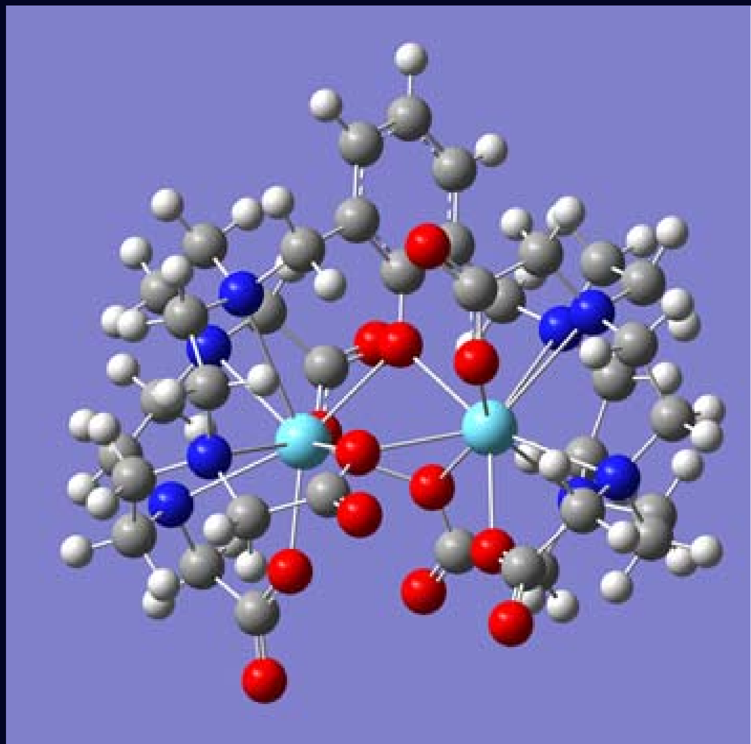
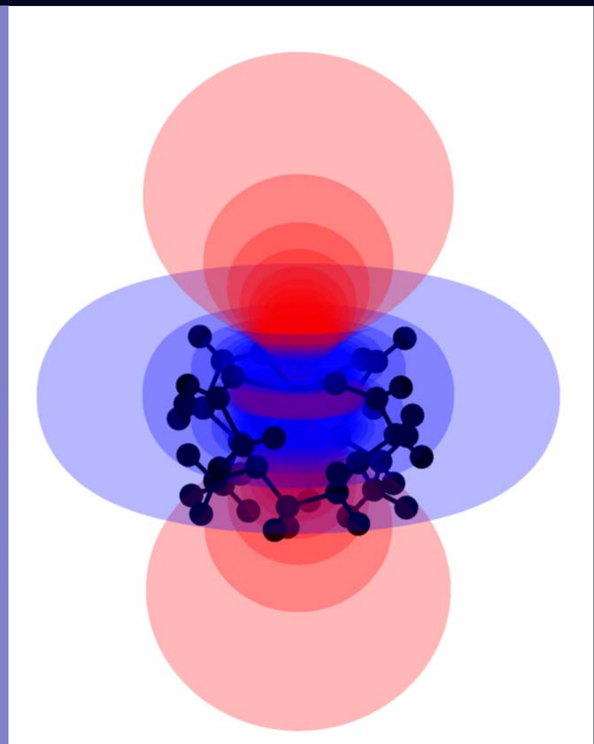
Probing the Solution Speciation and Coordination Environment of f-Element complexes by NMR and Emission Spectroscopy

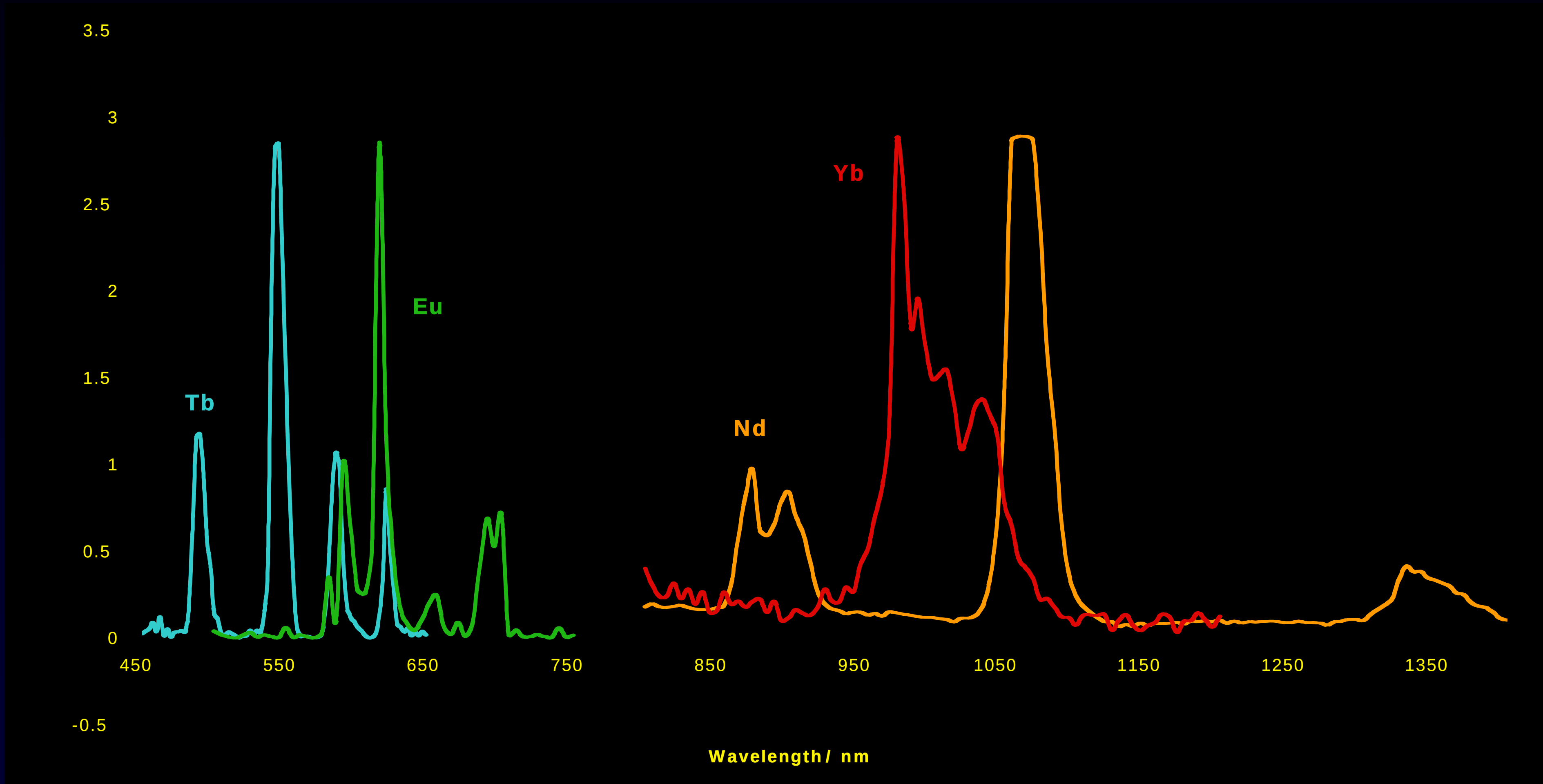




Louise Natrajan

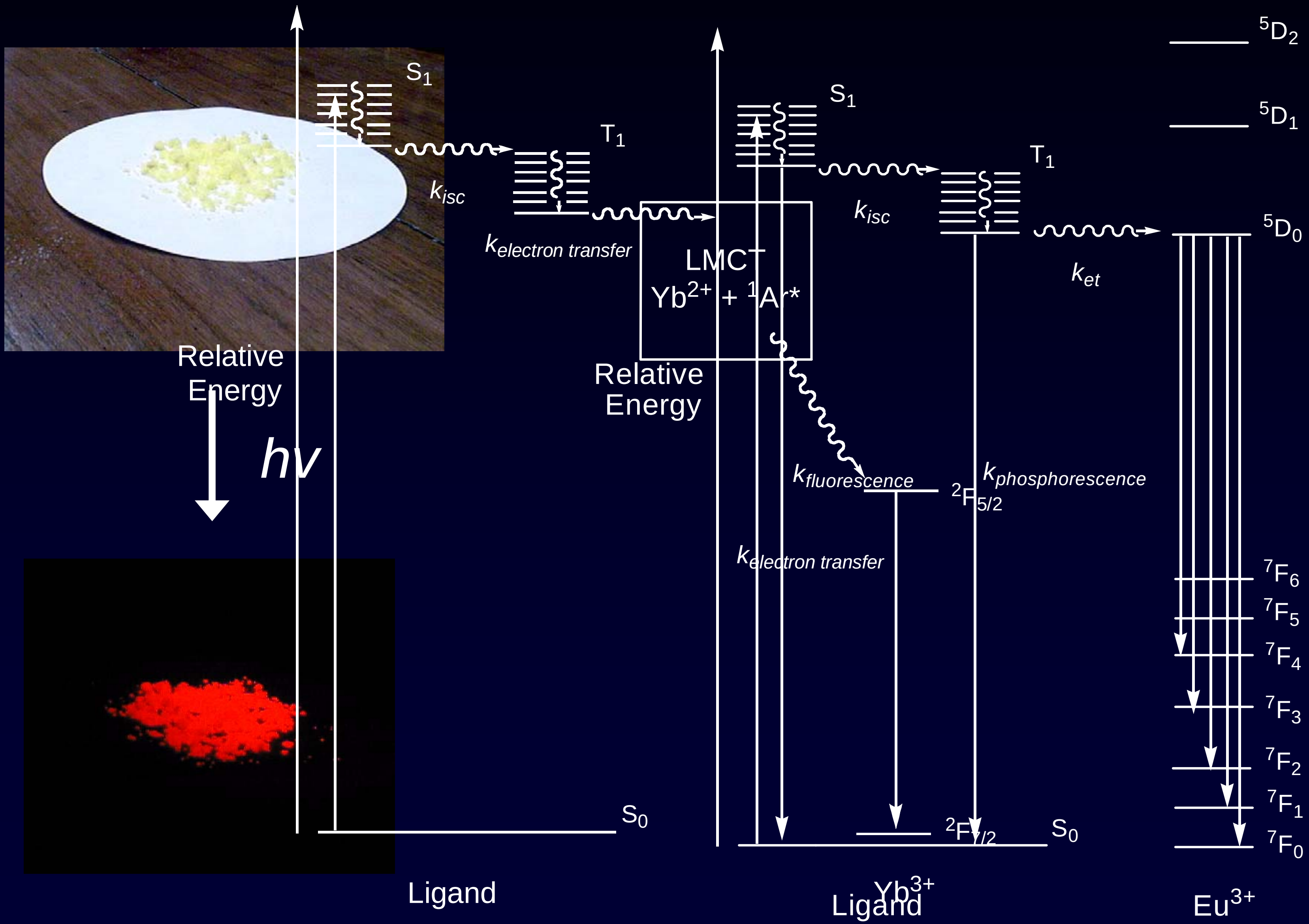
Karlsruhe, 27th January 2010

Lanthanide Luminescence



- Emission spectra span the visible and near IR regions
- Choice of sensitising chromophore important
- Lifetimes range nanosecond to millisecond order

Lanthanide Luminescence



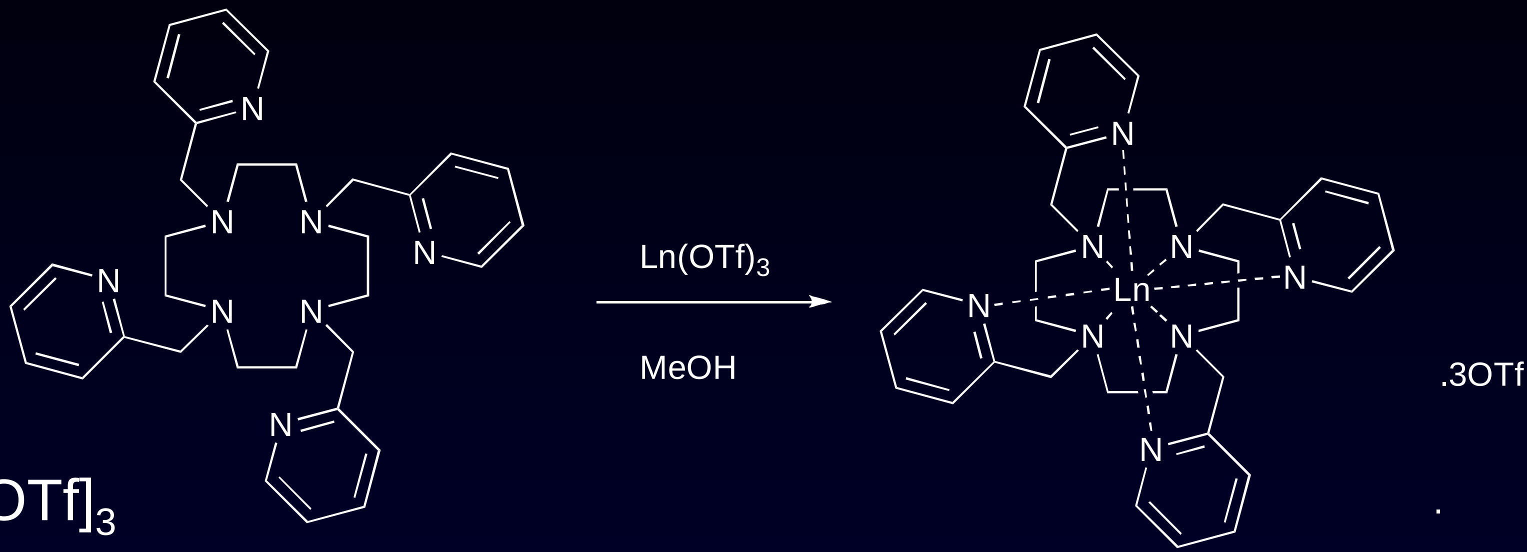
LMCT mediated energy transfer mechanism

Faulkner *et al.*, *Dalton Trans.*, 2009, 3890.

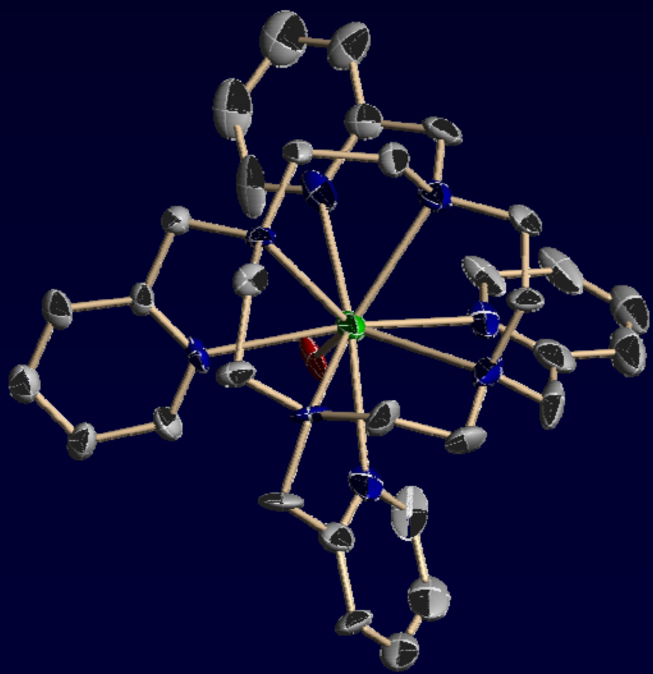
http://int.ch.liv.ac.uk/Lanthanide/Lanthanides

Tetra Picolyl Substituted Cyclen

L^{py}



$[Yb(L^{py})(OH_2)][OTf]_3$



Ln = La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Tm, Er, Yb

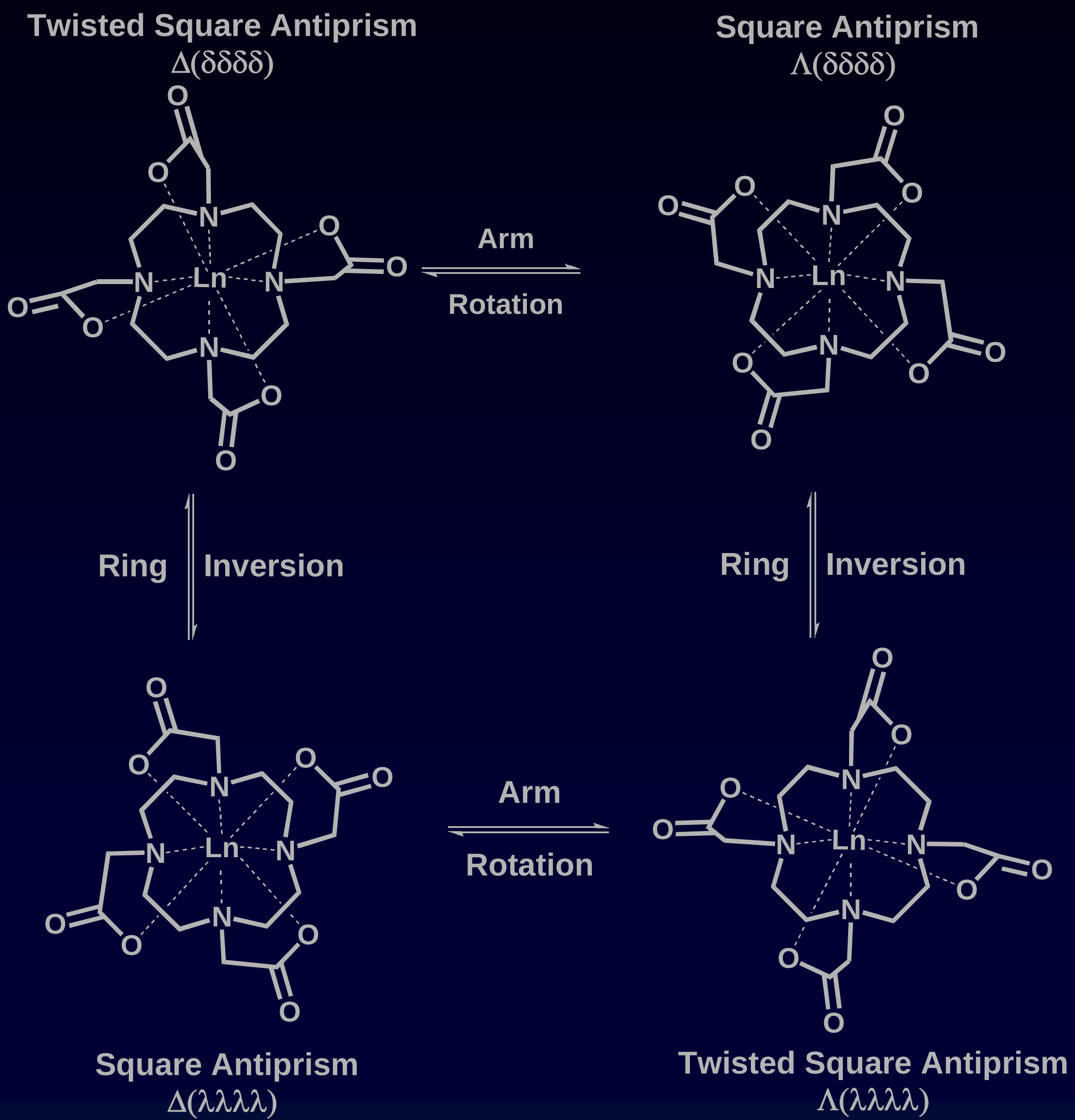
Mono-capped SAP (ϕ = 39°)

- Ave. Yb-N_{cyclen} 2.63 Å
- Ave Yb-N_{py} 2.52 Å
- Yb-OH_2 2.40 Å

Nd TSAP	(ϕ = 24°)
Eu TSAP	(ϕ = 25°)
Gd SAP	(ϕ = 36°)
Tb SAP	(ϕ = 37°)
Er SAP	(ϕ = 38°)

Change in solid state coordination geometry across the series

Solution Coordination Isomerism



- Four stereoisomers
- Interconversion by pendant arm rotation and ring inversion
- TSAP faster H_2O exchange
- Same isomerism for DO3A complexes

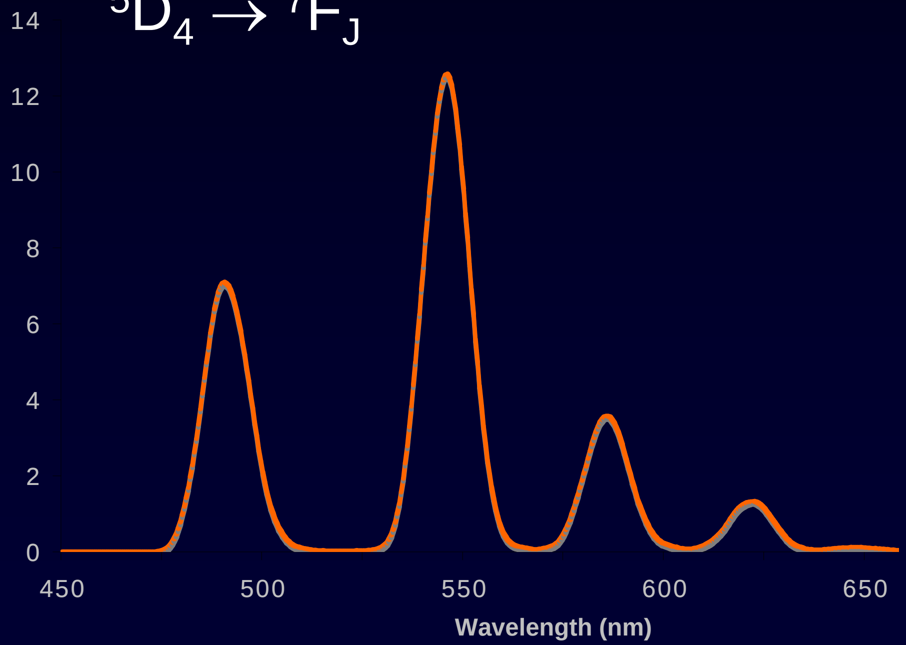
Dalton Trans. 2005, 3829.

Solution Studies

Steady state and time resolved luminescence studies:

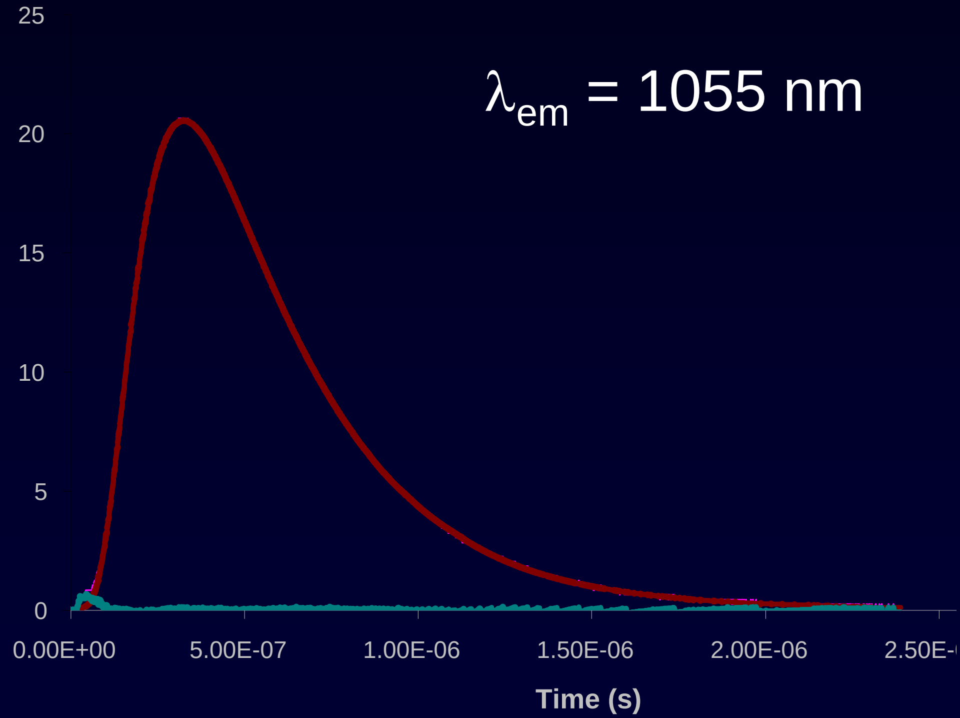
$[Tb(L^{Py})(OTf)].2OTf/H_2O$

$^5D_4 \rightarrow {}^7F_J$



$[Nd(L^{Py})(OTf)].2OTf/D_2O$

$\lambda_{em} = 1055$ nm



- •Kinetic traces for Yb, Pr and Nd fitted to a bi-exponential decay
- •Eu and Tb follow mono-exponential decay kinetics

Lifetime Measurements

Complex	$\tau_{H2O}/\mu s$	$\tau_{D2O}/\mu s$	q_{H2O}
Nd	0.22 50 %	0.35 50 %	0.0
	0.09 50 %	0.17 50 %	0.4
Pr	-	0.08 67 %	-
	-	0.12 33 %	-
Eu	720	1130	0.4
Tb	2060	2540	0.2
Yb	1.63	4.47	0.3

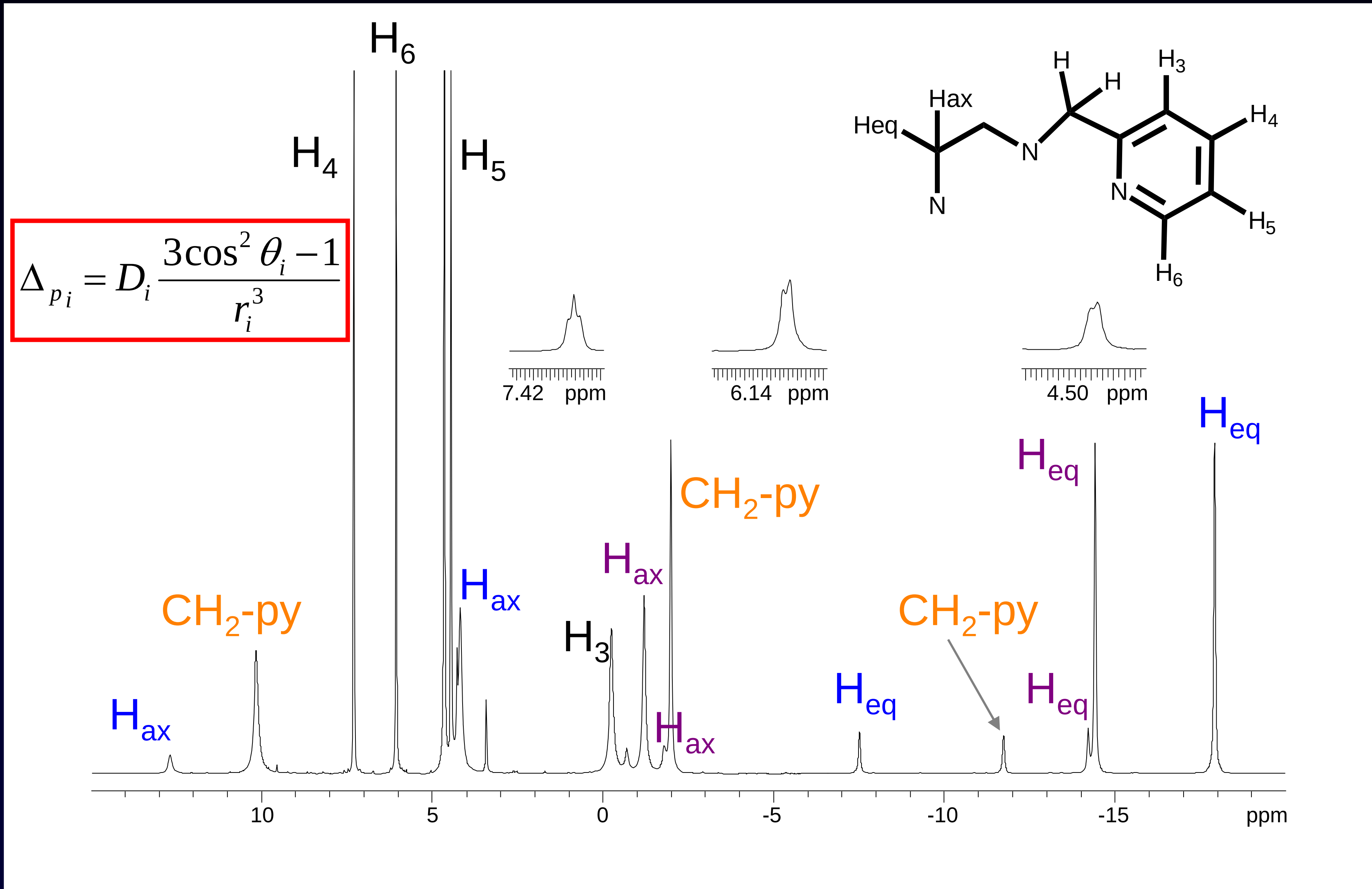
$q = A(k_{H2O} - k_{D2O} - B)$ (Eu, Tb)

$q = A(k_{H2O} - k_{D2O}) - B$ (Nd)

Number of inner sphere H_2O molecules approximates to 0

J. Chem. Soc., Perkin Trans 2., 1999, 493.

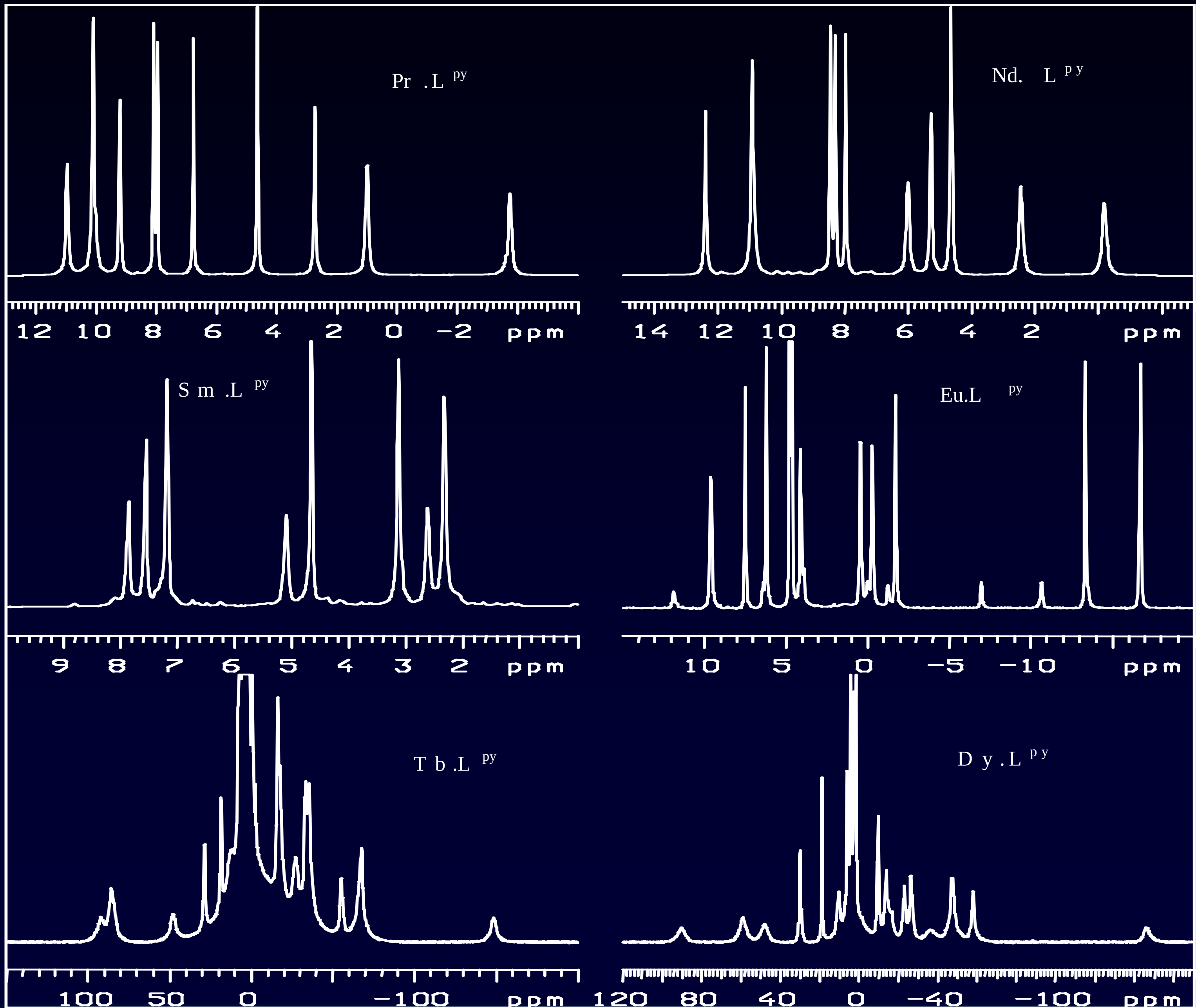
^{1}H NMR Spectrum of Eu(L^{py})/D_2O



$$\Delta_{p_i} = D_i \frac{3\cos^2\theta_i - 1}{r_i^3}$$

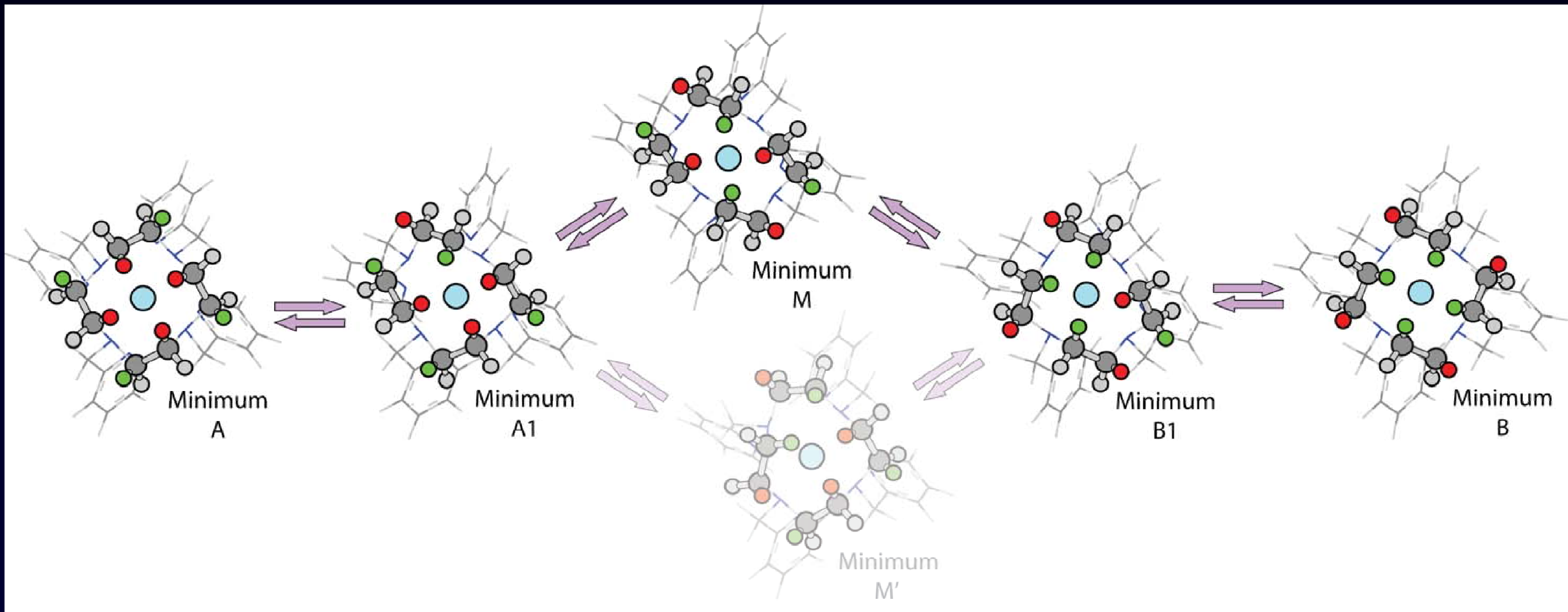
Solution conformation different to solid state geometry

^{1}H NMR Spectra of Ln(L^{py})/D_2O



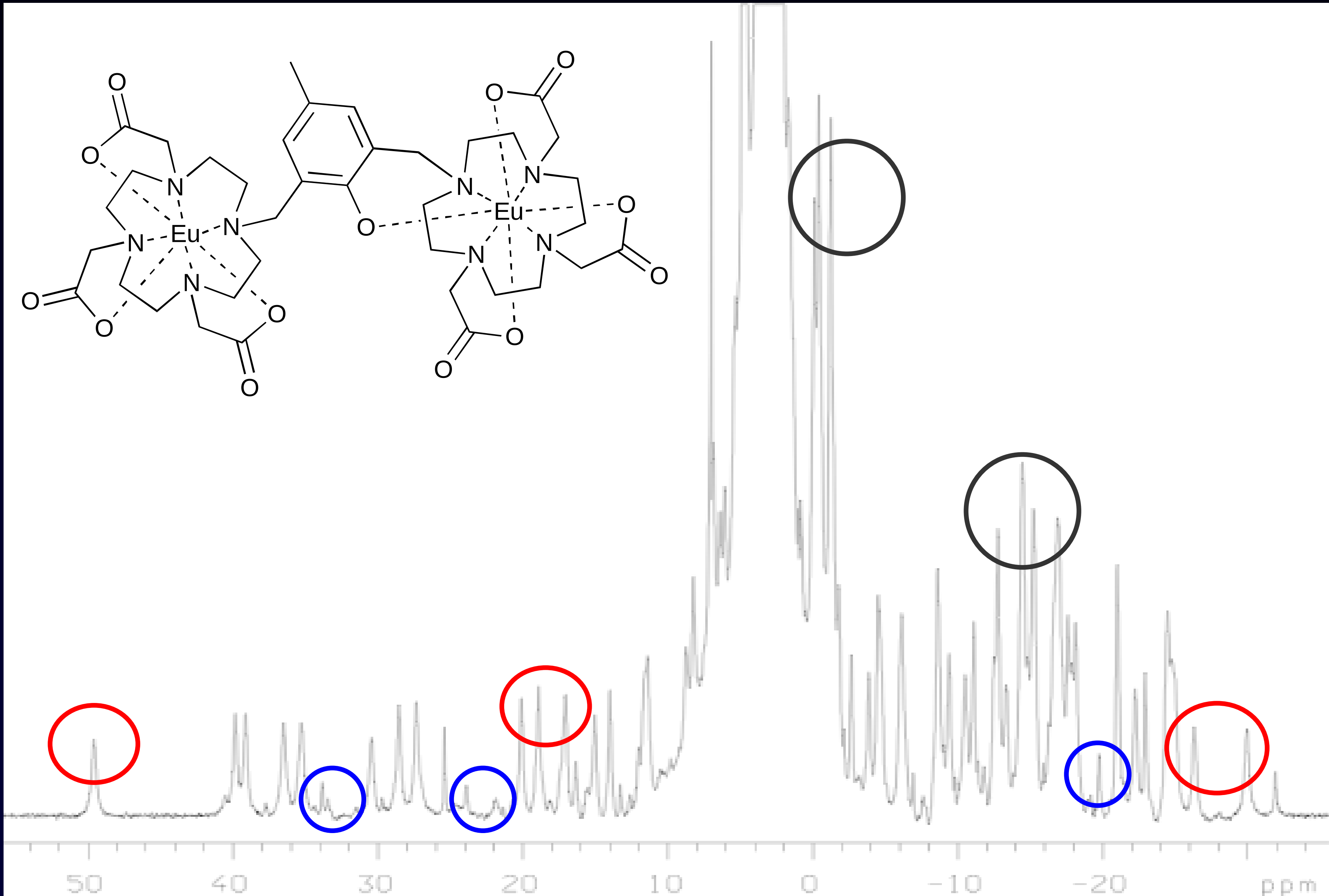
DFT Calculations of Y(L^{py})

DFT scan through cyclen ring isomerisation pathway

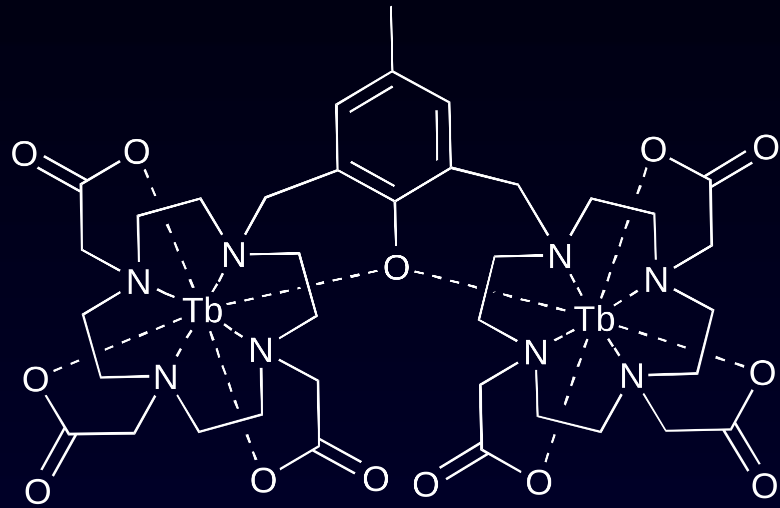


The isomerisation process is a sequence of single-joint inversion pathways

Bimetallic Complexes: ^{1}H NMR



Luminescence Studies



τ_{H2O} 0.51 & 1.67 μs

τ_{D2O} 1.17 & 4.95 μs

q = 0.3 & 1

Differentiated binding sites

τ_{H2O} 2.26 ms

τ_{D2O} 2.55 ms

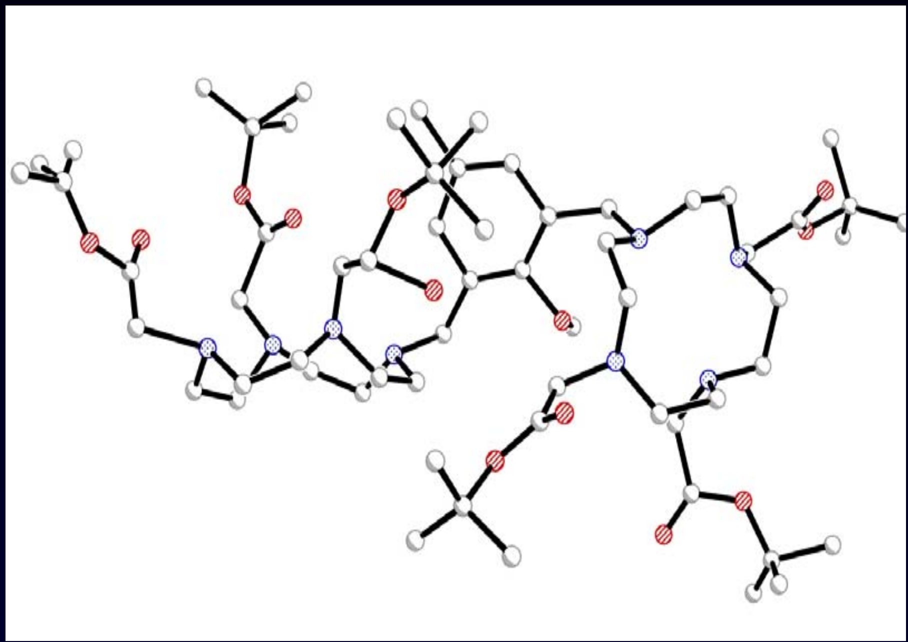
q = 0

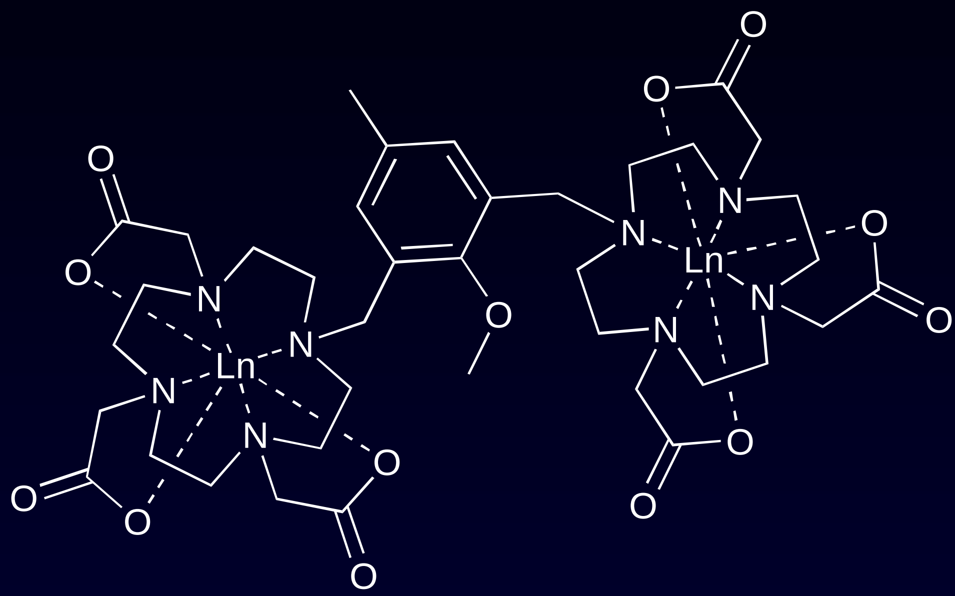
Non-distinguishable binding sites

Open *vs.* closed conformation

Pope *et al*., *Chem. Commun*., 2003, 125.

Anisole Derivative





Eu τ_{H2O} 0.50 ms, τ_{D2O} 1.45 ms, q = 1.3

Tb τ_{H2O} 1.31 ms, τ_{D2O} 1.87 ms, q = 0.8

Yb τ_{H2O} 1.42 μs, τ_{D2O} 4.63 μs, q = 0.4

Removal of coordinative ability of phenol

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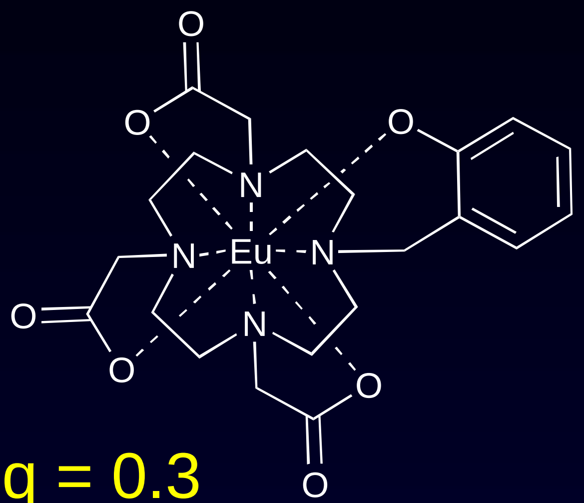
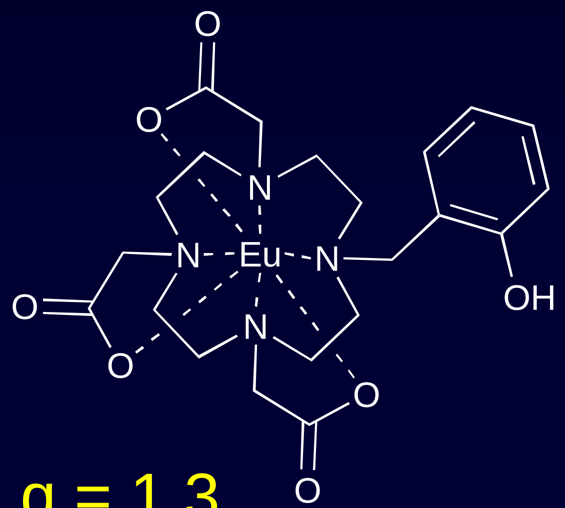
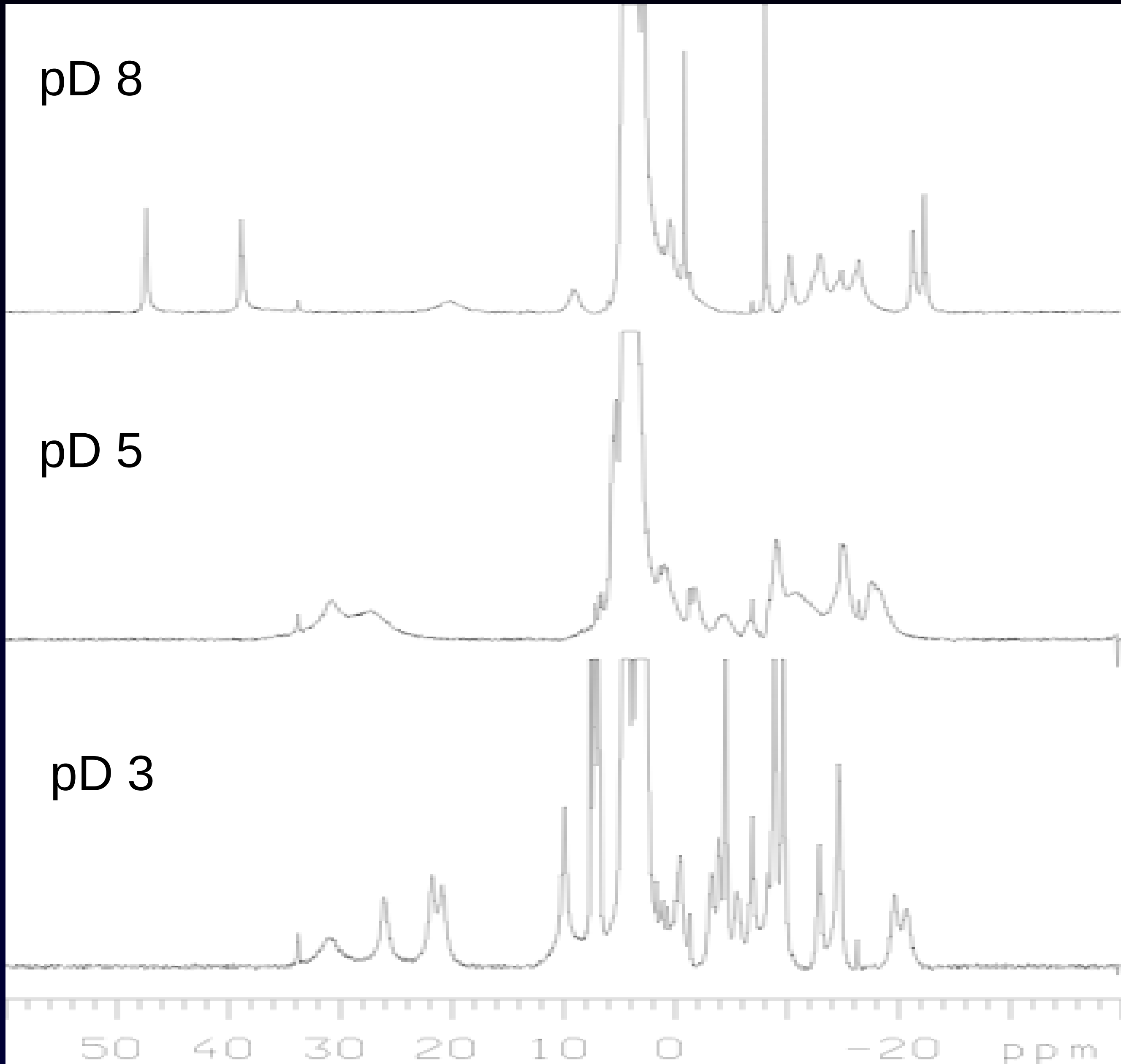
pH Dependence of ^{1}H NMR Spectra



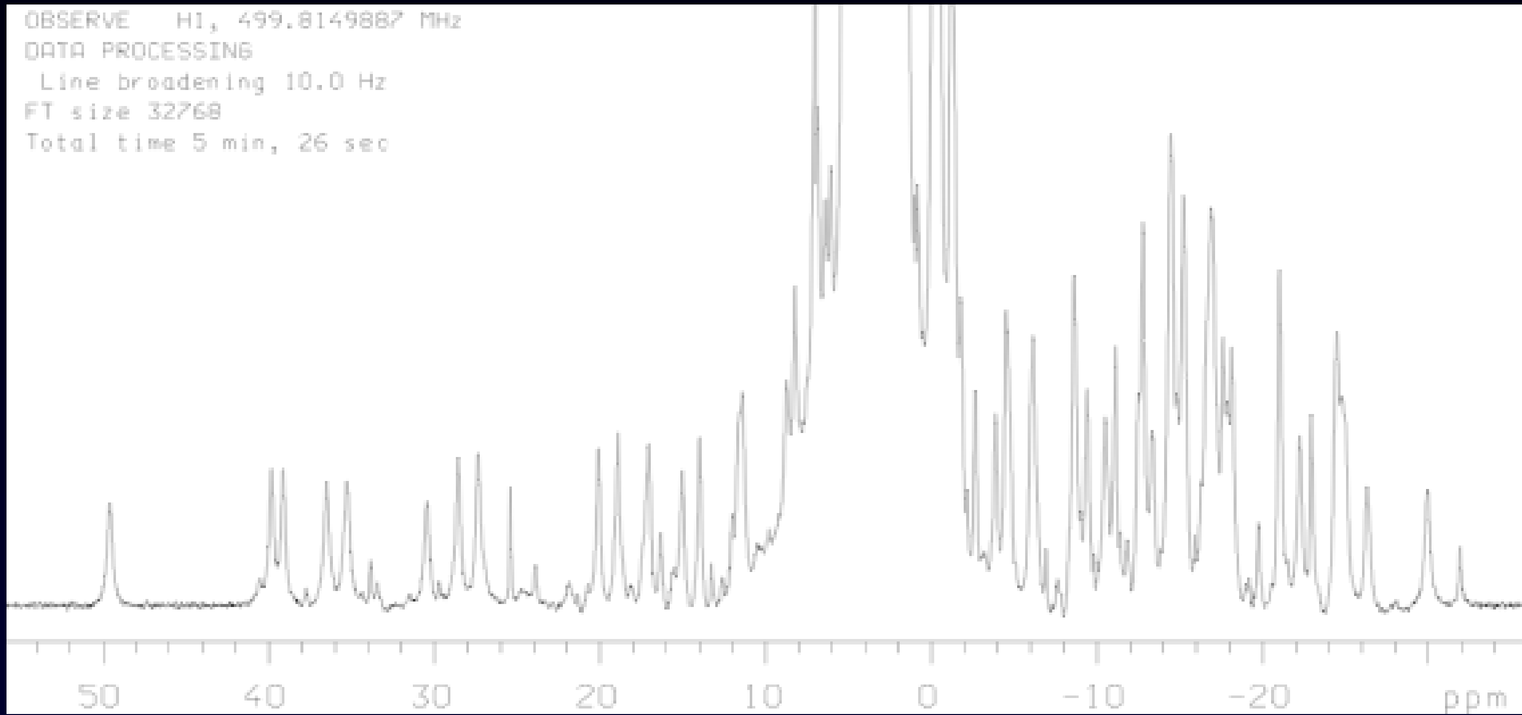
q = 0.3

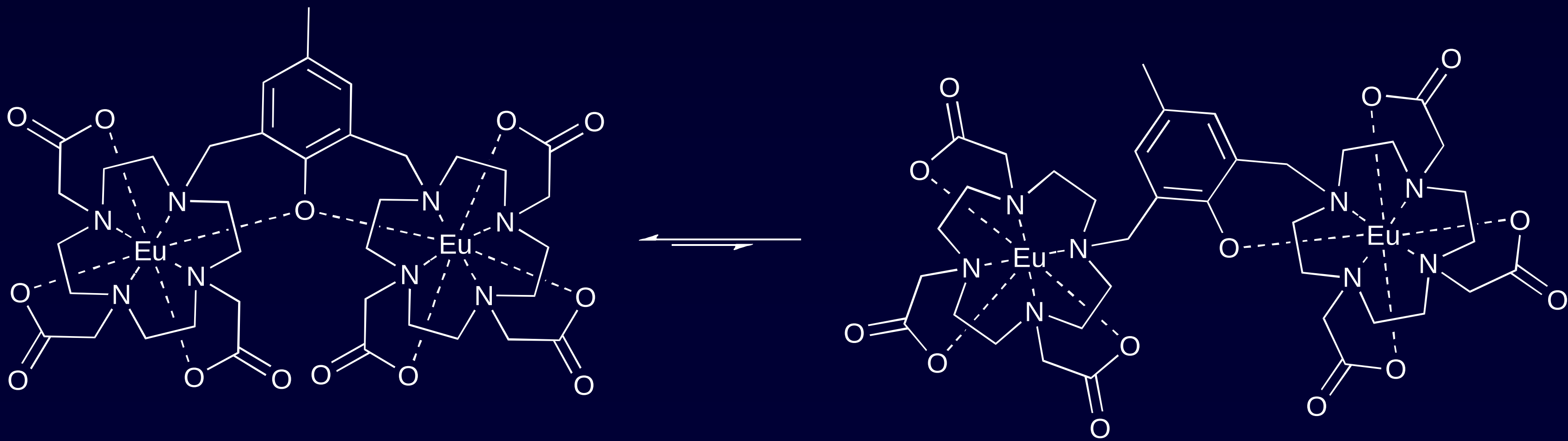


q = 1.3



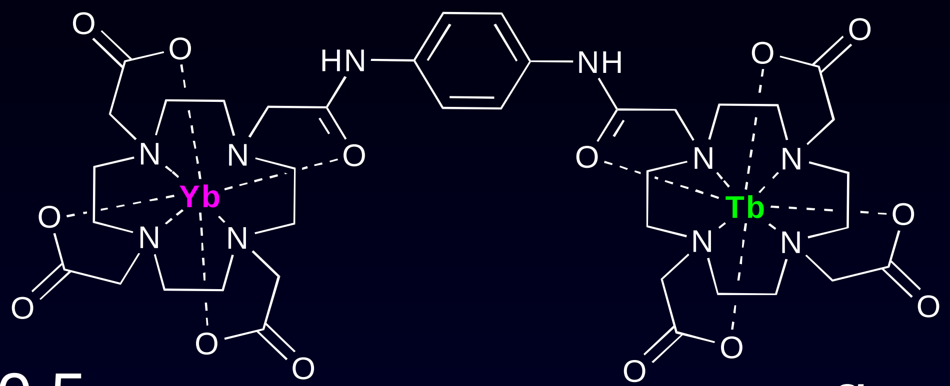
^{1}H NMR Spectra Independent of pH





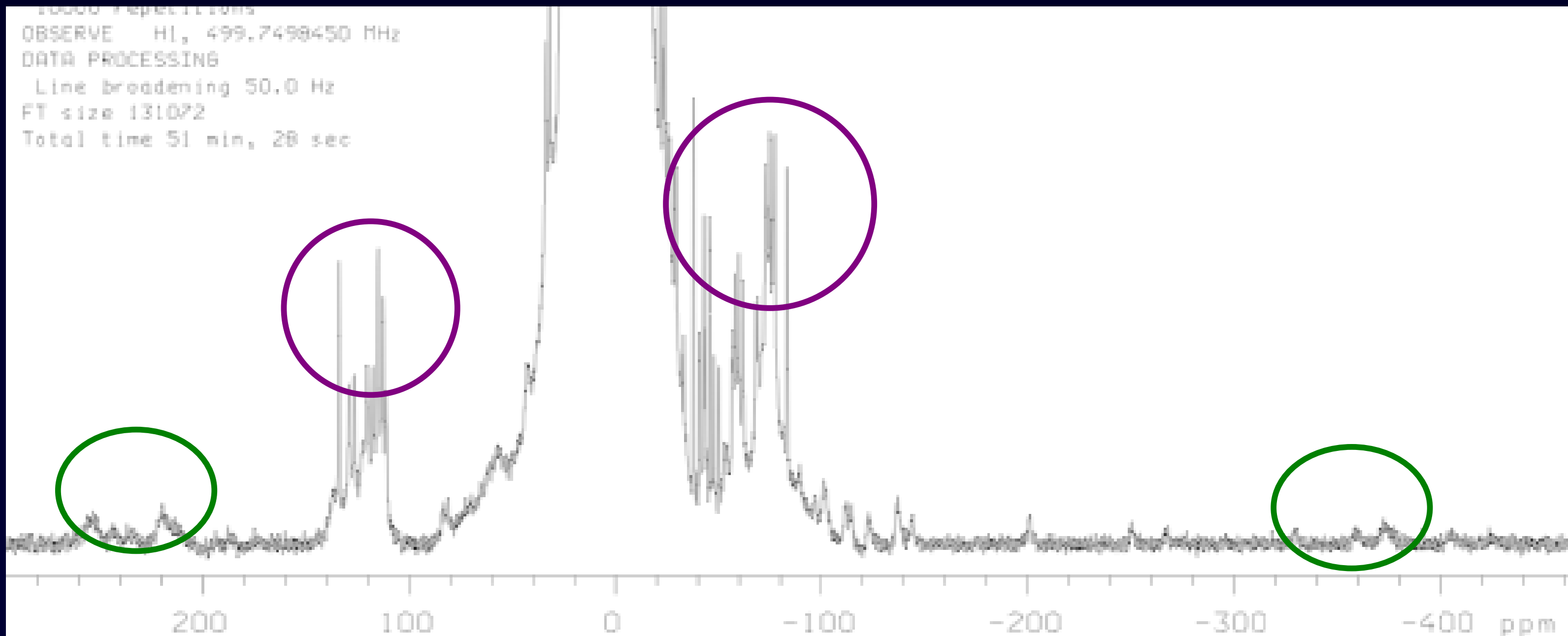
Selective Introduction of Ln^{3+}

Orthogonal protections



$q_{Yb} = 0.5$

$q_{Tb} = 0.6$



Natrajan*et al.*, *Chem. Commun.*, 2009, 6020.

The University of Manchester

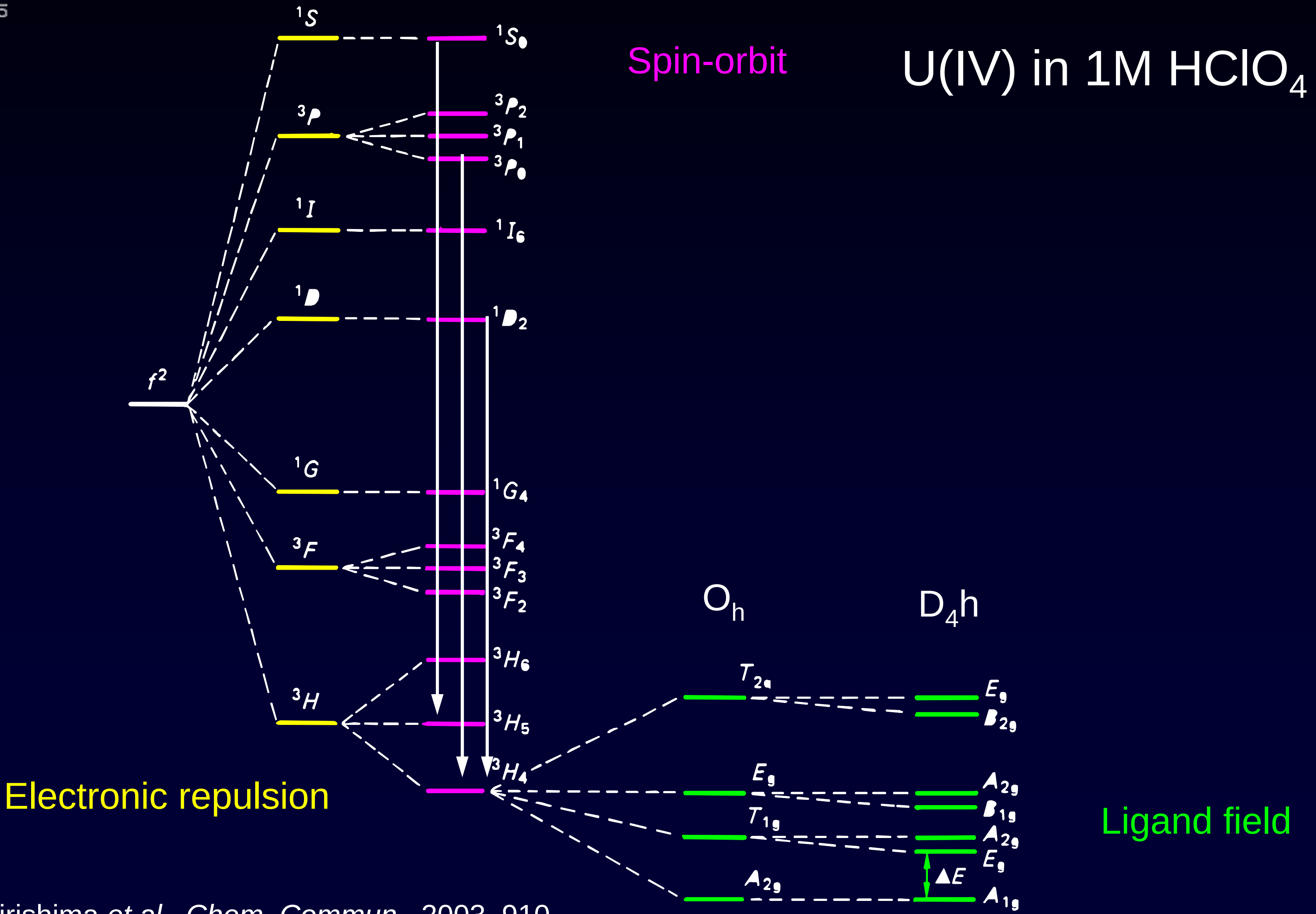
MANCHESTER 1824

Summary

- Solid state structures of complexes with L^{py} do not provide an ideal model for solution behaviour
- Unusual donor sets change the nature of the anisotropy
- In bimetallic systems, solution isomerism is more complicated and NMR spectra are more difficult to interpret
- Emission spectroscopy can be used to study dynamic solution behaviour
- Complementary technique with NMR spectroscopy

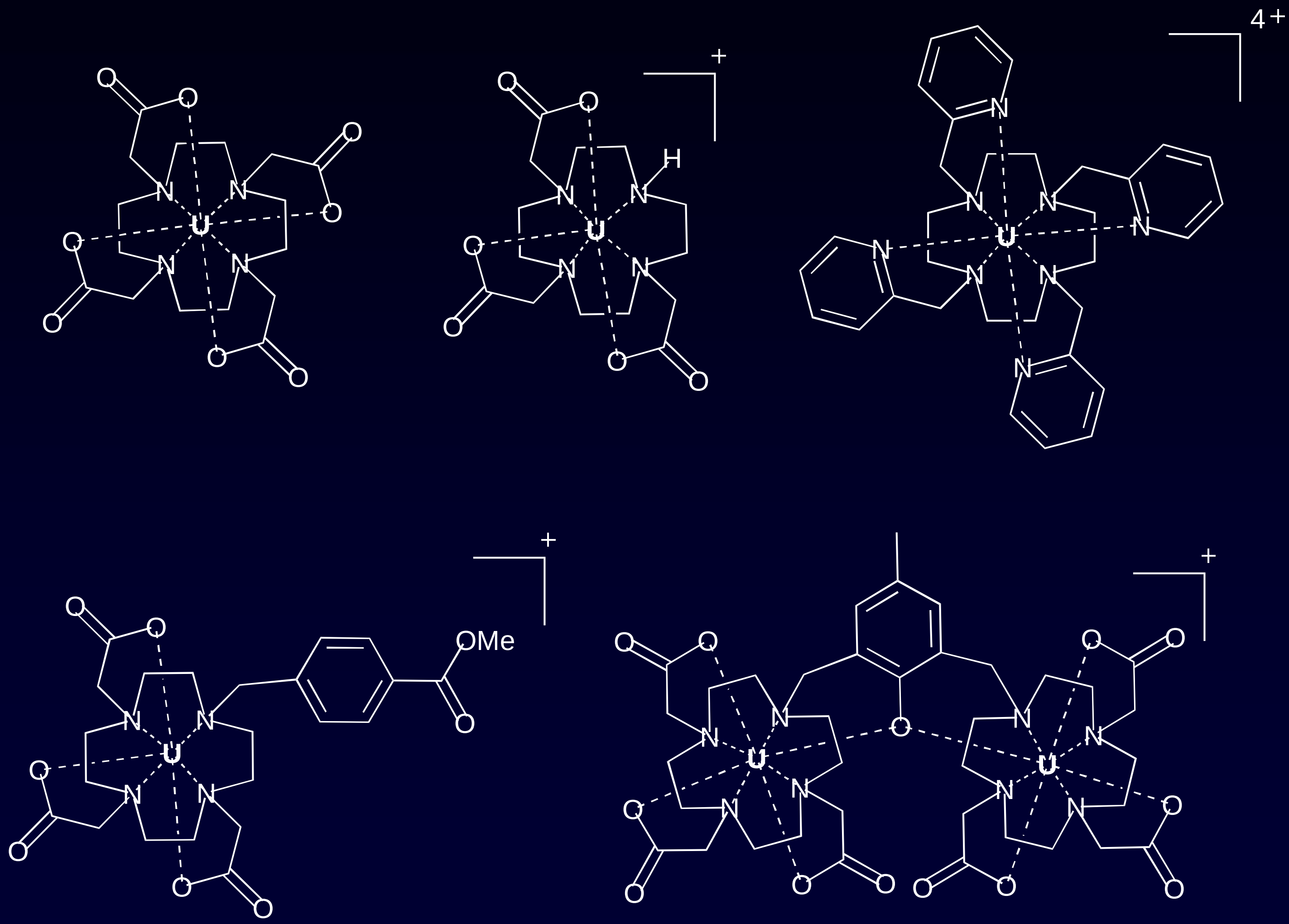
Luminescence Studies of Uranium(IV) Complexes

Uranium(IV) (f^2)



Kirishima *et al*., *Chem. Commun*., 2003, 910.

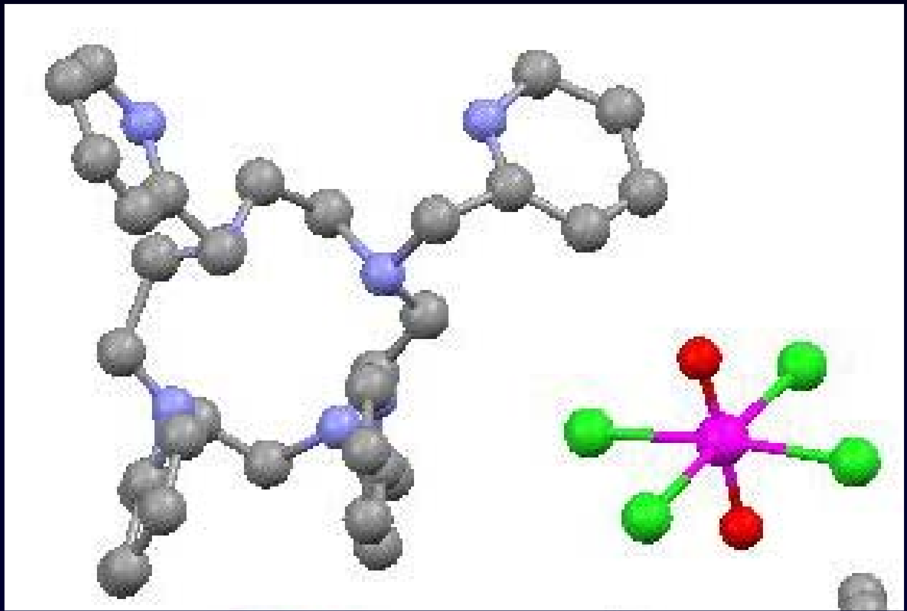
Uranium(IV) Complexes



Complexes prepared by reaction of K salt of ligand wih UCl_4

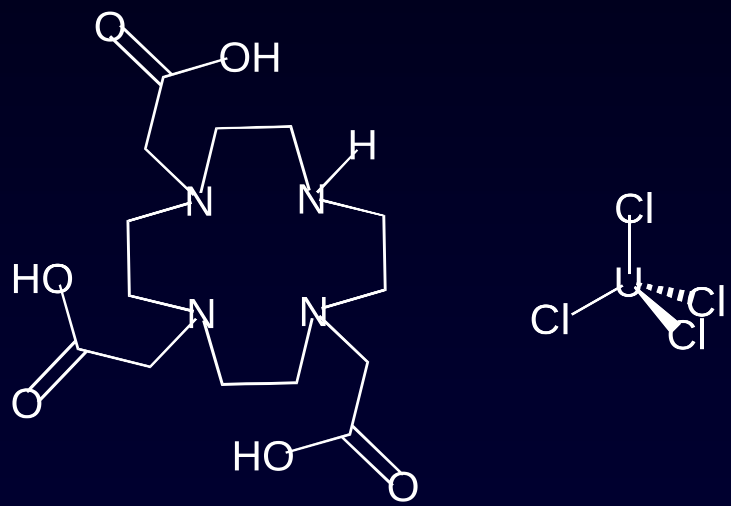
X-ray Crystal Structures

Hydrolysis of U(IV) to UO_2(VI) occurs with L^{py}



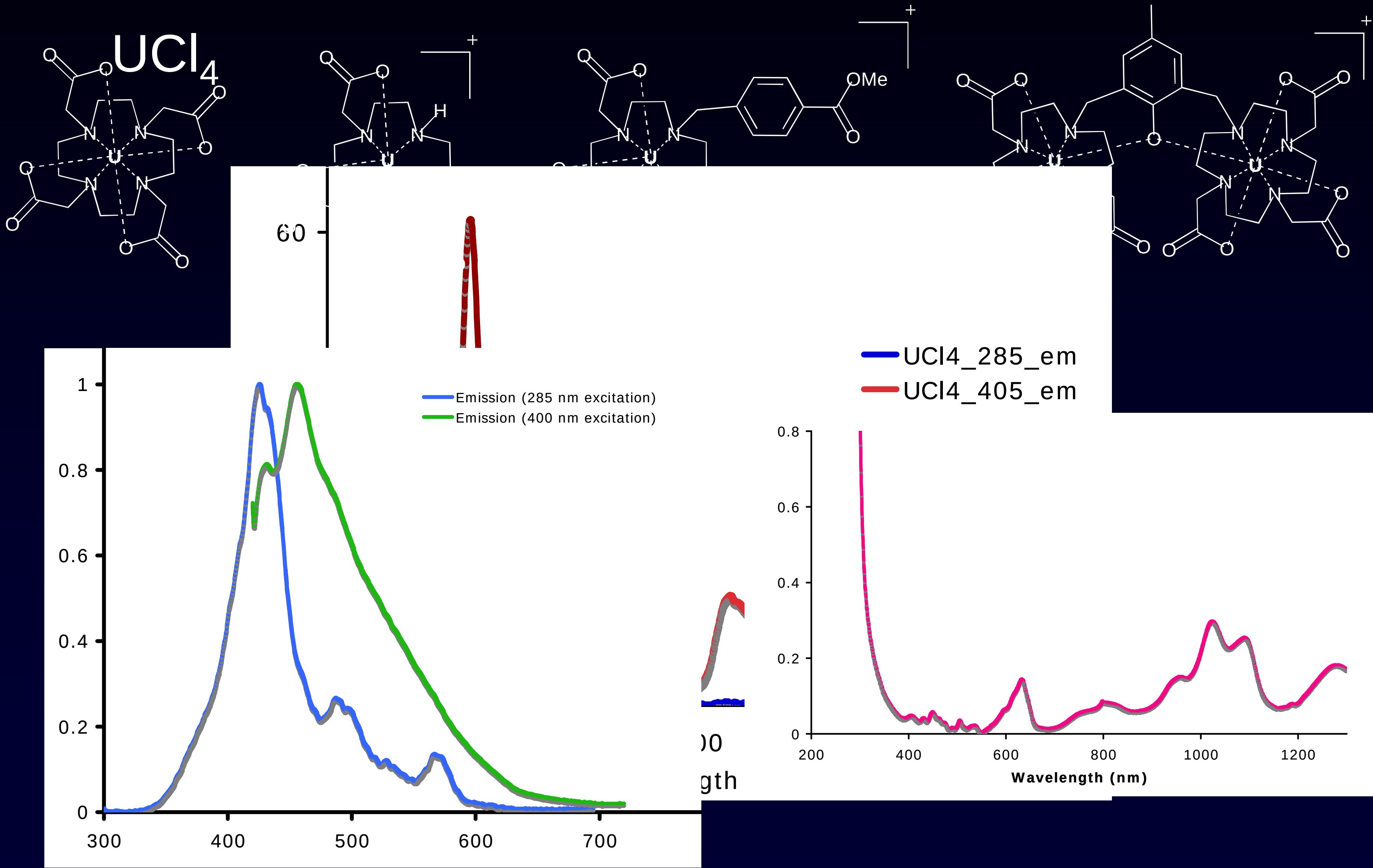
X-ray crystal structure

of $[H_2L^{py}][UO_2Cl_4]$



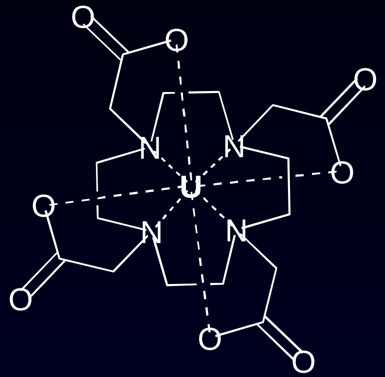
Co-crystallisation of H_3DO3A and UCl_4 occurs; ^{1}H NMR suggests equilibrium mixture with complex

Emission Spectra (MeOH and DMF)

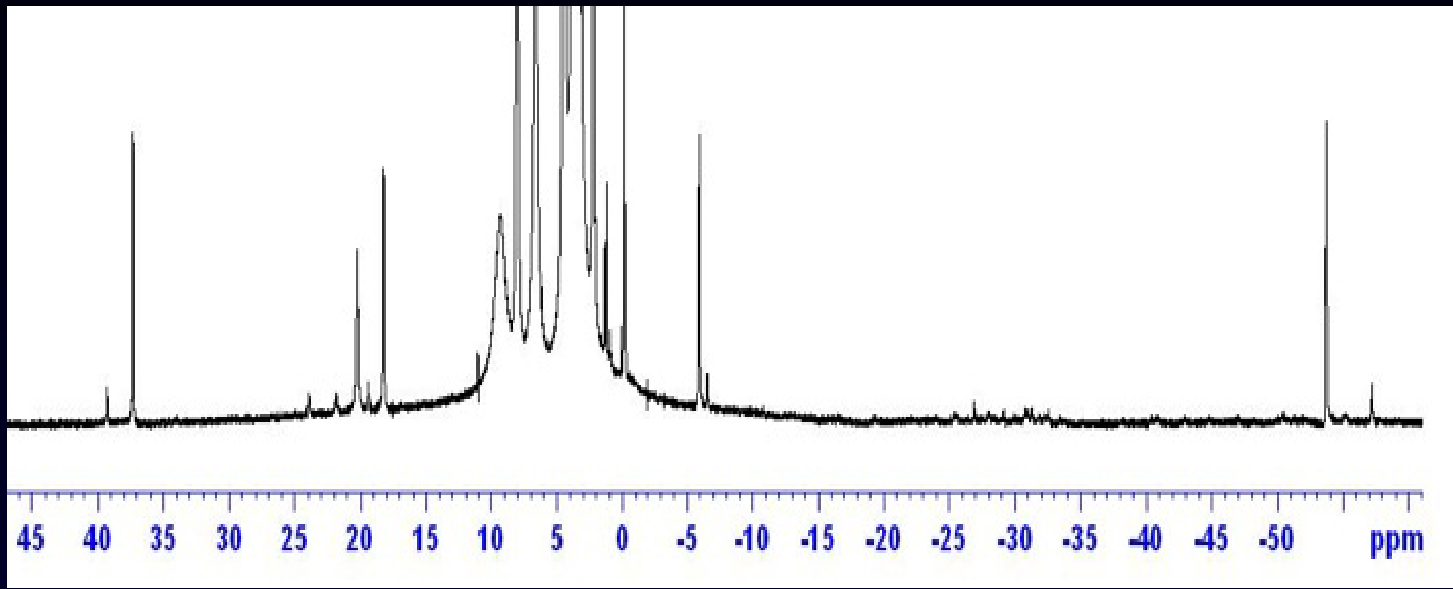


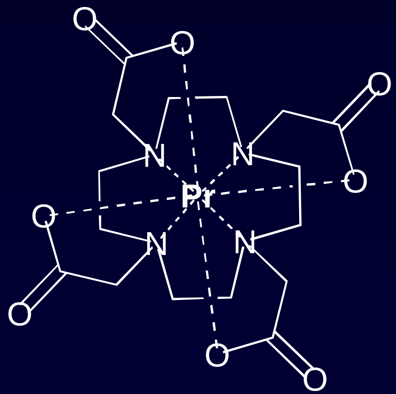
λ_{exc}= 375 and 405 nm; all lifetimes are ~ 2-10 ns (400 - 900 nm)

NMR Spectra (MeOD)

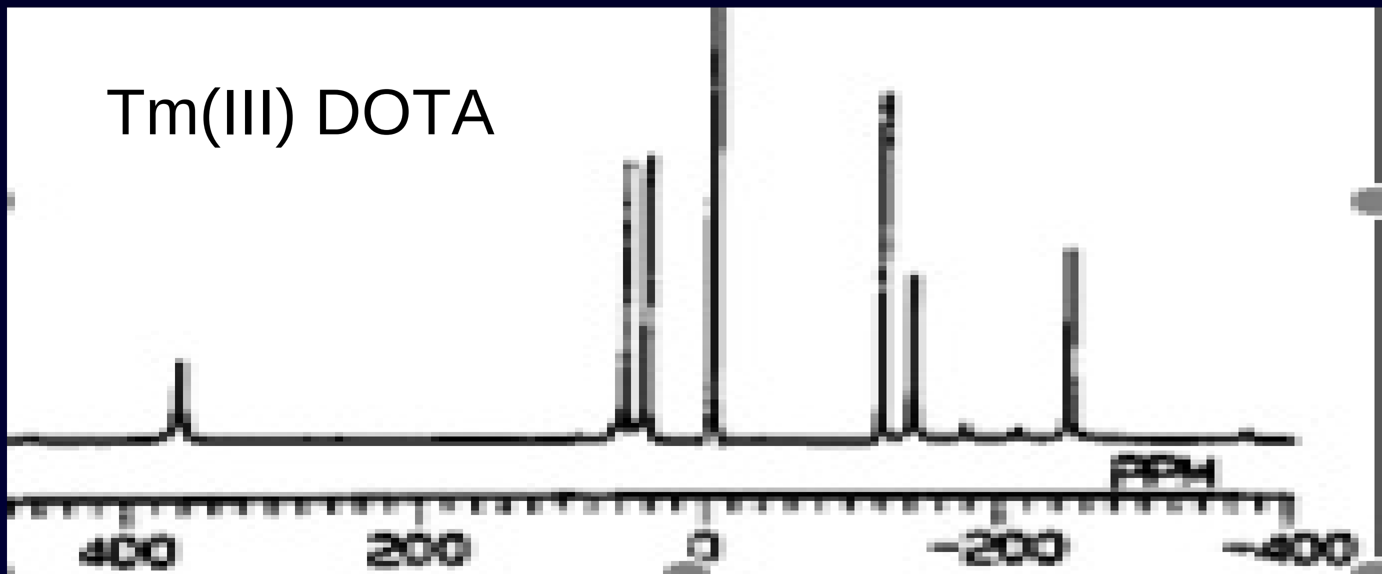


U(IV) DOTA



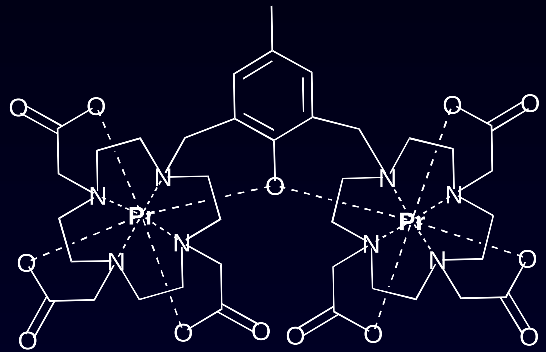


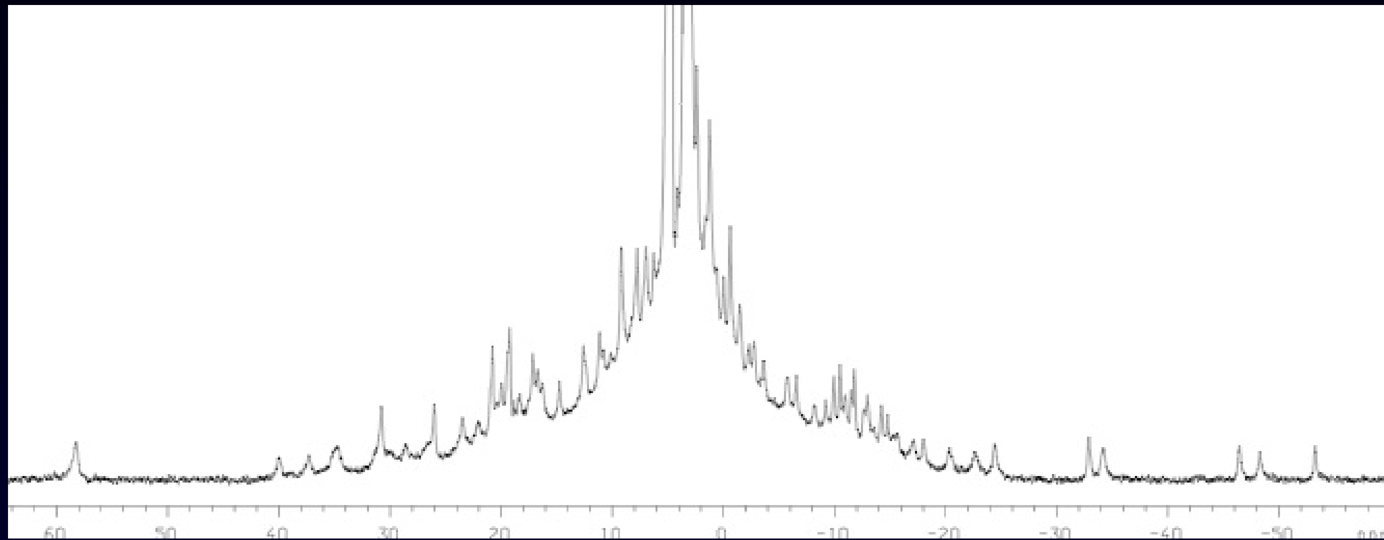
Pr(III) DOTA

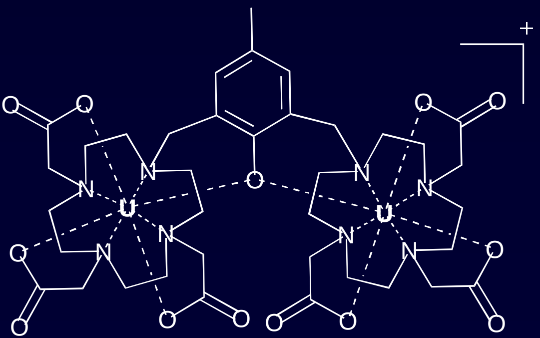


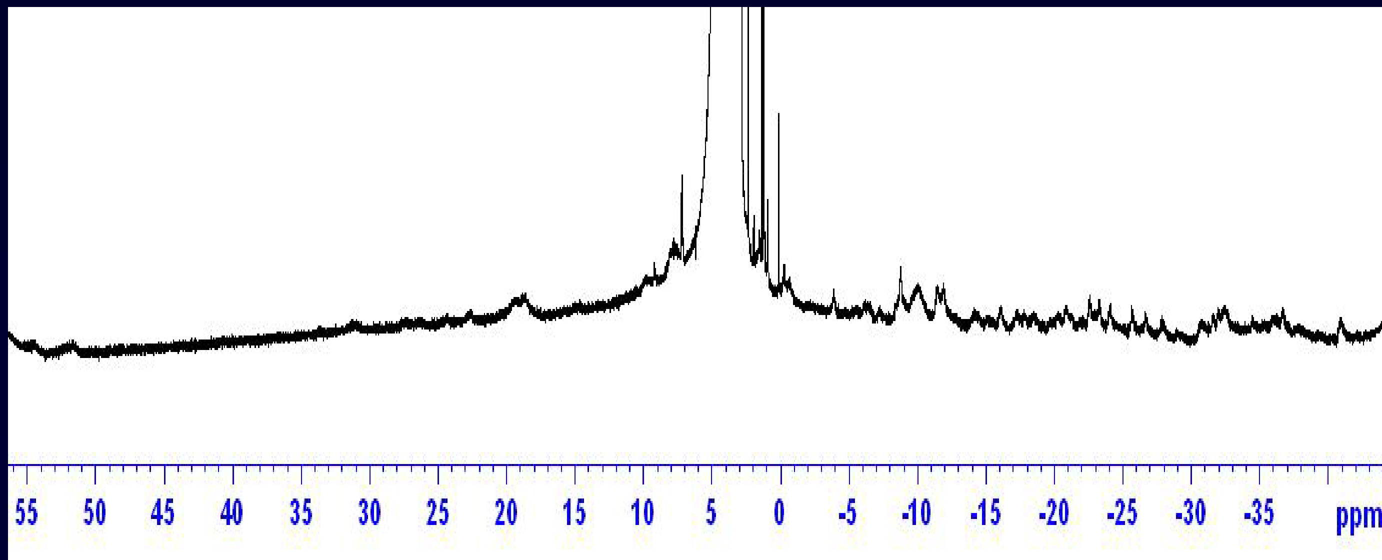
Aime *et al.*, *Inorg. Chem.*, 1992, **31**, 4291

NMR Spectra









Summary

- Several macrocyclic uranium(IV) complexes have been synthesised
- These show long-lived visible emission (ILCT and f-f)
- Intra f-f transitions exhibit charge transfer character
- Emission spectroscopy can be used as a probe for actinide speciation
- ^{1}H NMR spectra of symmetric systems are structurally informative
- ^{1}H NMR spectra of DO3A systems appear similar to the Ln^{3+} series

Acknowledgements

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Mike Redmond

David Collison

The University of Manchester

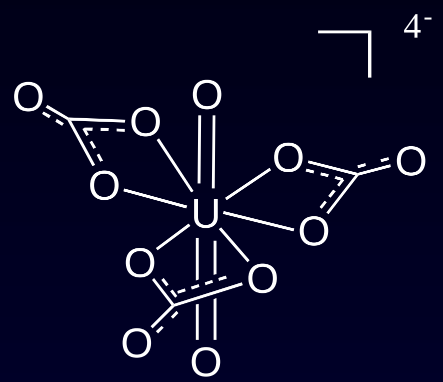
The Leverhulme Trust

EPSRC Engineering and Physical Sciences Research Council


Hurrah!
You did it
Go Ape!

Uranyl(VI) Luminescence

$5f^0$



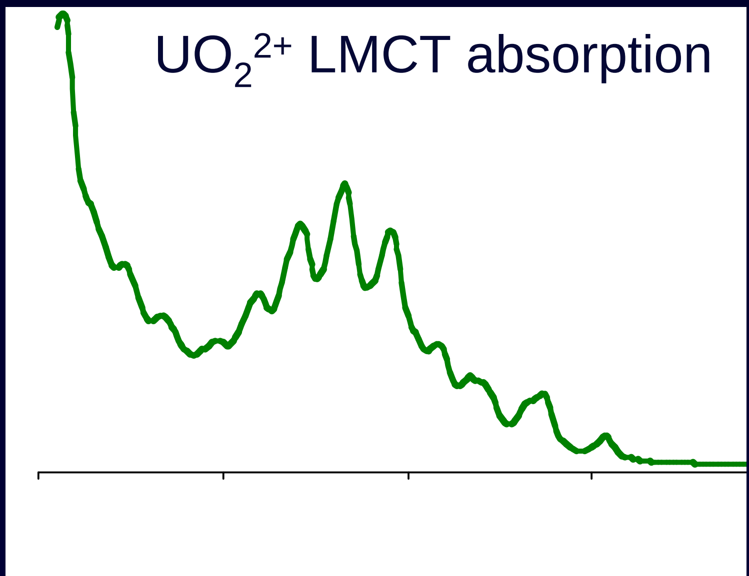
$h\upsilon$

LMCT

UO_2^{2+*}

Photochemistry

Luminescent Probe

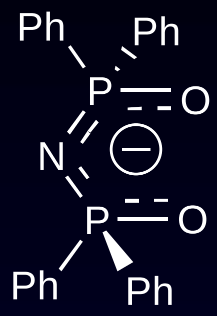


Characteristic green emission

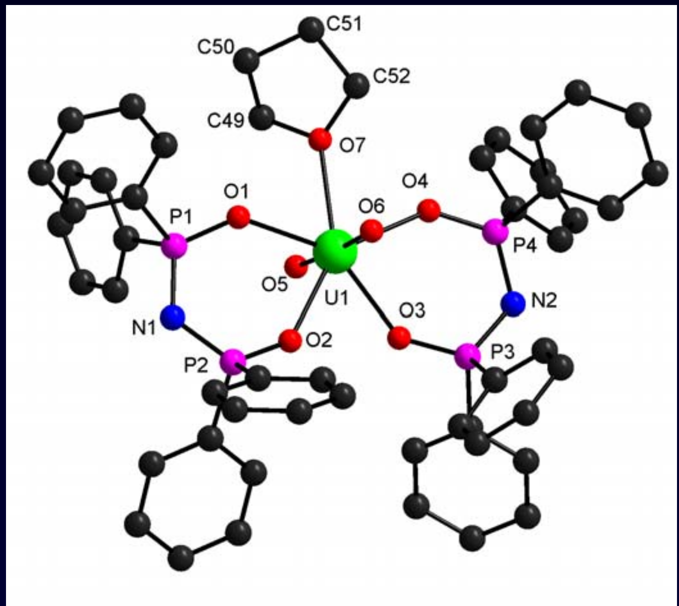
Long lived triplet excited state (μs - s)

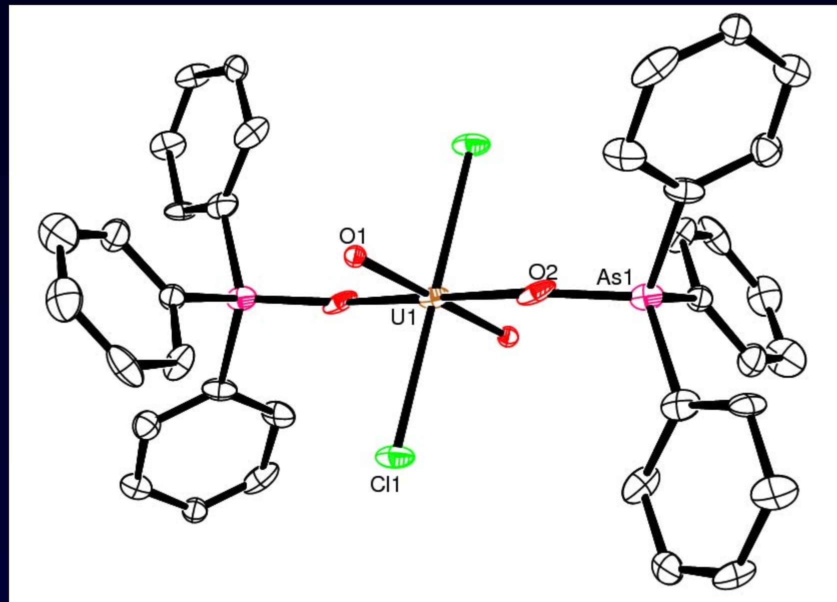
J. Photochem. Photobiol., 1990, **52**, 293.

Uranyl(VI) Complexes

L = 

$Ph_3P{=}O$ $Ph_3As{=}O$ $Ph_3P{=}NH$





M. Redmond

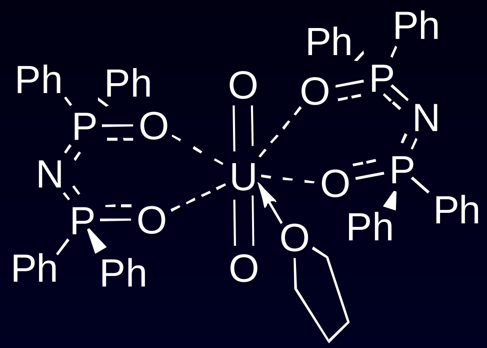
$[UO_2(TPIP)_2(thf)]$

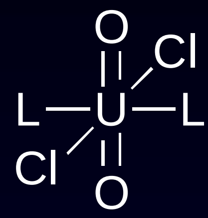
$[UO_2(OAsPh_3)_2Cl_2]$

S. Cornet

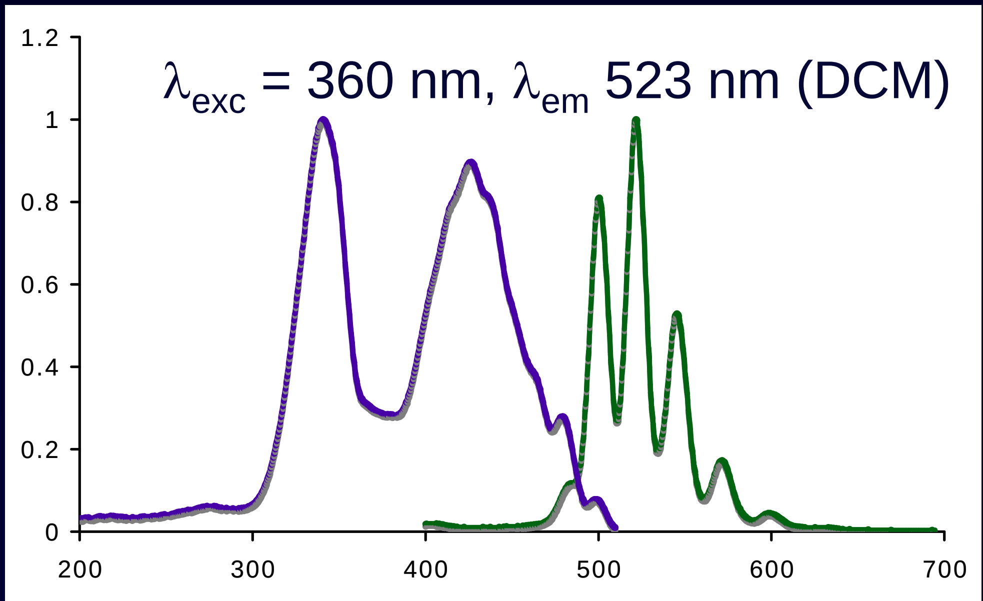
Ligands relevant to the PUREX process

Emission Spectra



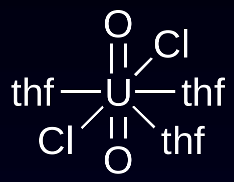
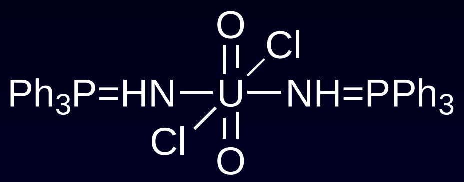
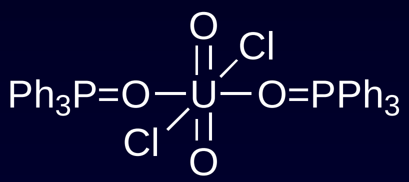
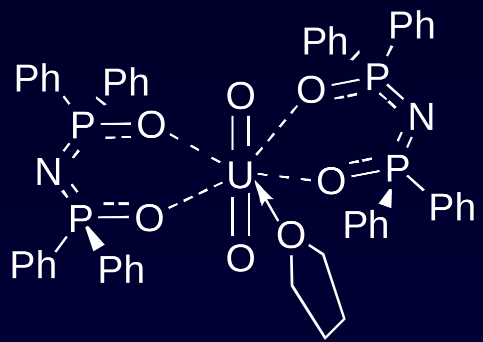
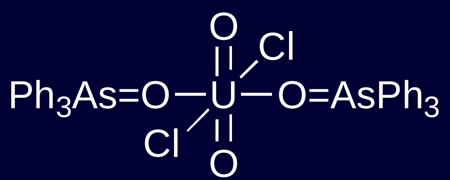


L	λ_{em}
Cl	504 nm
$Ph_3P{=}NH$	517 nm
Ph_3PO	529 nm
Ph_3AsO	531 nm



All complexes show well resolved uranyl LMCT emission

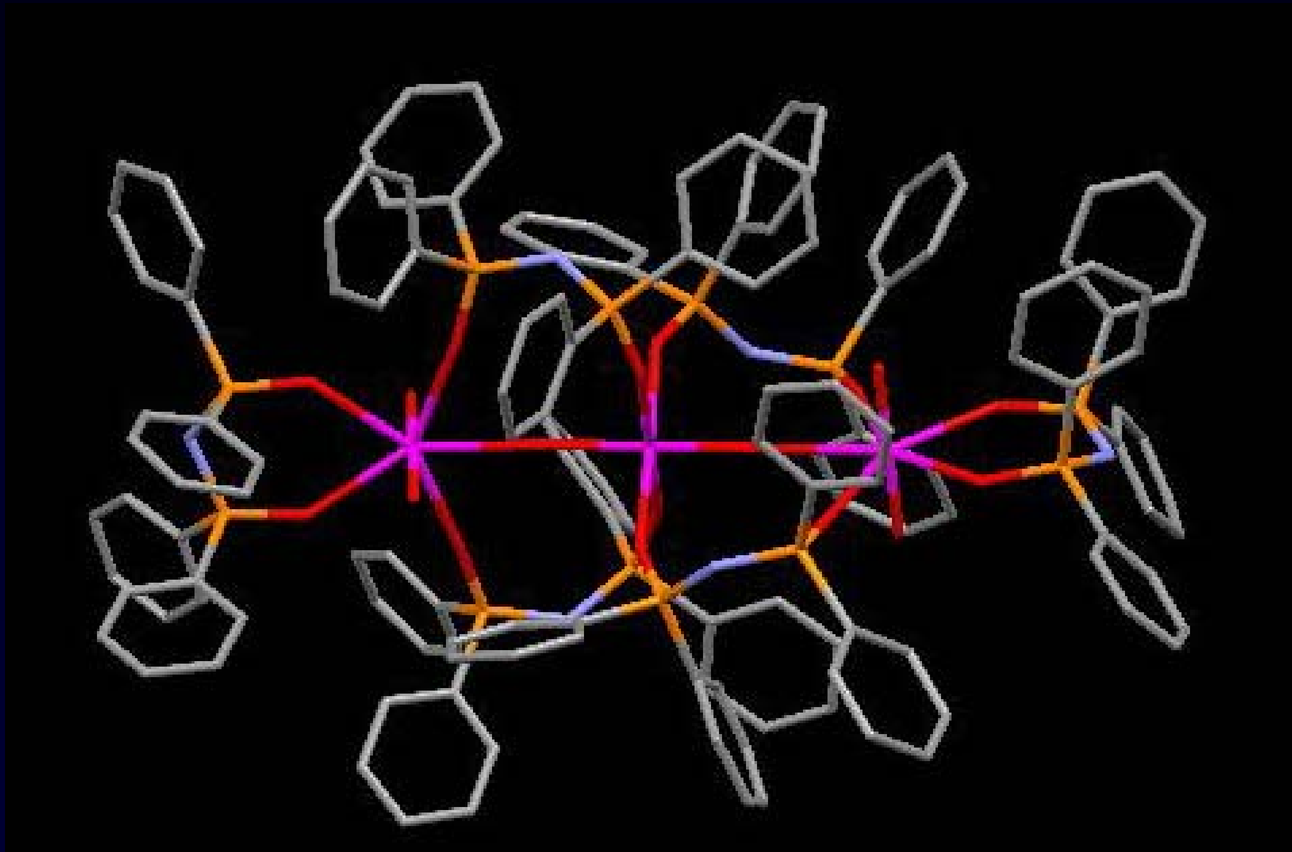
Luminescence Lifetimes

	τ_1 (μs)	τ_2 (μs)	χ^2
	0.15 (46 %)	0.04 (54 %)	1.520
	0.87 (93 %)	0.19 (7 %)	1.063
	1.42 (75 %)	0.13 (25 %)	1.001
	2.00	-	1.008
	3.46	-	1.097

λ_{exc} 405 nm, λ_{em} 450 - 550 nm

Future Outlook

$[UO_2(TPIP)_2]_3$



Using luminescence as a probe of nuclearity and speciation

Cea-Olivers *et al*., *Inorg. Chem. Commun*., 2005, **8**, 205.