About OMICS Group

OMICS Group International is an amalgamation of Open Access publications and worldwide international science conferences and events. Established in the year 2007 with the sole aim of making the information on Sciences and technology 'Open Access', OMICS Group publishes 400 online open access scholarly journals in all aspects of Science, Engineering, Management and Technology journals. OMICS Group has been instrumental in taking the knowledge on Science & technology to the doorsteps of ordinary men and women. Research Scholars, Students, Libraries, Educational Institutions, Research centers and the industry are main stakeholders that benefitted greatly from this knowledge dissemination. OMICS Group also organizes 300 International conferences annually across the globe, where knowledge transfer takes place through debates, round table discussions, poster presentations, workshops, symposia and exhibitions.

About OMICS Group Conferences

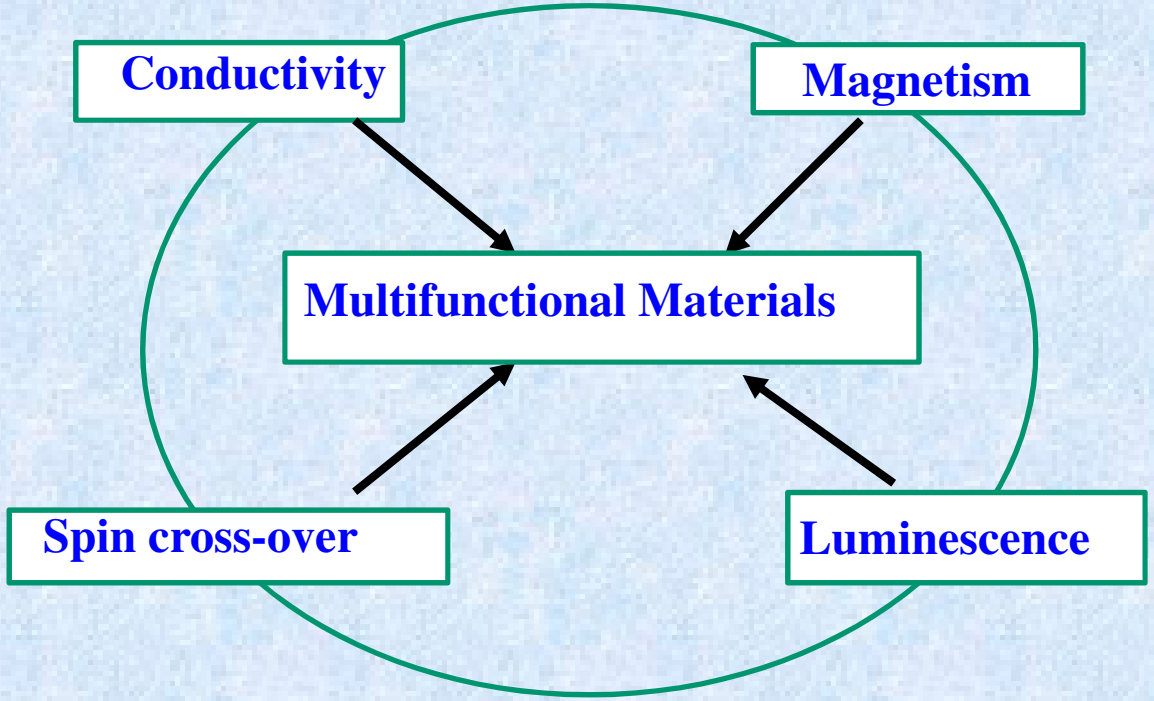
OMICS Group International is a pioneer and leading science event organizer, which publishes around 400 open access journals and conducts over 300 Medical, Clinical, Engineering, Life Sciences, Phrama scientific conferences all over the globe annually with the support of more than 1000 scientific associations and 30,000 editorial board members and 3.5 million followers to its credit.

OMICS Group has organized 500 conferences, workshops and national symposiums across the major cities including San Francisco, Las Vegas, San Antonio, Omaha, Orlando, Raleigh, Santa Clara, Chicago, Philadelphia, Baltimore, United Kingdom, Valencia, Dubai, Beijing, Hyderabad, Bengaluru and Mumbai.

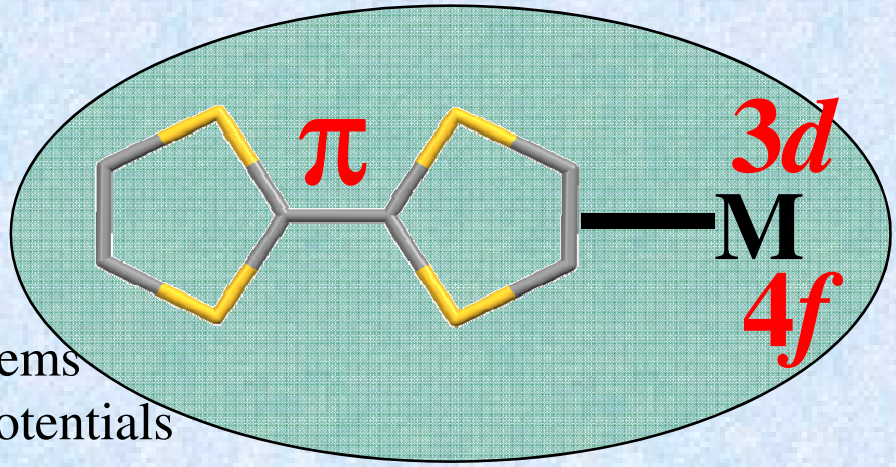
UMR 6226 CNRS_Université de Rennes1

Correlation Between Magnetism and Luminescence in Redox Active Single Molecule Magnet.

Lahcène Ouahab



Multifunctional Molecular Systems : Molecules and Materials

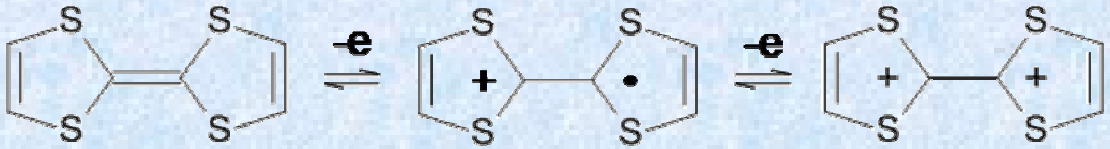


TTFs

- Planar molecules
- Delocalized π systems
- accessible redox potentials
- Stable radical cations

Charge transfer complexes

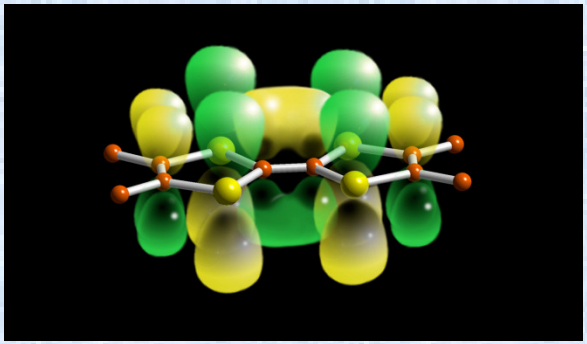
Mixte valence compounds



Lanthanides

- Luminescence
- High magnetic moment
- Strong Anisotropy

SMM and SIM



*** Use of TTF derivatives as organic antenna for the sensitization of the Ln Luminescence**

*** TTF containing Ln complexes as redox-active S M M**

*** Combination of luminescence and magnetism and conductivity**

Sciences Chimiques UMR CNRS 6226 de Rennes

OUTLINE

- **Introduction**
- **TTF for sensitization of Ln(III) Luminescence**

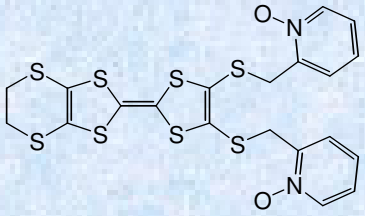
  $[Ln(hfac)_3(L)_2]$;
  Ln(III) = Er, Yb

- **SMM in *4f* complexes with TTFs**
  - *Solid state vs. solution*
  - *Radical cation*

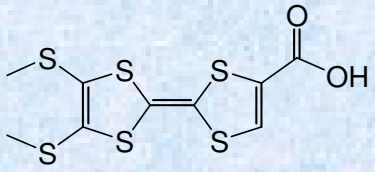
- **Redox-active Luminescente SMM**

  $[Yb(hfac)_3(L^1)]_2$

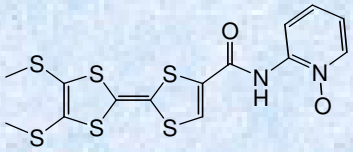
  $[Yb(tta)_2(\mu\text{-}L^2)(L^3)]_2 \bullet 2(CH_2Cl_2)$



L^1



L^2

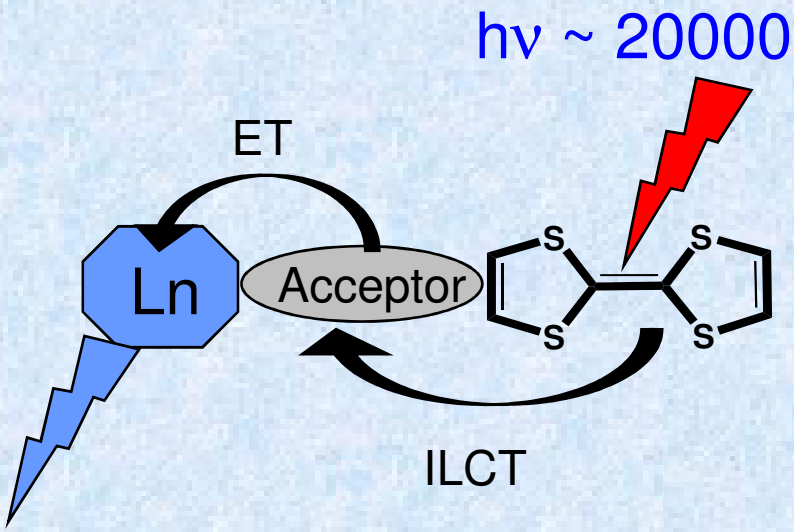


L^3

- **Conclusion**

LUMINESCENCE

Due to the weak absorption coefficient for the *f-f* transitions, the luminescence of the lanthanides is sensitized via a π system



Use of the TTF core as organic antenna

Limited choice to the Near IR emissive lanthanide ions due to absorption in the visible energy range

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LUMINESCENCE OF LANTHANIDES

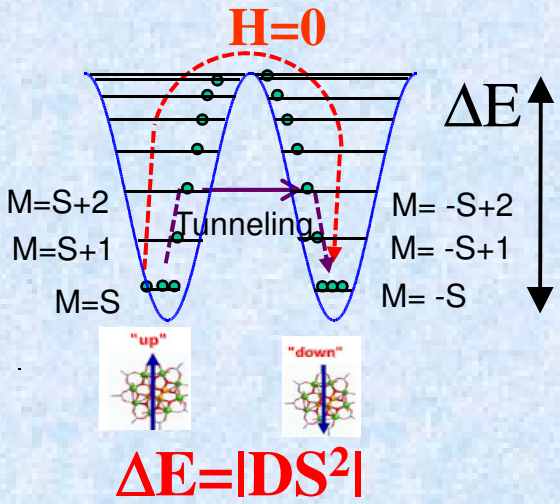
Table 1 Main luminescent transitions of trivalent lanthanide aquo ions[15,18–20]

Ln	Excited state[a]	τ_{Rad}/ms[b]	End state[c]		Lumin. type[d]	λ/nm[e]	Emission color
Pr	$^1G_4$	n.a.	^3H_J	4–6	P	1300	NIR
	$^1D_2$	n.a.	^3F_J	2–4	P	890, 1060	NIR
	$^3P_0$	n.a.	^3H_J	4–6	F	525–680	Orange
Nd	$^4F_{3/2}$	0.42	^4I_J	9/2–15/2	F	1060	NIR
Sm	$^4G_{5/2}$	6.26	^6H_J	5/2–15/2	P	590	Orange
Eu	$^5D_0$	9.67	^7F_J	0–6	P	620	Red
Gd	$^6P_{7/2}$	10.9	$^8S_{7/2}$		P	312	UV
Tb	$^5D_4$	9.02	^7F_J	6–0	P	550	Green
Dy	$^4F_{9/2}$	1.85	^6H_J	15/2–5/2	P	570	Yellow-orange
Ho	$^5F_5$	n.a.	^5I_J	8–4	F	970, 1450	NIR
	$^5S_2$	0.37	^5I_J	8–4	F	540	Green
Er	$^4S_{3/2}$	0.66	^4I_J	15/2–9/2	F		
	$^4I_{13/2}$	n.a.	$^4I_{15/2}$		F	1530	NIR
Tm	$^1G_4$	n.a.	^3H_J	6–4	P		
Yb	$^2F_{5/2}$	1.2[f]	$^2F_{7/2}$		F	980	NIR

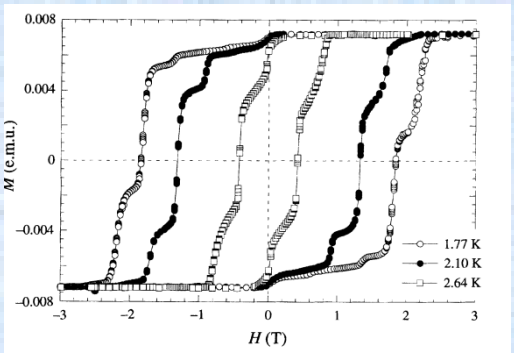
J.-C. G. Bünzli et *al. Chem Rev. Soc.* **2005**, *34*, 1048

Single Molecule Magnet

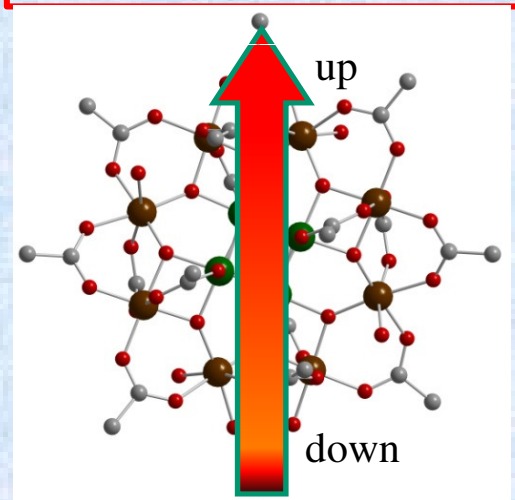
Molecule exhibiting a slow relaxation of the magnetization induced by the combination of High spin value (S) + magnetic anisotropy (D). These features create an energy barrier between S up and S down, leading to a hysterisis loop with reversal of the magnetization



$\Delta E = |DS^2|$



$Mn_{12}O_{12}(Oac)_{16}(H_2O)_4$



$(4Mn^{IV} + 8Mn^{III})$

S = 10

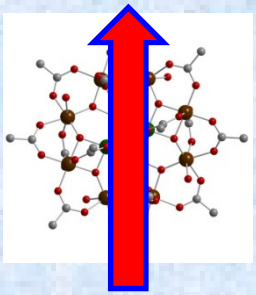
T. Lis, *Acta Cryst.* (1980). B36, 2042 , R. Sessoli, D. Gatteschi *et al. Nature, 1993*

How to Evidence Single Molecule Magnet

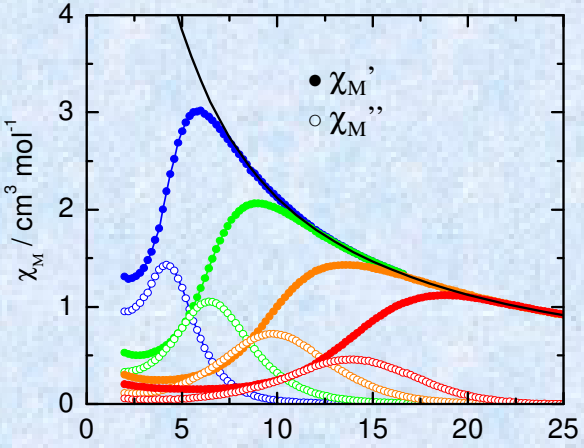
ac magnetic field

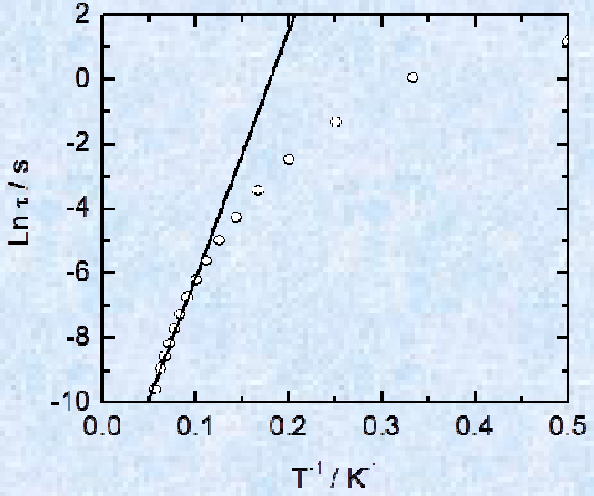
$$\chi_{ac} = |\chi|\, e^{-i\theta}$$

$$\chi_{ac} = \underbrace{|\chi| cos\theta}_{\chi'} - i\, \underbrace{|\chi|\, sin\theta}_{\chi''}$$



H



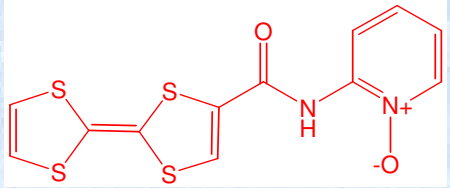


$$\frac{1}{\tau} = \frac{1}{\tau_{TA}} + \frac{1}{\tau_{TI}} \qquad \tau_{TA} = \tau_0 \exp\left(-\frac{\Delta}{T}\right)$$

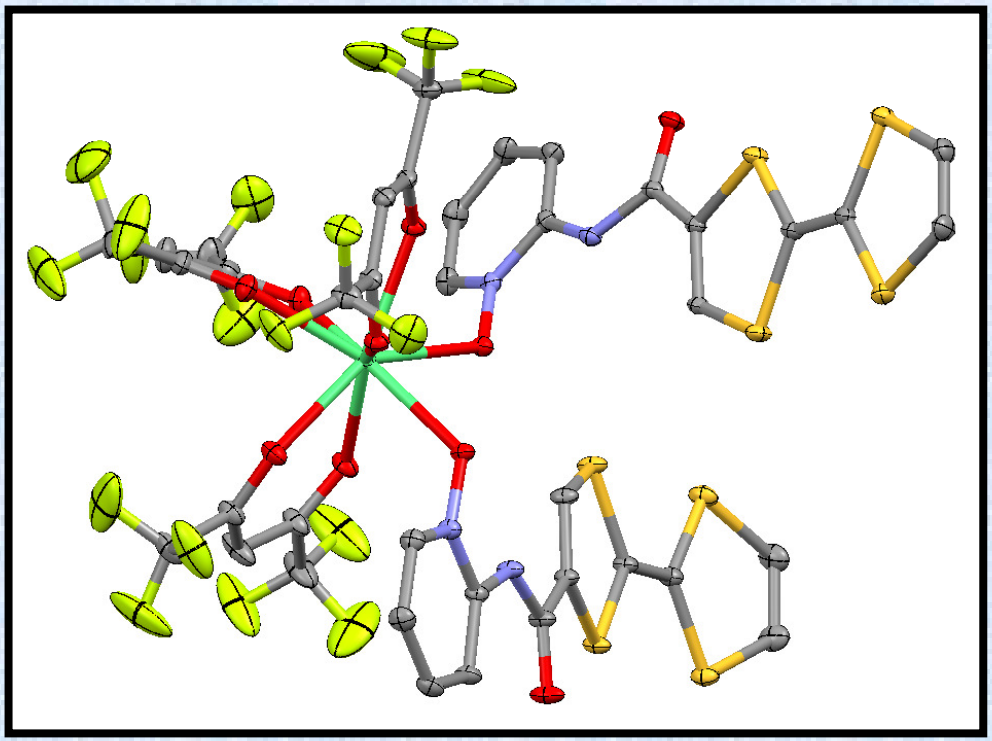
τ ; Δ

TTFs as antenna for the sensitization of Ln luminescence

$[Ln(hfac)_3(H_2O)_n]$ + 3-chloro-benzoïc acid +



(L)

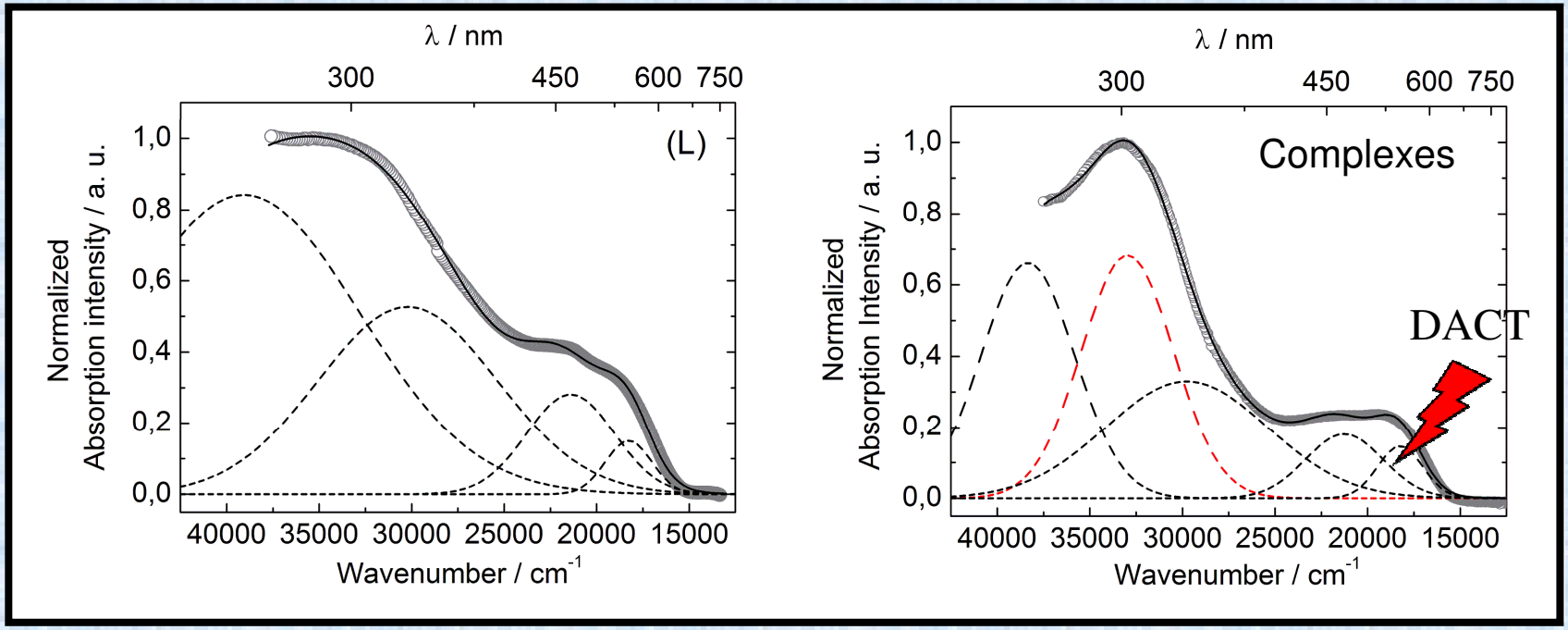


$[Ln(hfac)_3(L)_2]$

Ln(III) = Dy, Y, Er , Yb

Chem. Eur. J. **2010**, *16*, 11769

ABSORPTION PROPERTIES



Measurements done in solid-state to prevent any risks of dissociation for the coordination complexes

EMISSION PROPERTIES

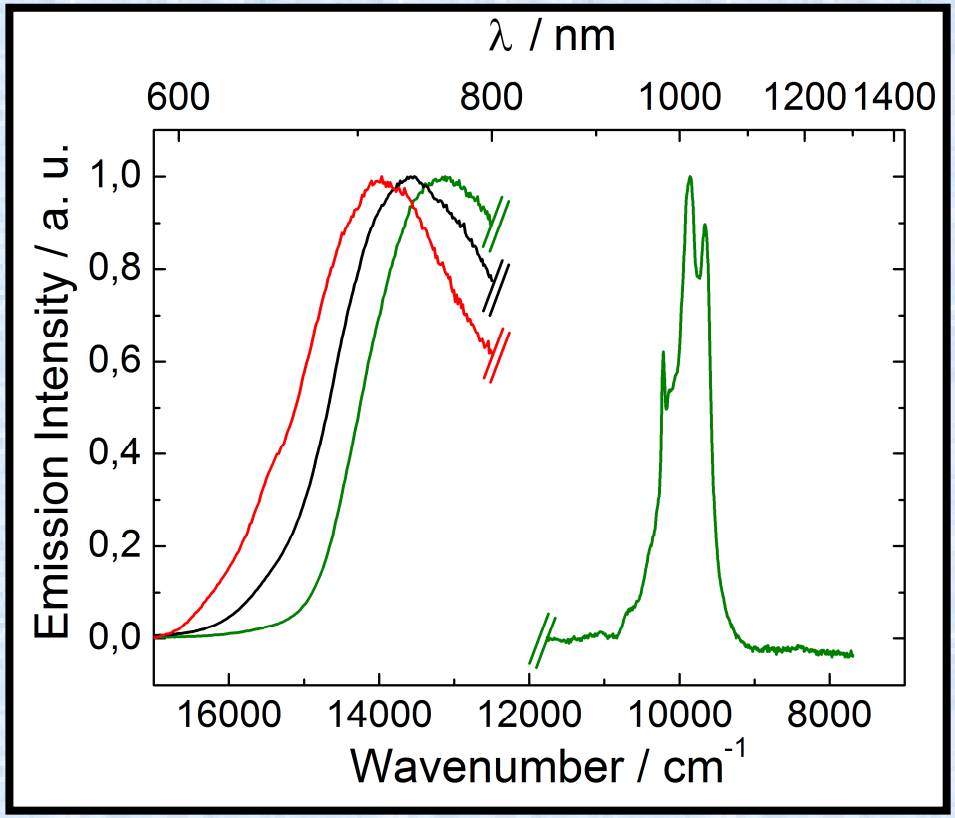
Free Ligand
Y(III) complex
Yb(III) complex

Irradiation at 19600 cm^{-1}

Fluorescence of the ligand at 13986, 13568 and 13157 cm^{-1}

+

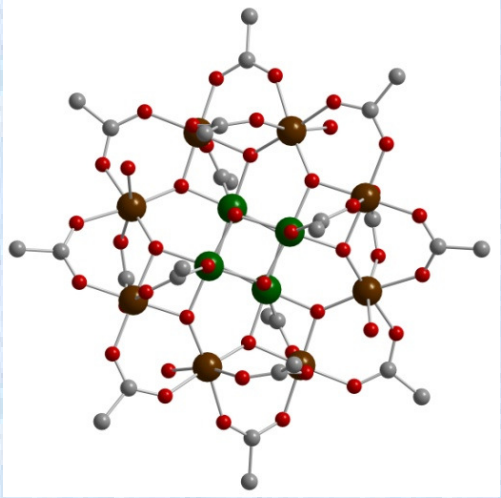
Luminescence of the Yb(III) ion at 9860 cm^{-1} attributed to the $^2F_{5/2} \rightarrow {}^2F_{7/2}$ excitations



Ln(III) / TTF-BASED

SINGLE MOLECULE MAGNET

$Mn_{12}O_{12}(Oac)_{16}(H_2O)_4$



($4Mn^{IV}$ + $8Mn^{III}$)

S = 10

thousands papers

R. Sessoli, D. Gatteschi *et al. Nature, 1993*

Electro-active Luminescente Single Molecule Magnets

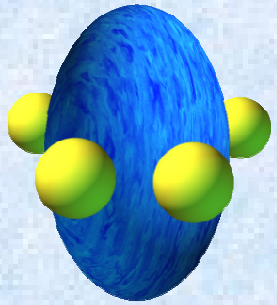
Dy(III), Tb(III) ⇒ SMM but Luminescence in yellow-orange-green where TTF ligands absorb

Yb(III), Nd(III) ⇒ Luminescence in NIR But not convenient for SMM

Yb(III)

Equatorial environnement might be a serious candidate to promote ising type anisotropy

J. D. Rinehart and J. R. Long, *Chem. Sci.*, 2011, **2**, 2078.



Prolate

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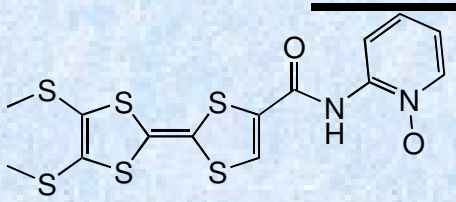
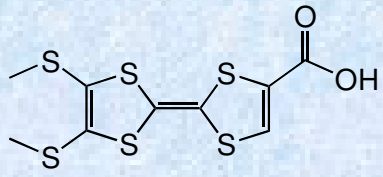
$[Yb(tta)_2(\mu\text{-}L^2)(L^3)]_2 \bullet 2(CH_2Cl_2)$



L^3

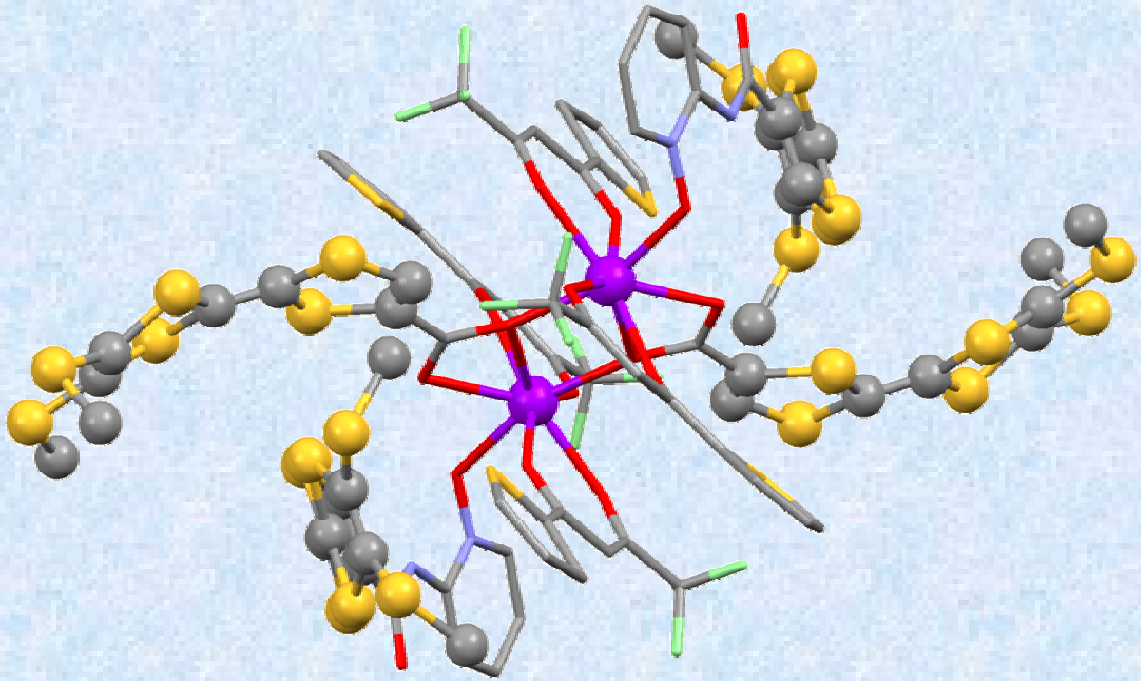


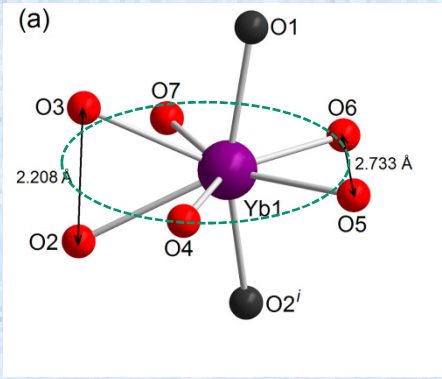
L^2

$$+ \; Yb(tta)_3.2H_2O \xrightarrow{CH_2Cl_2/n\text{-hexane}} [Yb(tta)_2(L^2)(L^3]_2.2CH_2Cl_2$$

L^3 = bismethylthio-tetrathiafulvalene-amido-2-pyridine-*N*-oxide

L^2 = bismethylthio-tetrathiafulvalene-carboxylate

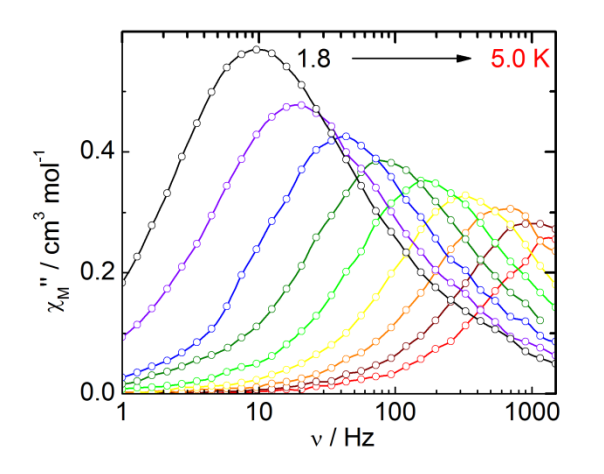


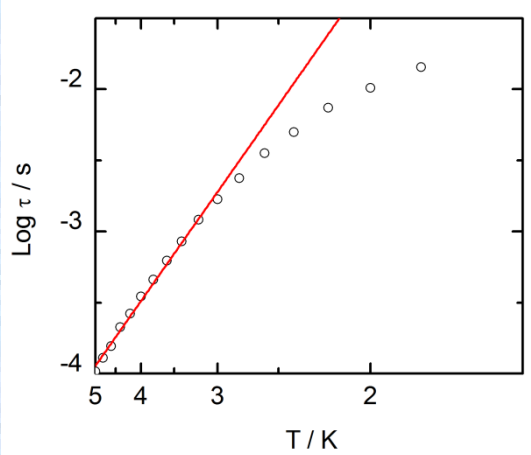


Planar distortion of the D_{2d} dodecahedron

Chem Commun., 2013, *49*, 615-617

DYNAMIC MAGNETIC PROPERTIES

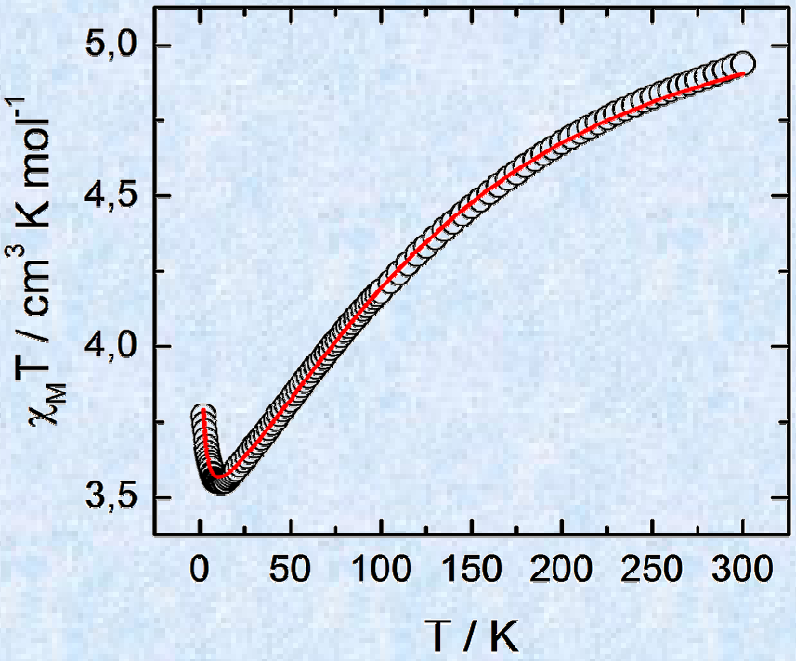


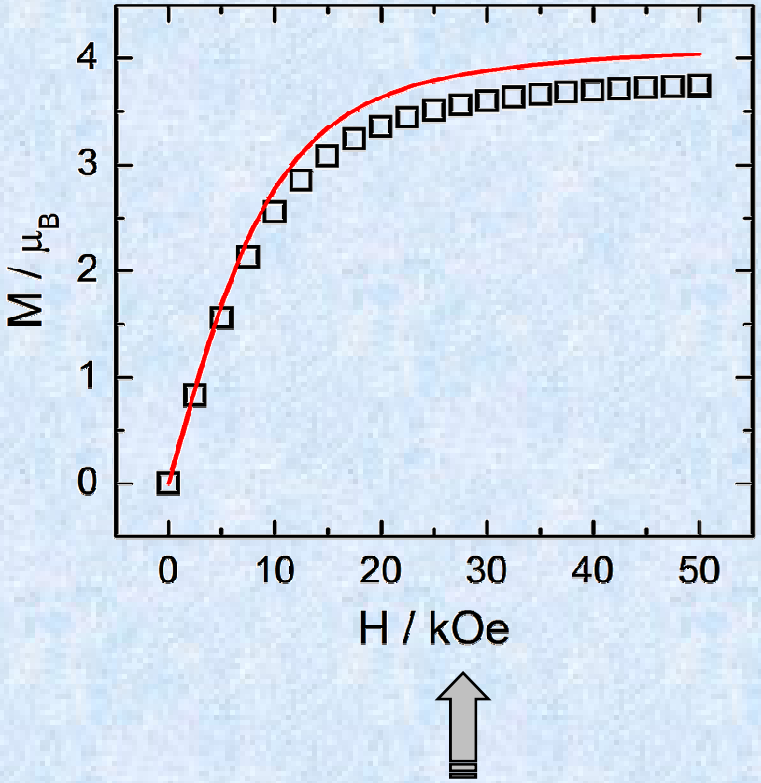


$\tau_0 = 1.7(3)\times10^{-6}$ s

$\Delta = 14.7(5)$ cm^{-1}

STATIC MAGNETIC PROPERTIES

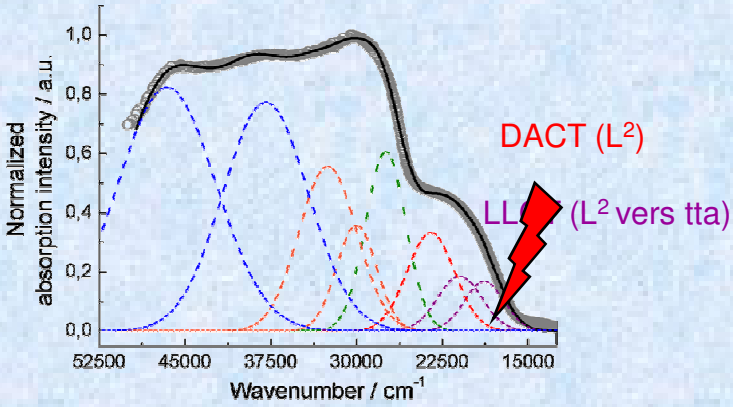




Steven's Technique ⇒ The ground state is $M_J = \pm 7/2$

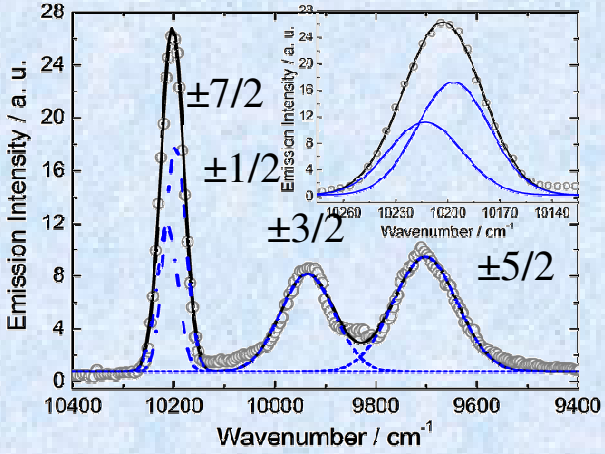
PHOTO-PHYSICAL PROPERTIES

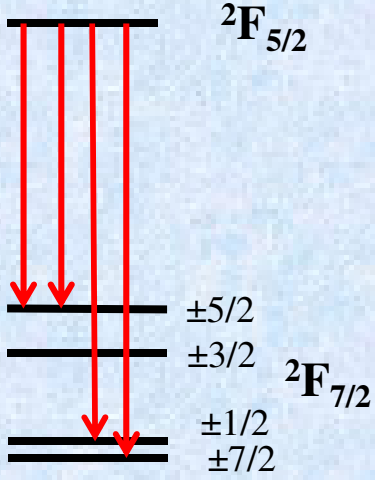
ABSORPTION



EMISSION

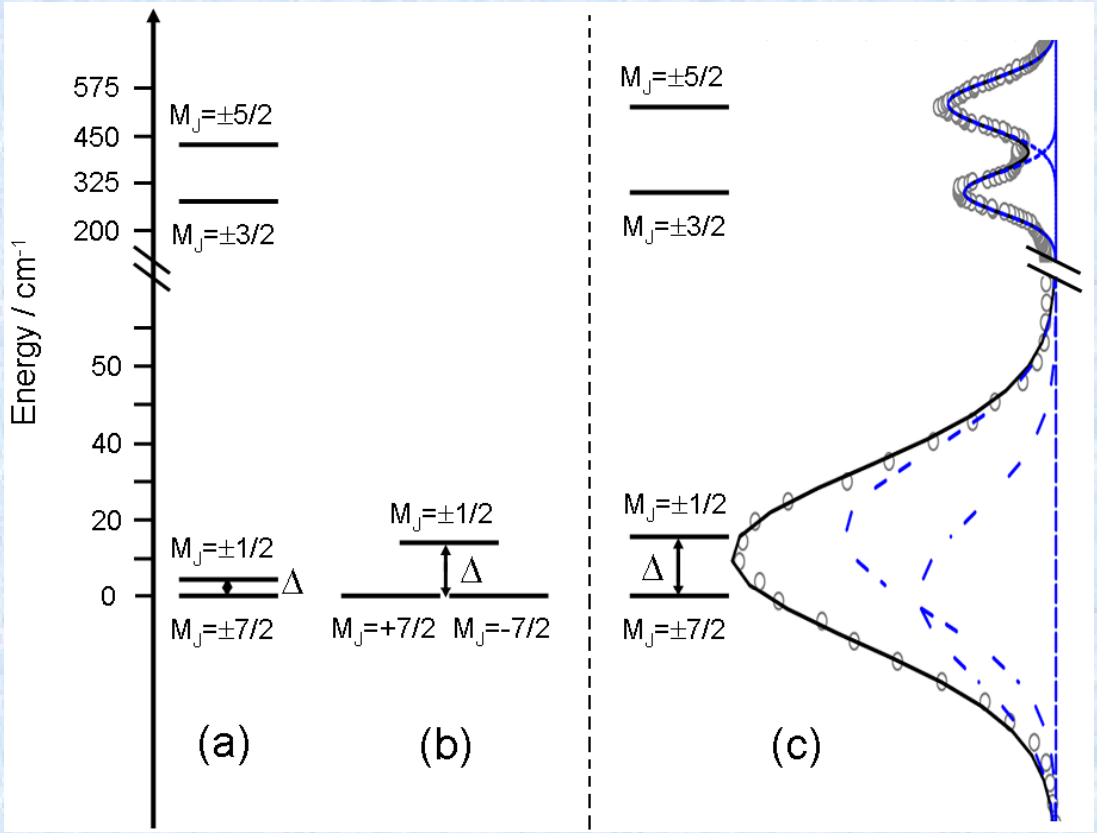
Irradiation at 20000 cm^{-1}





Luminescence of the Yb(III) ion at 9860 cm^{-1} attributed to the $^2F_{5/2} \rightarrow {}^2F_{7/2}$ excitations

MAGNETO-EMISSION CORRELATION

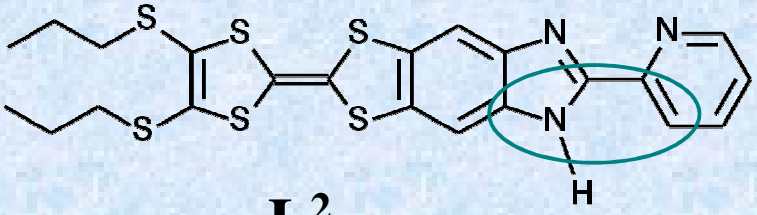


Energy splitting of the M_J level of the $^2F_{7/2}$ ground state multiplet determined from the dc fit (Δ=2.57 cm^{-1}) (a) ac fit (Δ=14 cm^{-1}) (b) and luminescence spectrum (Δ=16 cm^{-1}) (c).

redox-active luminescent Yb(III) SMM with very good agreement between magnetic and optical properties

Chem Commun., 2013, *49*, 615-617

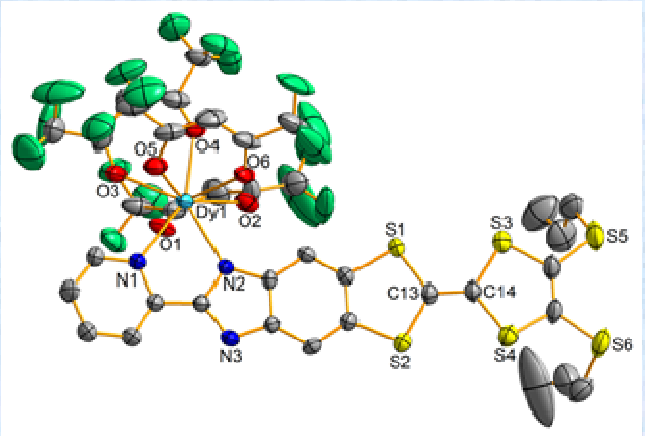
…. In solution memory effect

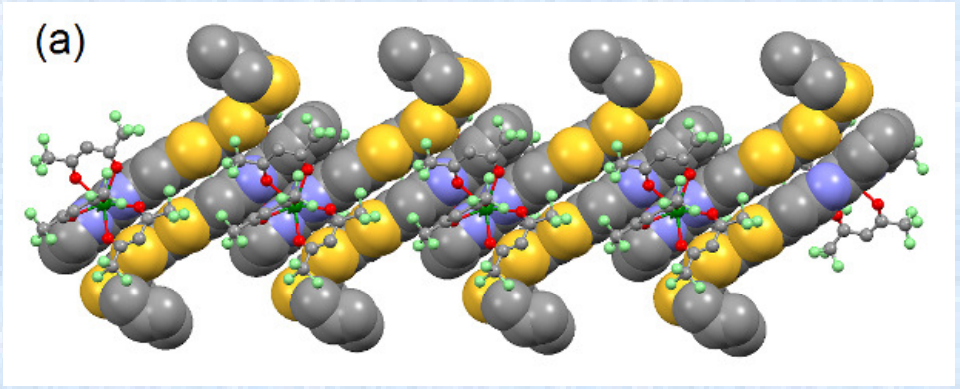


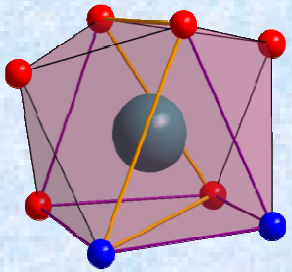
L²

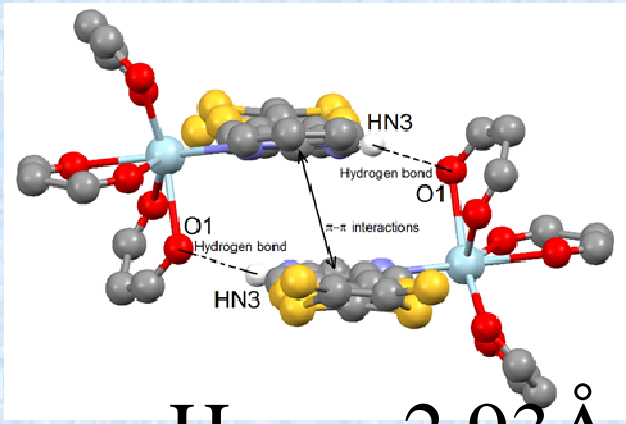
+ $Ln(hfac)_3 \cdot 2H_2O$

$Ln(hfac)_3L^2$; Ln^{III} = Y, Dy, Er, Yb





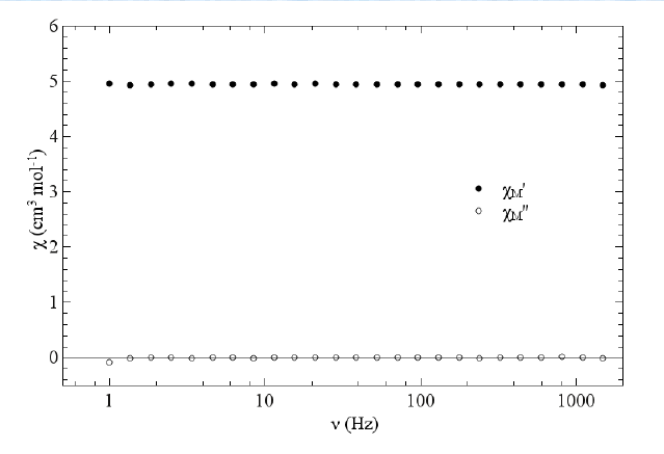




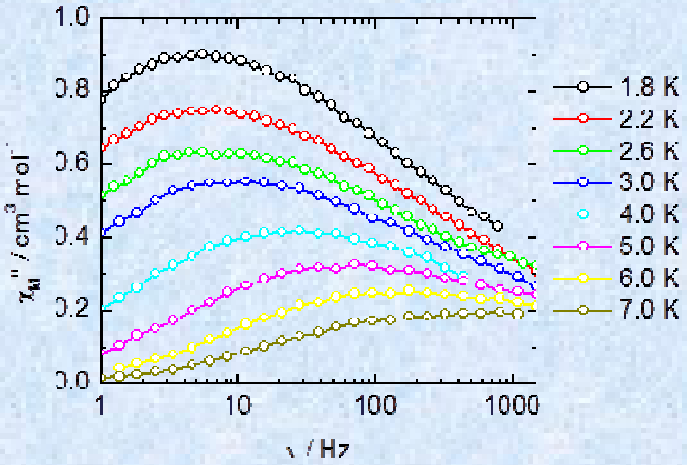
Deformed C_{2v} symmetry

$O_{hfac} \cdots H_{NH}$ = 2.93Å

$Dy(hfac)_3L^2$



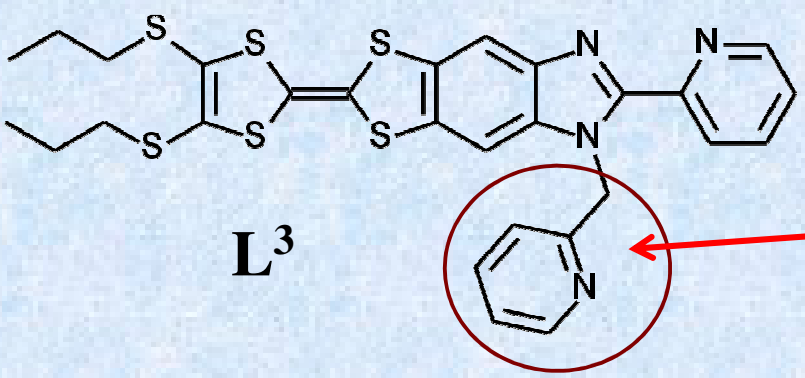
Solid state



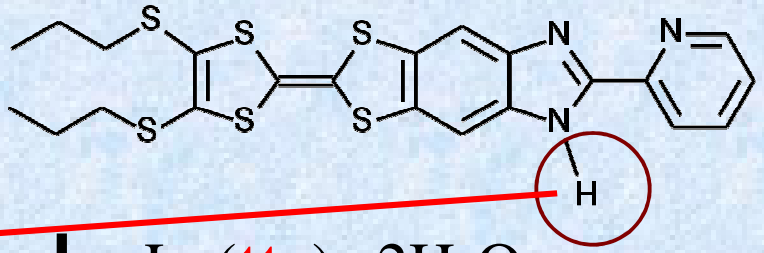
In solution

Δ= 12(1) K

τ_0= 1.9(4).10^{-6} s)

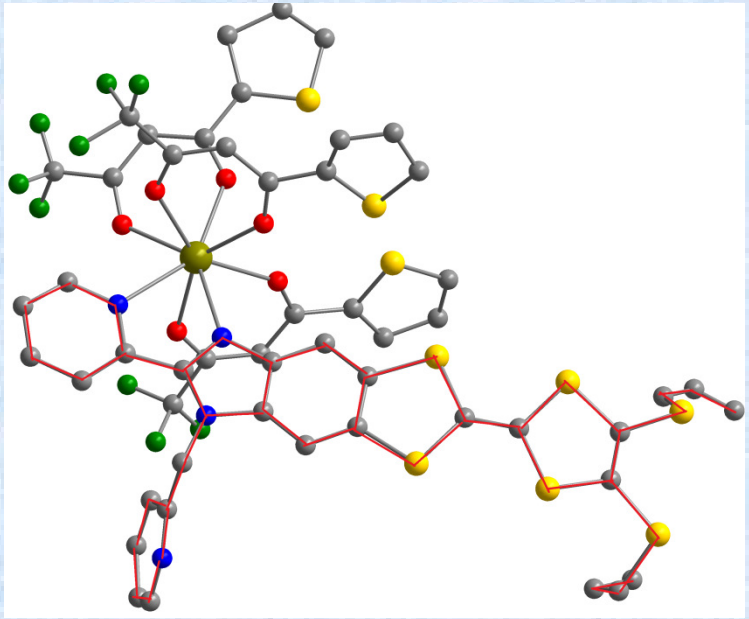


L^3

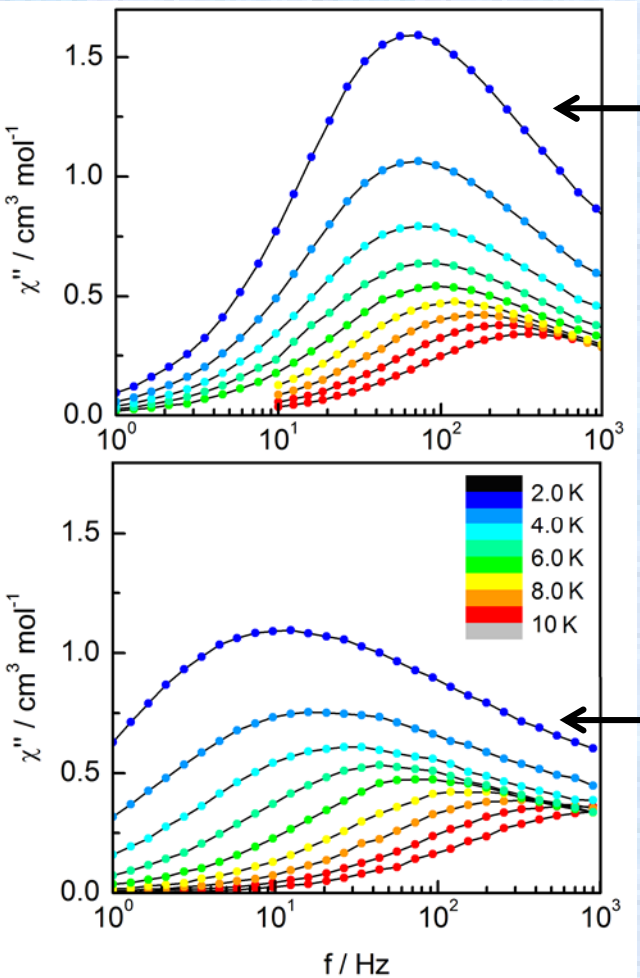


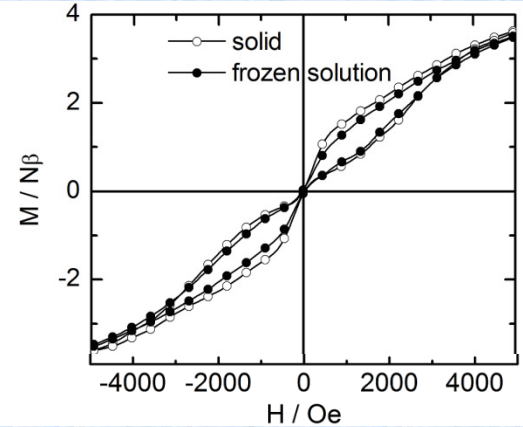
+ $Ln(tta)_3 \cdot 2H_2O$

$[Dy(tta)_3(\mathbf{L_3})] \cdot C_6H_{14}$



$[Dy(tta)_3(L)]\cdot C_6H_{14}$





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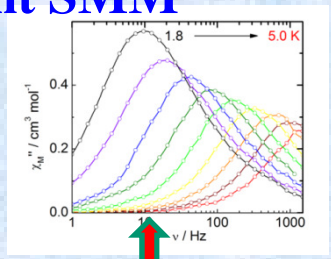
SUMMARY

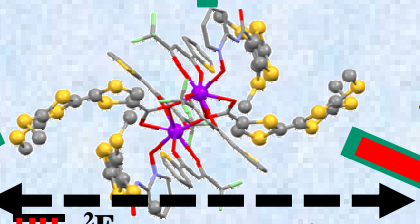
Redox active luminescent SMM

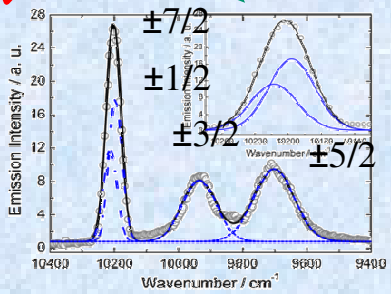
SMM

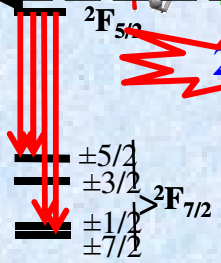


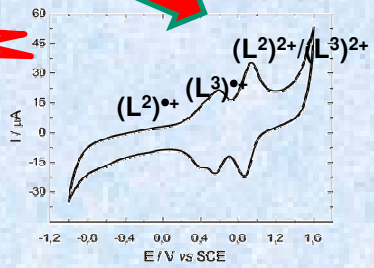
Luminescence

redox

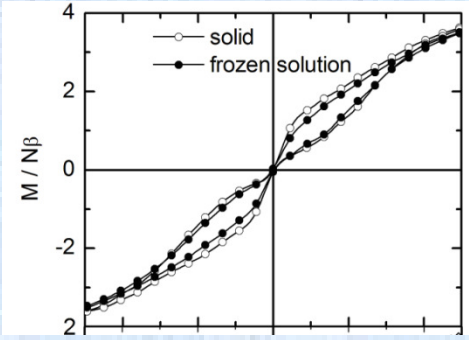








SMM and memory effect in solution



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Institut des Sciences Chimiques de Rennes UMR CNRS 6226

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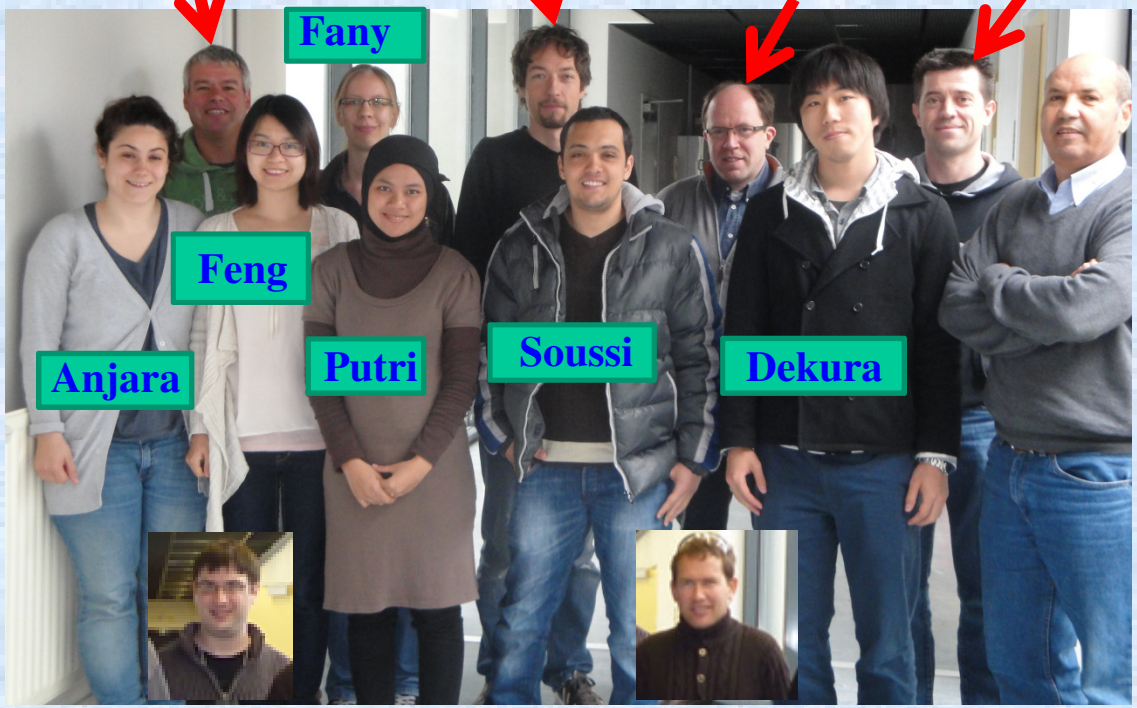
O. Cador



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Dr. Borris Leguennic; Rennes

Julie Jung, Rennes

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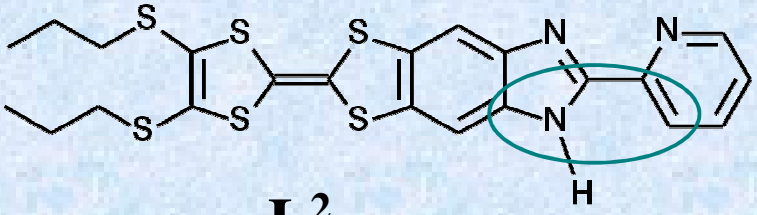
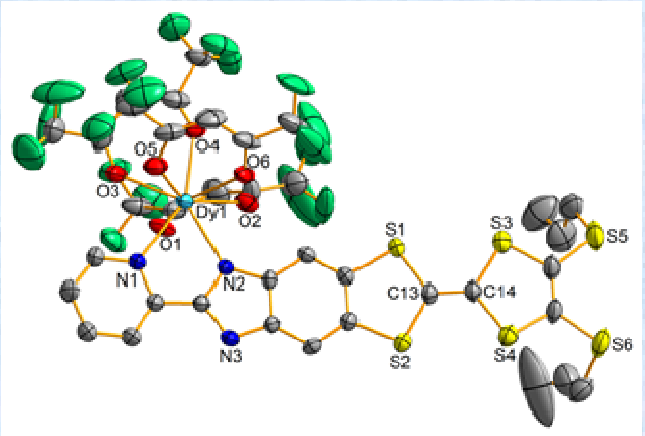
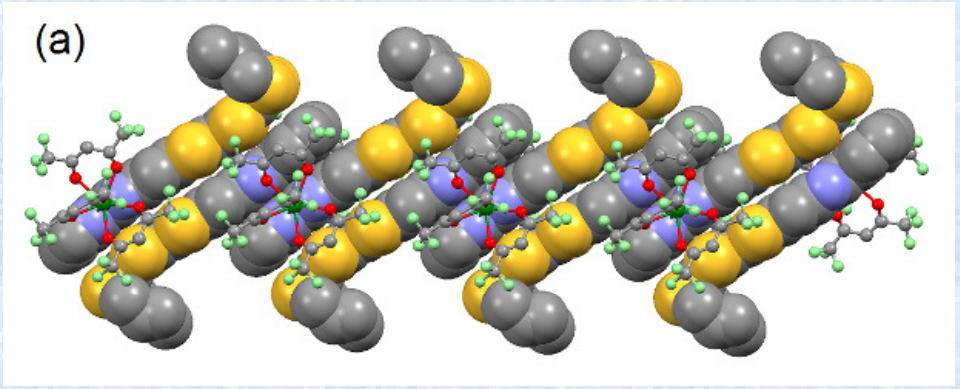


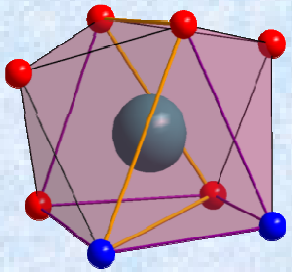
L²

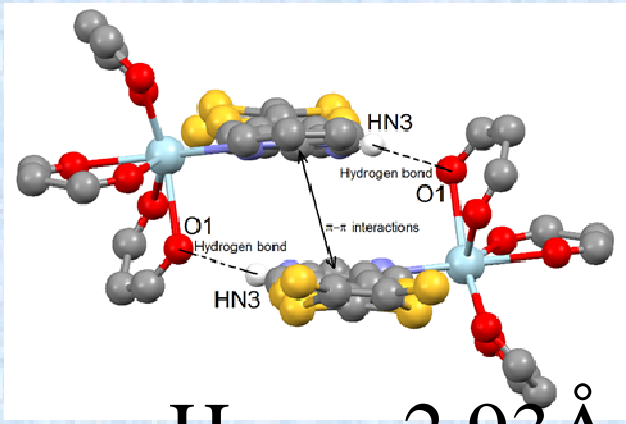
+ $Ln(hfac)_3 \cdot 2H_2O$

$Ln(hfac)_3L^2$; Ln^{III} = Y, Dy, Er, Yb





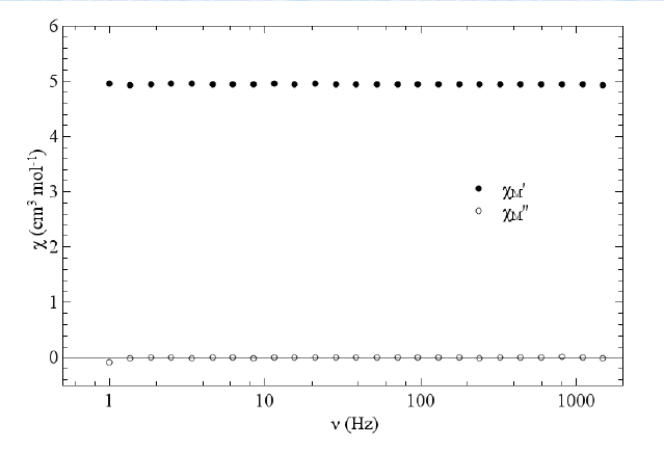




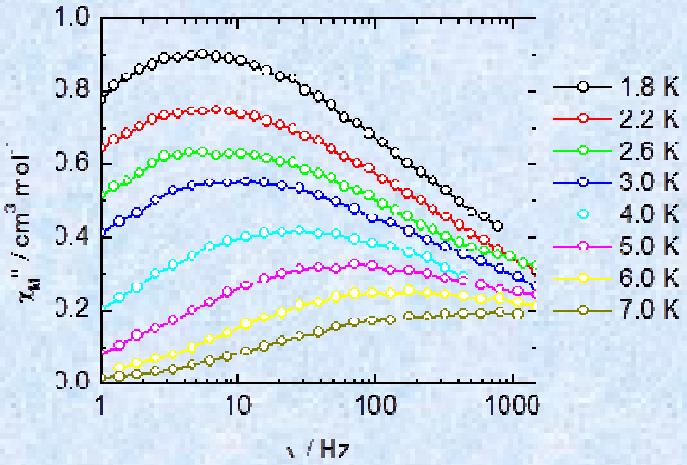
Deformed C_{2v} symmetry

$O_{hfac} \cdots H_{NH}$ = 2.93Å

$Dy(hfac)_3L^2$



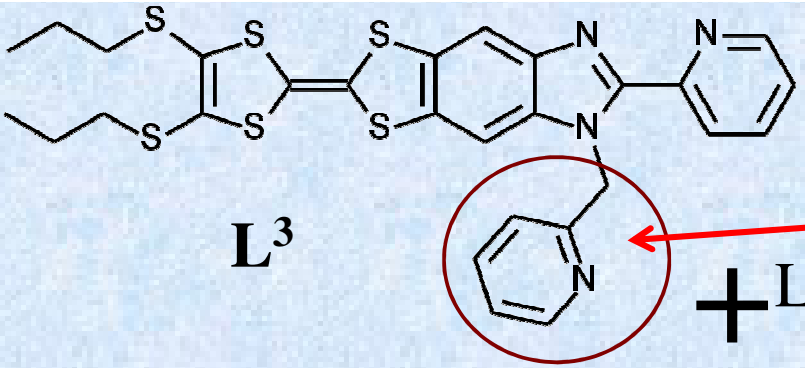
Solid state



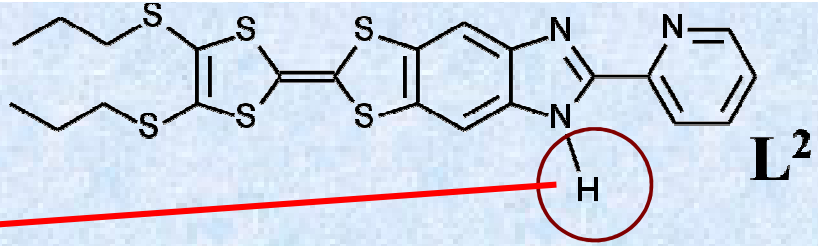
In solution

Δ= 12(1) K

τ_0= 1.9(4).10^{-6} s)



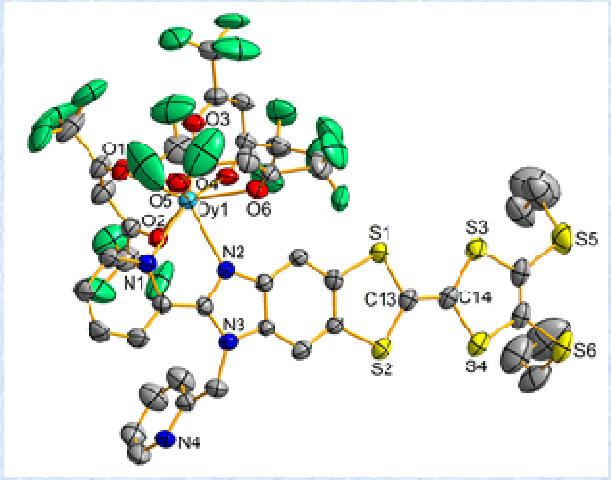
L^3

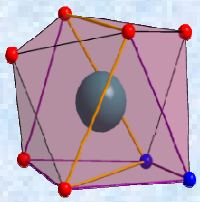


L^2

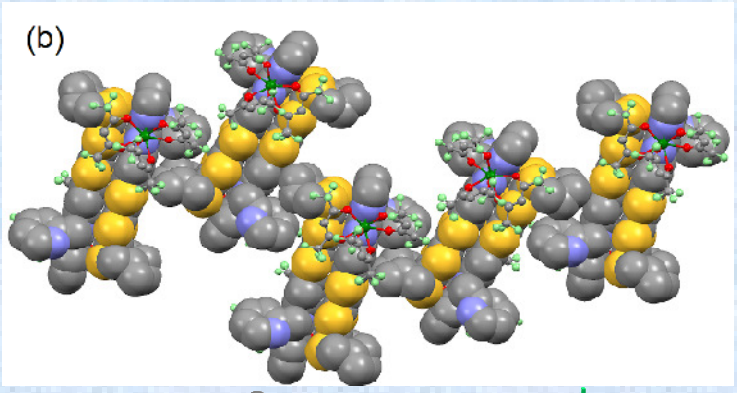
+ $Ln(hfac)_3 \cdot 2H_2O$

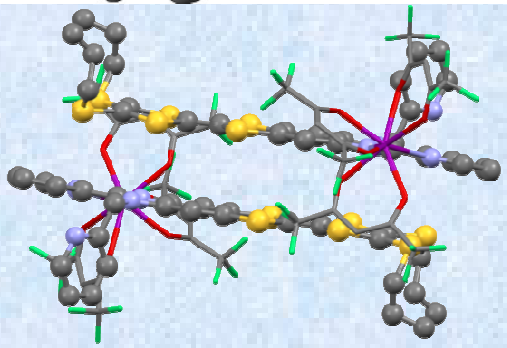
$Ln(hfac)_3L^3$; Ln^{III} = Y, Dy, Er, Yb





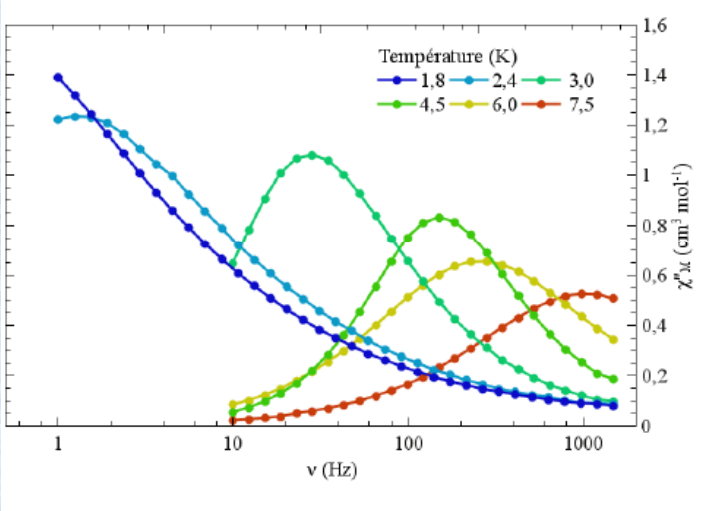
Deformed C_{2v} symmetry





No hydrogen bonds

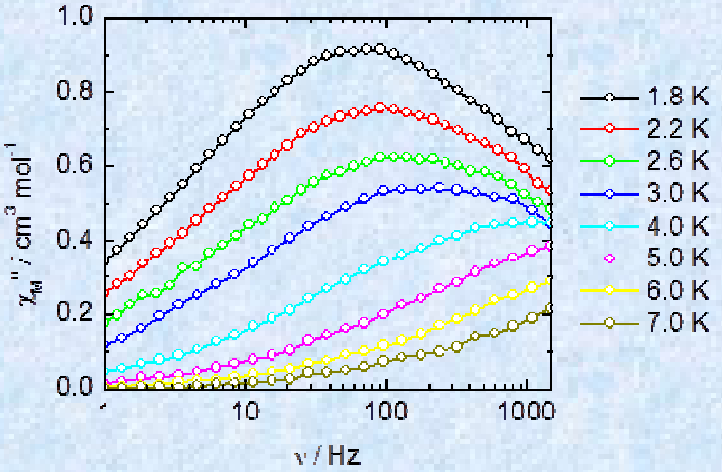
$Dy(hfac)_3L^3$



Solid state

Δ= 17(2) K

τ_0= 9.5(2).10^{-6} s)

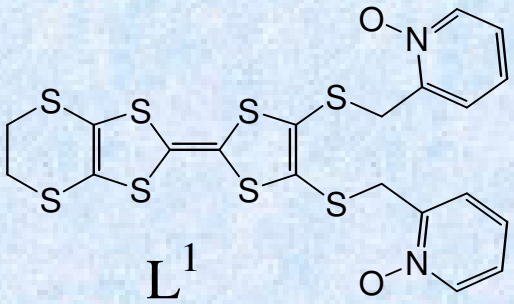


In solution

Δ= 15(2) K

τ_0= 1.5(3).10^{-6} s)

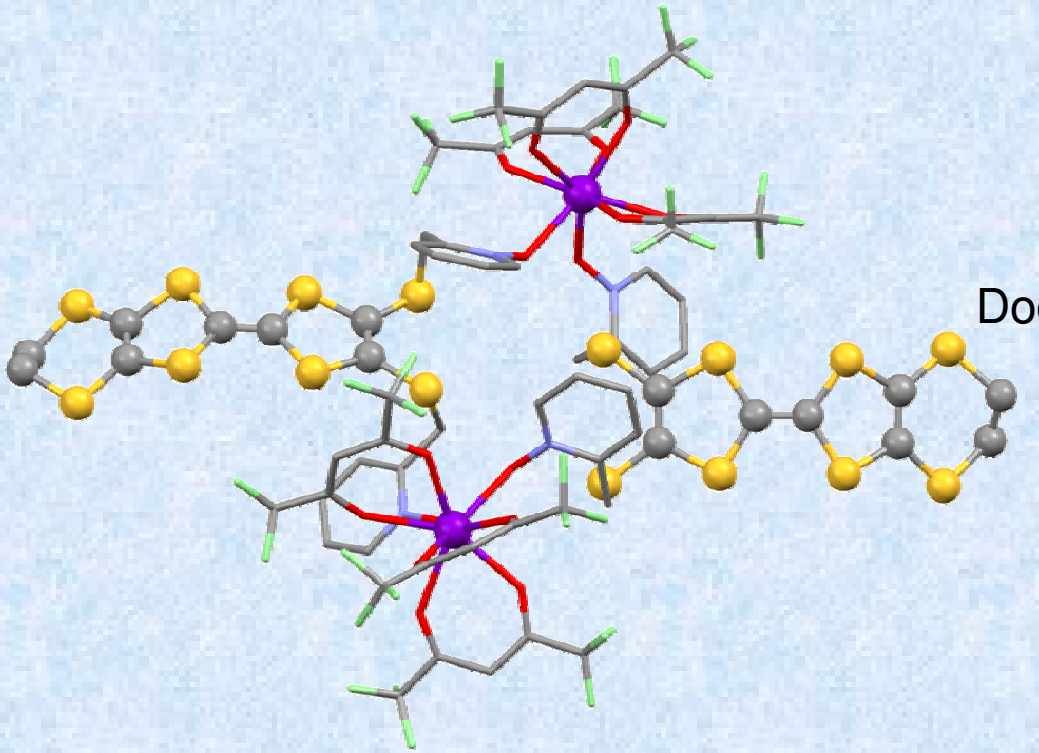
$[Yb_2(hfac)_6(L^1)_2]$



L^1

$+ Yb(hfac)_3.2H_2O \xrightarrow{CH_2Cl_2/n\text{-hexane}} [Yb_2(hfac)_6(L^1)_2]$

L^1 = ethylenedithio-tetrathiafulvalene-dimethylthio-2-pyridine-*N*-oxide

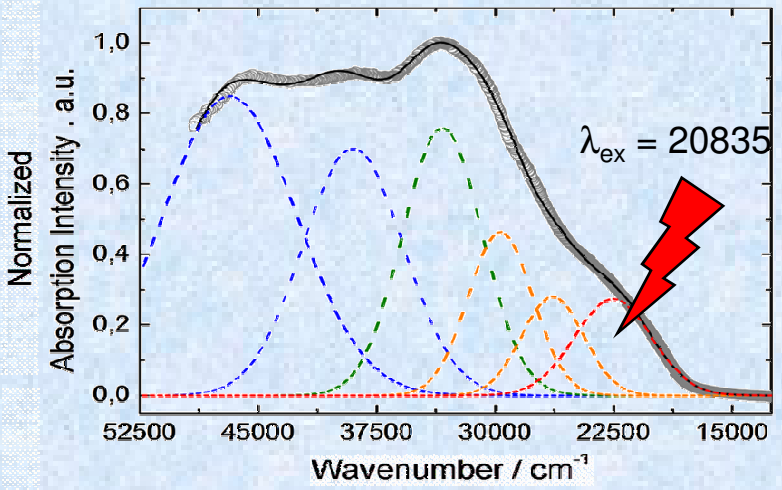


Dodecahedron with a D_{2d} symmetry

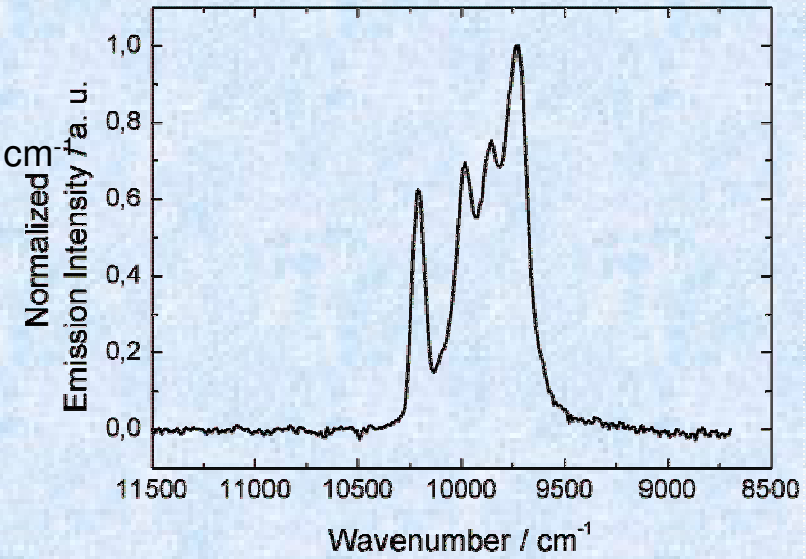
***Inorg. Chem.*, 2013**, *52*, 5978

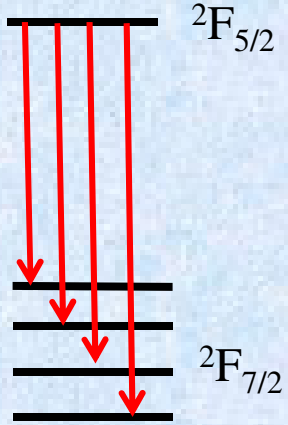
PHOTO-PHYSICAL PROPERTIES

Absorption



Emission





TTF to Py-*N*-oxide charge Transfer

Intra-TTF transitions

Intra-hfac transitions

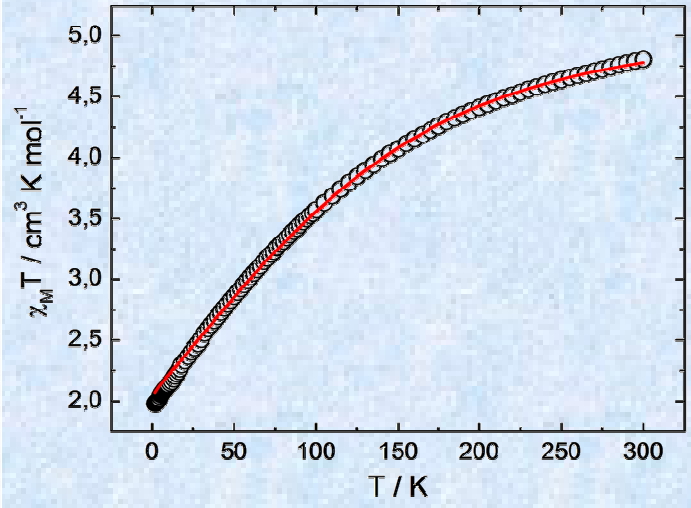
Intra-Py-*N*-oxide transitions

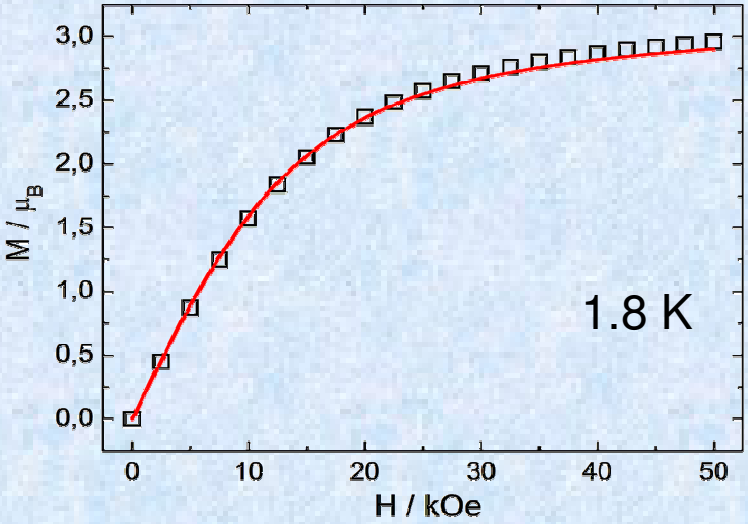
Luminescence of the Yb(III) ion at 9860 cm^{-1} attributed to the $^2F_{5/2} \rightarrow {}^2F_{7/2}$ excitations

dc MAGNETIC PROPERTIES

$$\hat{H} = \sum_{i=1}^{2}\left(B_2^0 \hat{O}_{2i}^0 + B_2^2 \hat{O}_{2i}^2 + B_4^0 \hat{O}_{4i}^0 + B_4^2 \hat{O}_{4i}^2 + B_4^4 \hat{O}_{4i}^4 + B_6^0 \hat{O}_{6i}^0 + B_6^2 \hat{O}_{6i}^2 + B_6^4 \hat{O}_{6i}^4 + B_6^6 \hat{O}_{6i}^2 \right)$$

$$+\beta\left(g_J \hat{J}_1 + g_J \hat{J}_2 \right) \cdot \vec{H} - J\ \hat{J}_1 \cdot \hat{J}_2$$





No out-of-phase signal

B_2^0	0.4826 cm^{-1}
B_4^0	0.316 cm^{-1}
B_6^0	2.313×10^{-3} cm^{-1}
g	8/7 (fixed)
J	0 cm^{-1} (fixed)

The ground state is $M_J = \pm 5/2$

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