3/2$ $S_{rad}^{SQ}=1/2$

HT state

Dapporo et al. *Chem. Eur. J.* **2008** 14 10915

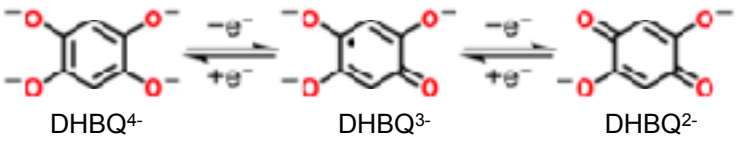


Valence Tautomerism: intramolecular ET between redox-active metal ion and ligand

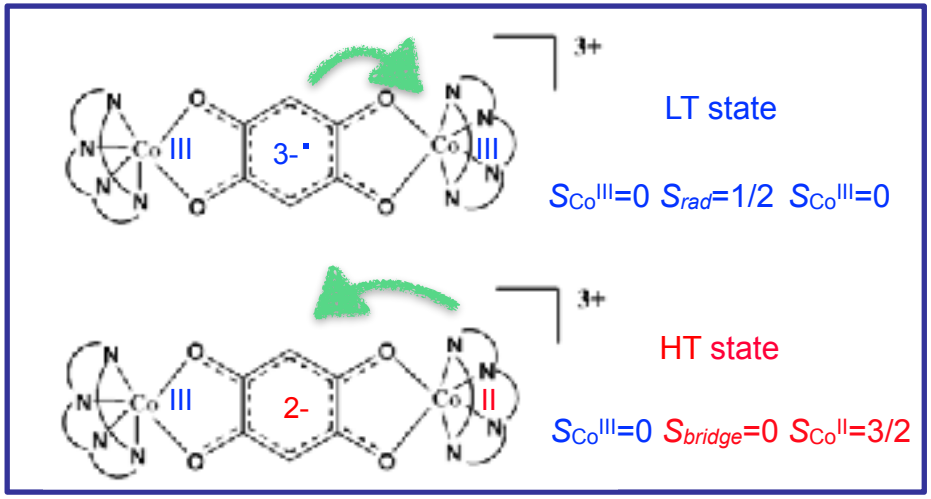
Gransbury G. and Boskovic C. *Encyclopedia of Inorganic and Bioinorganic Chemistry* **2021**, DOI: 10.1002/9781119951438.eibc2785

Me$_2$tpa: Tris(2pyridylmethyl)amine

Redox activity of a bridging ligand: towards dimers



Carbonera C. et al. *Angew. Chem. Int Ed.* **2004** 43 3136



Tao J. et al. *J. Am. Chem. Soc.* **2006** 128 1790

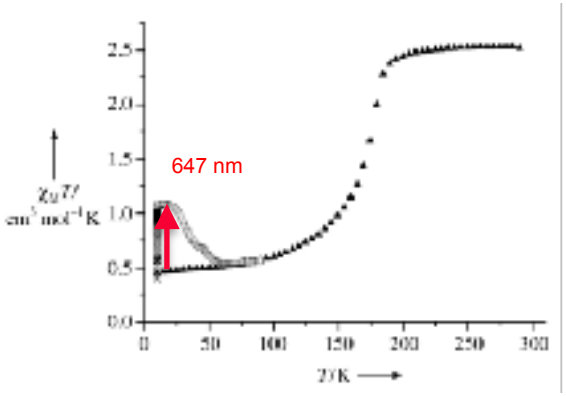
Synthesis

$$2\ [Co^{II}(cth)Cl_2] + (DHBQ)^{2-} \xrightarrow{KPF_6} [(cth)Co^{II})_2(DHBQ)](PF_6)_2$$

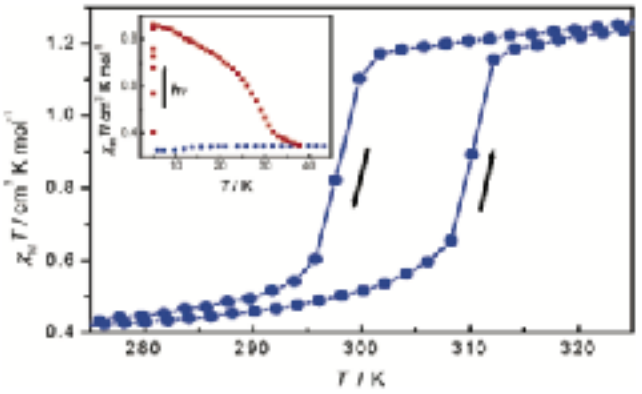
$$\xrightarrow{AgNO_3 \text{ then } KPF_6} [(cth)Co^{II,III})_2(DHBQ)](PF_6)_3$$

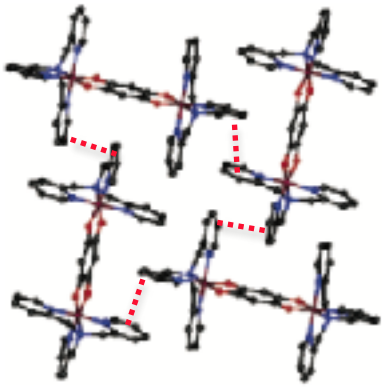
Magnetic properties

$[(TPA)Co)_2(DHBQ)](PF_6)_3$



Valence Tautomerism

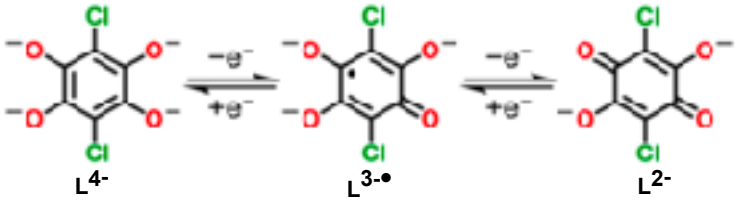




Cooperative Valence Tautomerism

Me2tpa: Tris(2pyridylmethyl)amine; cth = (dl)- 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane

Redox activity of a bridging ligand : towards extended networks

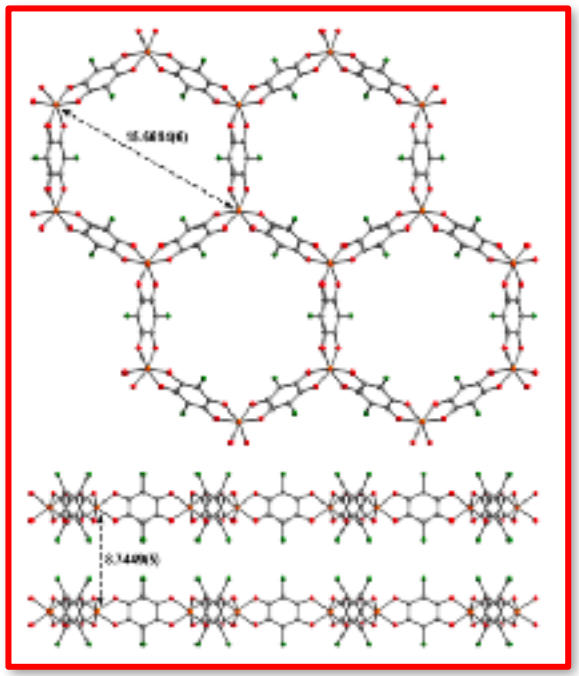


Jeon I.-R. et al. *J. Am. Chem. Soc.* **2015** 137 15699

De Gayner J. et al. *J. Am. Chem. Soc.* **2017** 139 4175

Synthesis

$Fe^{II}(BF_4)_2{\cdot}6H_2O + LH_2 \xrightarrow{DMF} (Me_2NH_2)_2[Fe^{III}_2(L^{3-\bullet})_2L]{\cdot}2H_2O{\cdot}6DMF$

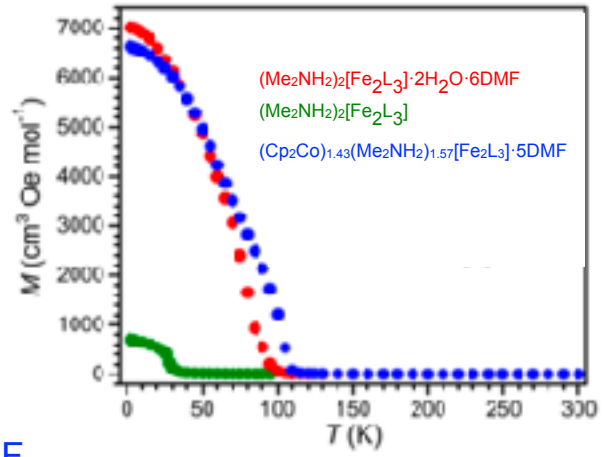


In situ ET Fe^{II} to L^{2-} revealed by SCXRD, Raman and Mossbauer studies

Post synthetic reduction

Cp_2Co in DMF

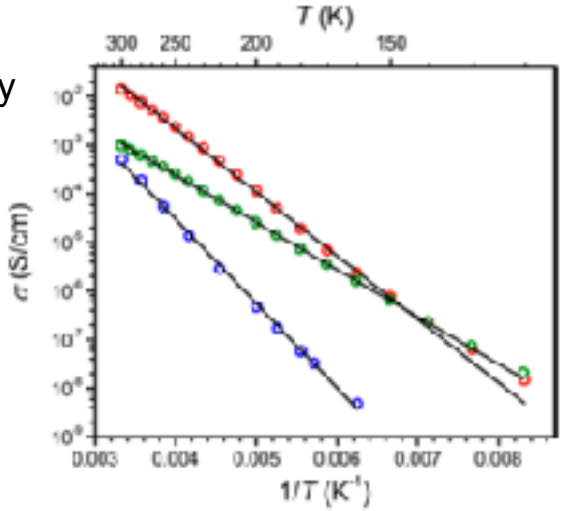
$(Cp_2Co)_{1.43}(Me_2NH_2)_{1.57}[Fe^{III}_2(L^{3-\bullet})_3]{\cdot}5DMF$



T_c = 100 K, σ_{RT} = 14 mS cm^{-1}

T_c = 105 K, σ_{RT} = 0.5 mS cm^{-1}

Radical bridges:
- strong interaction between Fe centers
- mixed valency $L^{2-}/L^{3-\bullet}$ high conductivity



New porous conducting ferrimagnets

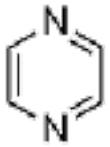
T_c above 100 K, σ_{RT} > few mS cm^{-1}

Murase R. et al. *Inorg. Chem.* **2017** 56 14373

LH_2: 2,5-dichloro-3,6-dihydroxo-1,4)benzoquinone, SCXRD: single crystal X-ray diffraction

Redox ligand activity always expected?

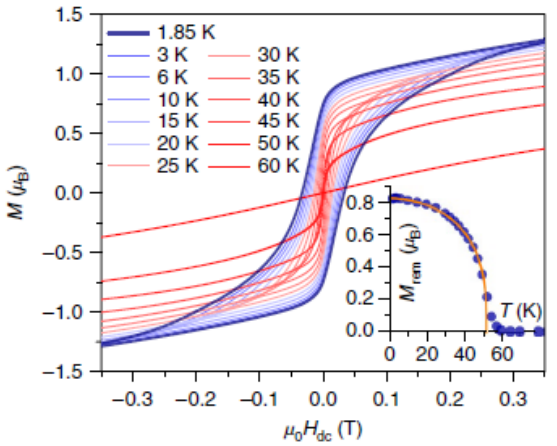
Pedersen K. et al. *Nature Chemistry* **2018** 10 1056

$Cr^{II}Cl_2$ + *n*  pyrazine

200°C

$Cr[(pyrazine)_2]Cl_2$

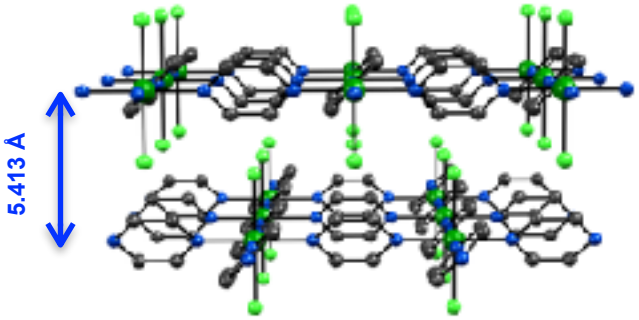
70% yield

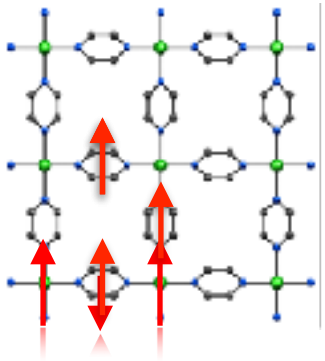


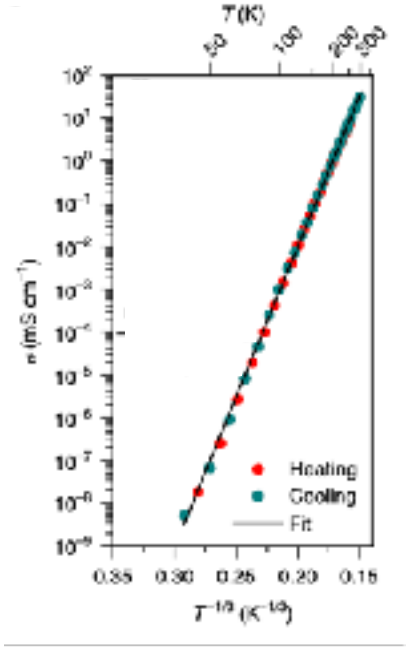
***in situ* ET between Cr^{II} and pyrazine revealed by XAS**

$Cr^{III}[(pyrazine)(pyrazine)^{-\bullet}]Cl_2$

High Resolution Powder X-Ray Diffraction



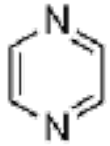




Semiconductor ferrimagnet

T_c = 52 K σ_{RT} = 32 mS cm^{-1}

XAS: X-ray absorption spectroscopy

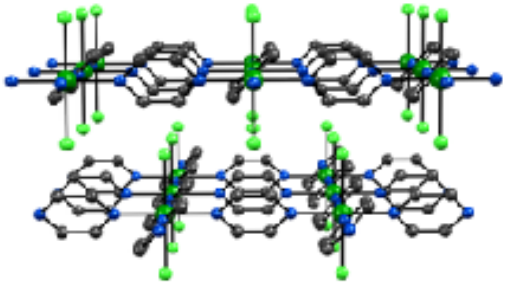
$Cr^{II}Cl_2$ + *n*  pyrazine

200°C

$Cr^{III}[(pyrazine)(pyrazine)^{-\bullet}]Cl_2$

70% yield

Semiconductor ferrimagnet
(52 K, 32 mS cm^{-1})



M(pyrazine)$_2$X$_2$

MCl$_2$

Cr(CH$_3$SO$_3$)$_2$

Perlepe P. et al. *Polyhedron* **2018** 153 248

Perlepe P. et al. *Nature Comm*, **2022** 13 5766

V analogue

$V^{II}[(pyrazine)_2]Cl_2$

Insulator antiferromagnet
T_N = 120 K

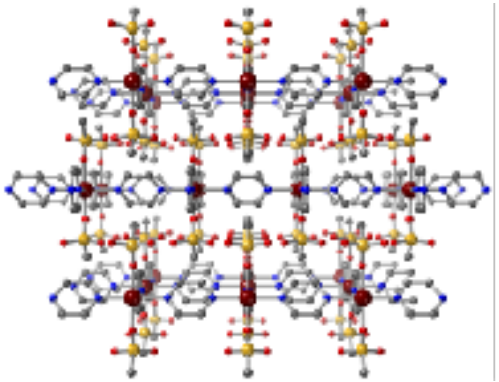
Ti analogue

$Ti^{III}[(pyrazine)(pyrazine)^{-\bullet}]Cl_2$

Metal (pauli) paramagnet
below 400 K
σ_{RT} = 5.3 S cm^{-1}

$CH_3SO_3^-$ analogue

$Cr^{II}[(pyrazine)_2](CH_3SO_3)_2$

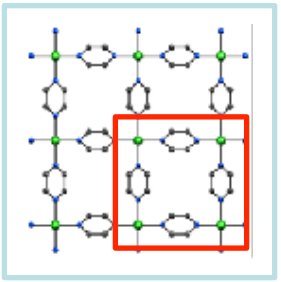


Insulator antiferromagnet
T_N = 10 K

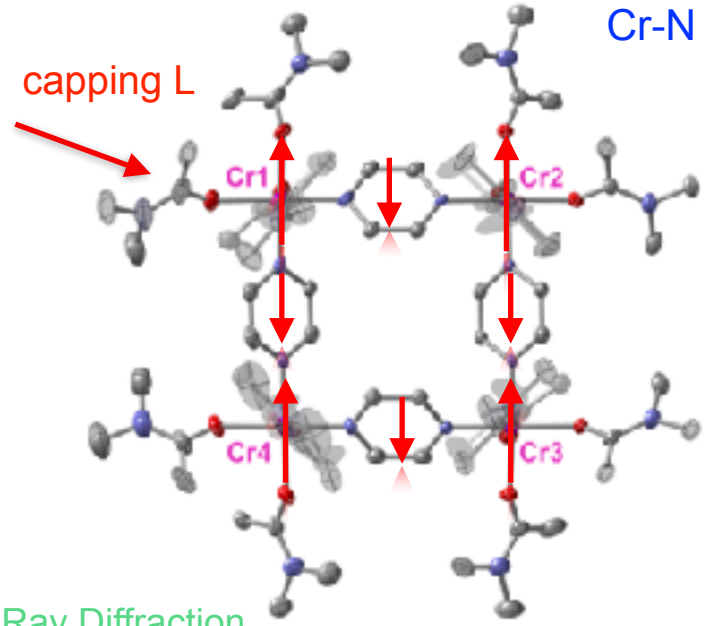
Lou D. et al *J. Am. Chem. Soc* **2024** 146 19649

$Cr^{II}(OTf)_2$ + *n* pyrazine (15 eq.) —diffusion method in DMA→ $[Cr^{III}_4[(pyrazine^{-\bullet})_4(DMA)_{16}](OTf)_8(pyrazine)(DMA)_{6.7}$

in situ ET between Cr^{II} and pyrazine

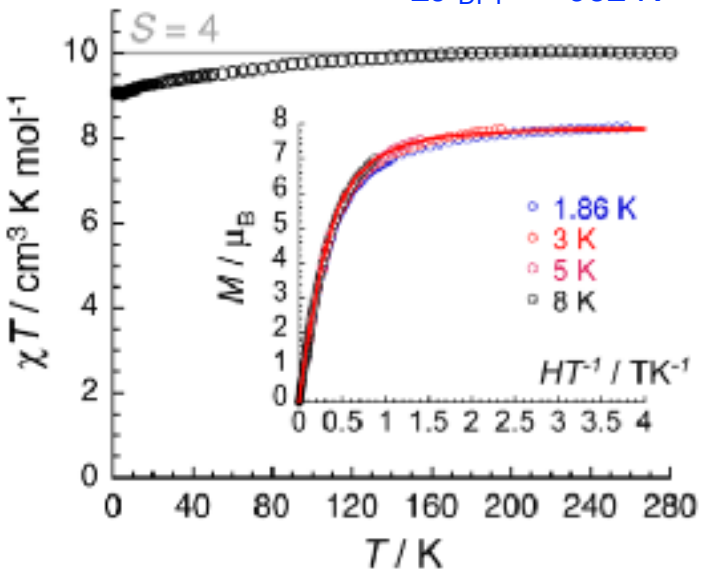


capping L



Cr-N average square 1.975 A → Cr^{III}
Cr-N in Cr^{II}-pyrazine systems : 2.162 A

$2J_{DFT}$ = −932 K

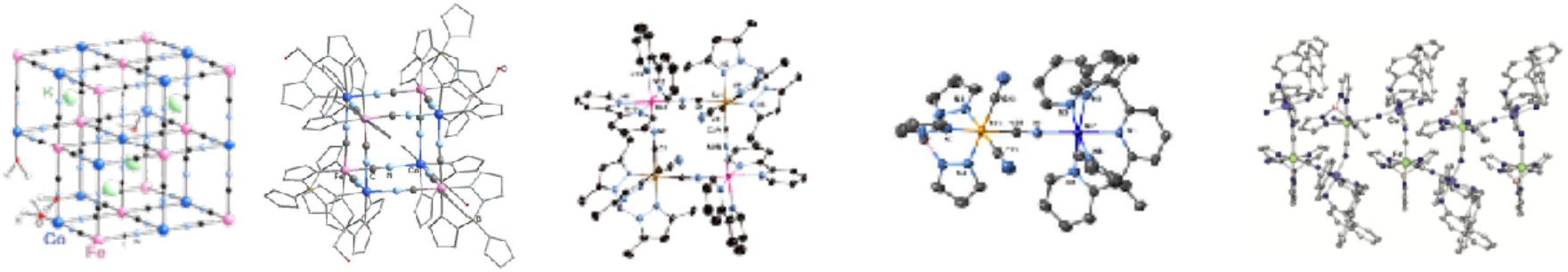


Single crystal X-Ray Diffraction
X-Ray absorption Spectroscopy
Bond Valence Shell method

Part I Metal-to-Metal ET networks and molecules

- Chemical design using the building block approach
- ET as an efficient tool for switching

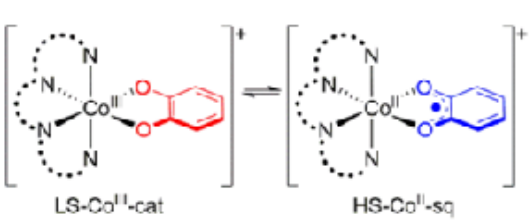
A large family of switchable Prussian Blue networks and molecular analogs

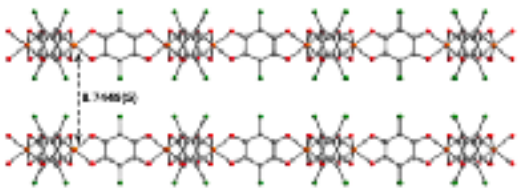


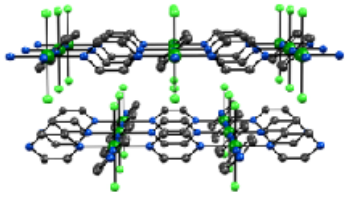
Part II Metal-to-Ligand and/or Ligand-to-Metal ET molecules and networks

- Chemical design using the building block approach
- ET as an efficient tool for switching (valence tautomerism)
- ET as an efficient tool for new conducting magnets

Ligand Redox activity : towards new functionalities







Highly 2D conductive magnets with high T_c

Xie L. S. et al. *Chem. Rev.* **2020** 120 8536

Murase R. et al. *Inorg. Chem.* **2017** 56 14373

Intrinsically Mixed-Valence Frameworks

Mixed-Valency via Post-synthetic Modification for conductivity

Post synthetic modifications for high T_c magnets

Perlepe P et al. *Science.* **2020** 370 587

$Cr^{III}[(pyrazine)(pyrazine)^{-\bullet}]Cl_2$ + LiRed → **$Li_{0.7}[Cr^{II}(pyrazine^{-\bullet})_2]Cl_{0.7}\bullet THF$** T_c = 515 K

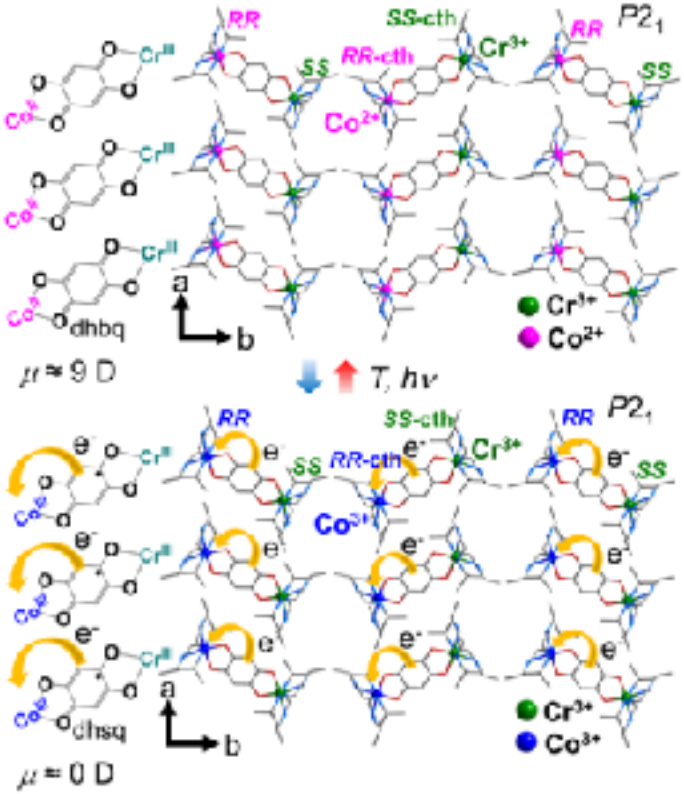
ET and chirality

Chirality: polar space group and ET unit orientation

Directional ET and pyroelectricity

Xie L. S. et al. *Chem. Sci.* **2023** 14 10631

Huang W. et al. *Chem. Soc. Rev.* **2021** 50 6832



The M3 team at the CRPP

Molecular Materials and Magnetism
http://m3.crpp.cnrs.fr/

Thank you for your attention!!!