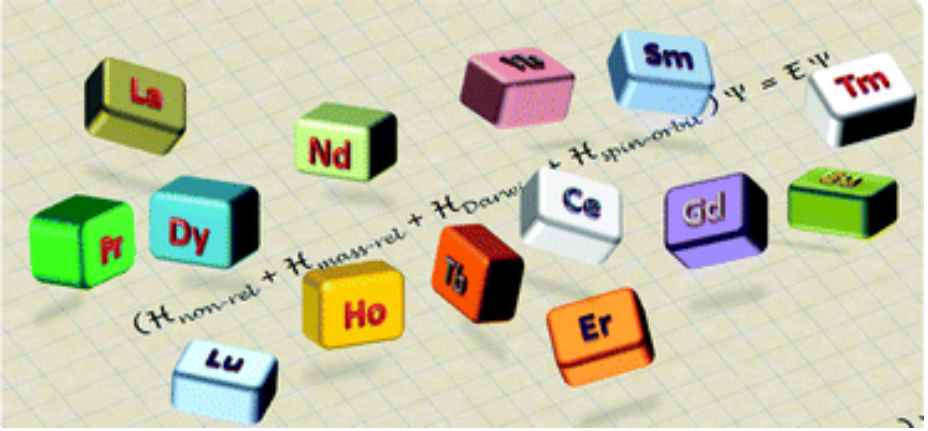
Introduction to the Magnetism of Lanthanides Ions



Kevin Bernot
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Basics of Rare-Earth & Lanthanide Elements

Rare-Earth & Lanthanides elements

Institut des Sciences Chimiques de Rennes
UMR CNRS 6226

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1.00794 1 H hydrogène																	4.002602 2 He hélium
2	6.941 3 Li lithium	9.012182 4 Be béryllium											10.811 5 B bore	12.0107 6 C carbone	14.0067 7 N azote	15.9994 8 O oxygène	18.998403 9 F fluor	20.1797 10 Ne néon
3	22.98976 11 Na sodium	24.3050 12 Mg magnésium											26.98153 13 Al aluminium	28.0855 14 Si silicium	30.97696 15 P phosphore	32.065 16 S soufre	35.453 17 Cl chlore	39.948 18 Ar argon
4	39.0983 19 K potassium	40.078 20 Ca calcium	44.95591 21 Sc scandium	47.867 22 Ti titane	50.9415 23 V vanadium	51.9962 24 Cr chrome	54.93804 25 Mn manganèse	55.845 26 Fe fer	58.93319 27 Co cobalt	58.6934 28 Ni nickel	63.546 29 Cu cuivre	65.38 30 Zn zinc	69.723 31 Ga gallium	72.64 32 Ge germanium	74.92160 33 As arsenic	78.96 34 Se sélénium	79.904 35 Br brome	83.798 36 Kr krypton
5	85.4678 37 Rb rubidium	87.62 38 Sr strontium	88.90585 39 Y yttrium	91.224 40 Zr zirconium	92.90638 41 Nb niobium	95.96 42 Mo molybdène	98 43 Tc technétium	101.07 44 Ru ruthénium	102.9055 45 Rh rhodium	106.42 46 Pd palladium	107.8682 47 Ag argent	112.441 48 Cd cadmium	114.818 49 In indium	118.710 50 Sn étain	121.760 51 Sb antimoine	127.60 52 Te tellure	126.9044 53 I iode	131.293 54 Xe xénon
6	132.9054 55 Cs césium	137.327 56 Ba barium	lanthanides 57-71	178.49 72 Hf hafnium	180.9478 73 Ta tantale	183.84 74 W tungstène	186.207 75 Re rhénium	190.23 76 Os osmium	192.217 77 Ir iridium	195.084 78 Pt platine	196.9665 79 Au or	200.59 80 Hg mercure	204.3833 81 Tl thallium	207.2 82 Pb plomb	208.9804 83 Bi bismuth	210 84 Po polonium	210 85 At astate	220 86 Rn radon
7	223 87 Fr francium	226 88 Ra radium	actinides 89-103	261 104 Rf rutherfordium	262 105 Db dubnium	266 106 Sg seaborgium	264 107 Bh bohrium	277 108 Hs hassium	268 109 Mt meitnérium	271 110 Ds darmstadium	272 111 Rg roentgenium	285 112 Cn copernicium	284 113 Nh nihonium	289 114 Fl flérovium	288 115 Mc moscovium	292 116 Lv livermorium	292 117 Ts tennessine	294 118 Og oganesson

138.9054 57 La lanthane	140.116 58 Ce	140.9076 59 Pr	144.242 60 Nd	145 61 Pm	150.36 62 Sm	151.964 63 Eu	157.25 64 Gd	158.9253 65 Tb	162.500 66 Dy	164.9303 67 Ho	167.259 68 Er	168.9342 69 Tm	173.054 70 Yb	174.9668 Lu
227 89 Ac actinium	232.0380 90 Th thorium	231.0358 91 Pa protactinium	238.0289 92 U uranium	237 93 Np neptunium	244 94 Pu plutonium	243 95 Am américium	247 96 Cm curium	247 97 Bk berkélium	251 98 Cf californium	252 99 Es einsteinium	257 100 Fm fermium	258 101 Md mendélévium	259 102 No nobélium	262 103 Lr lawrencium

Sources : IUPAC, Wikimedia Commons

Rare-Earths (RE)

Lanthanides (Ln)

Lanthanoids

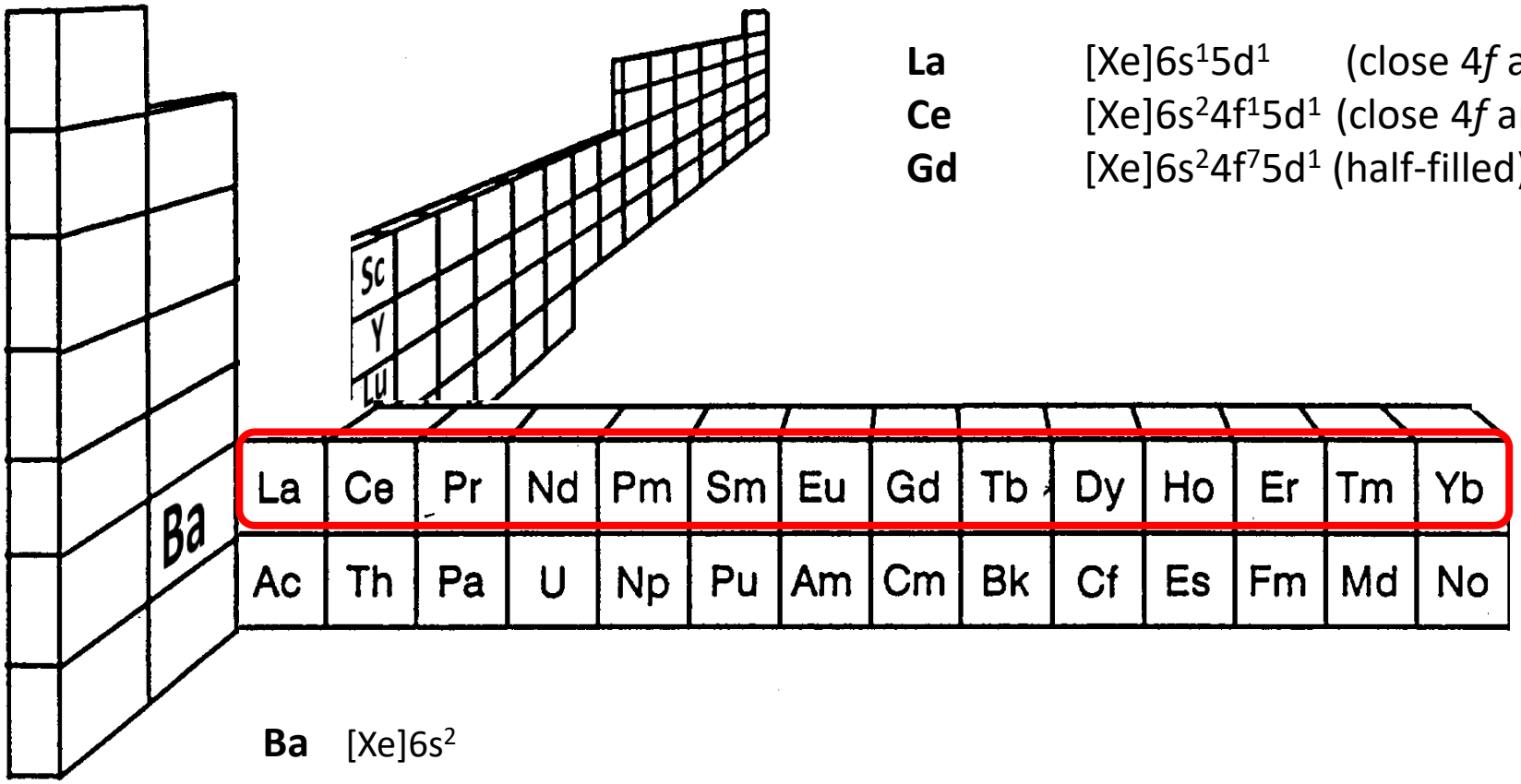
Ceric lanthanoids (Ce-Eu) → « big lanthanides »
Yttric lanthanoids (Gd-Lu) → « small lanthanides »

Think about periodic table in 3D…!

Sc	$[Ar]4s^2 3d^1$
Y	$[Kr]5s^2 4d^1$
Pr-Yb	$[Xe]6s^2 4f^n$ $\quad 3 \leq n \leq 14$
Lu	$[Xe]6s^2 4f^{14} 5d^1$

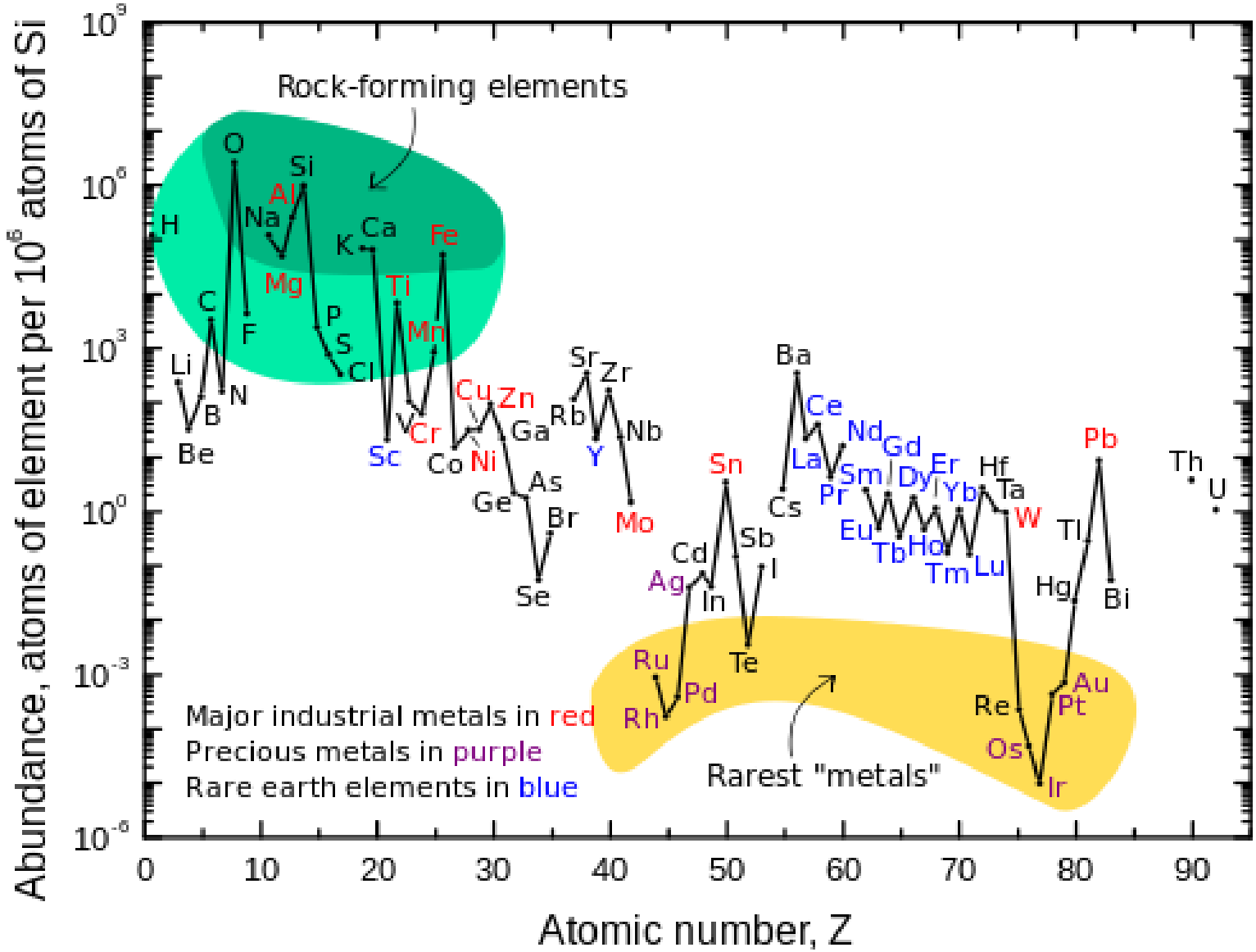
Exception to Klechkowski's rule:

La	$[Xe]6s^1 5d^1$	(close 4*f* and 5*d*)
Ce	$[Xe]6s^2 4f^1 5d^1$	(close 4*f* and 5*d*)
Gd	$[Xe]6s^2 4f^7 5d^1$	(half-filled)



Ba $[Xe]6s^2$

Rare-Earth elements are not…rare



http://en.wikipedia.org/wiki/Abundance_of_the_chemical_elements

Rare-Earth elements are rare…in every mine

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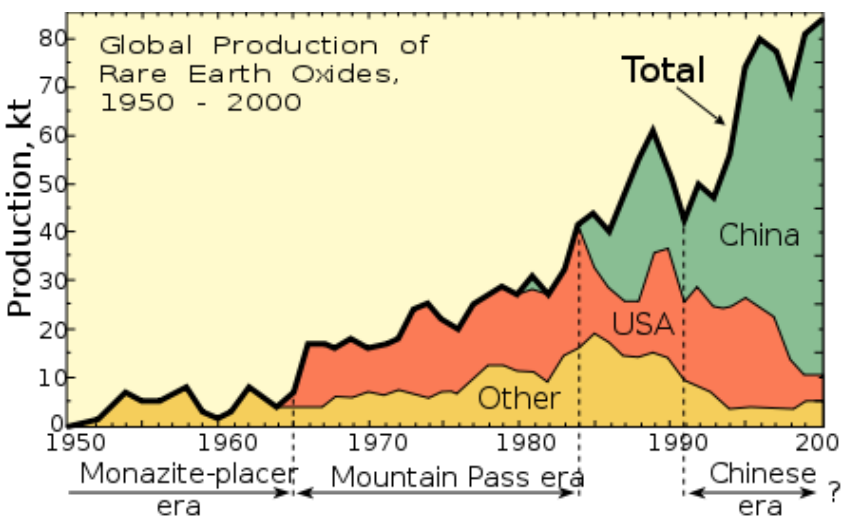
Oxydes de TR, Sc, Th et U	Formule	Teneur de l'écorce terrestre (en ppm)	Concentrés miniers (teneurs* en %)			Concentrés chimiques (teneurs* en %)			Prix des oxydes, en $/kg, 99 % de pureté, en juillet 2016
			Monazite	Bastnaésite	Loparite	Bayan Obo (Chine)	Mountain Pass (Etats -Unis)	Central Lanthanide Deposit, Mount Weld (Australie)	
Total oxyde de TR		150	~ 60	60-70	~ 32	100	100	100	
Lanthane	La_2O_3	18	24	32	28	23,0	34,0	23,88	5,1[1]
Cérium	CeO_2	46	46	49	57	50,0	48,8	47,55	5,2[1]
Praséodyme	Pr_6O_{11}	5,5	5	4	4	6,2	4,2	5,16	81,3[1]
Néodyme	Nd_2O_3	24	17	13,5	9	18,5	11,7	18,13	51[1]
Samarium	Sm_2O_3	6,5	2,5	0,5	0,9	0,8	0,79	2,44	15[1]
Europium	Eu_2O_3	0,5	0,05	0,1	0,1	0,2	0,13	0,53	285[1]
Gadolinium	Gd_2O_3	6,4	1,5	0,3	0,2	0,7	0,21	1,09	45[1]
Terbium	Tb_4O_7	0,9	0,04	0,01	0,07	0,1		0,09	559[1]
Dysprosium	Dy_2O_3	5	0,7	0,03	0,09	0,1		0,25	259[1]
Holmium	Ho_2O_3	1,2	0,05	0,01	0,03			0,03	82[2]
Erbium	Er_2O_3	4	0,2	0,01	0,07			0,06	37[1]
Thulium	Tm_2O_3	0,4	0,01	0,02	0,07			0,01	275[2]
Ytterbium	Yb_2O_3	2,7	0,1	0,01	0,3			0,03	65[2]
Lutécium	Lu_2O_3	0,8	0,04	0,01	0,05			0	1 550[2]
Yttrium	Y_2O_3	28	2,4	0,1	0,15		0,12	0,76	34[1]
Thorium	ThO_2	10	6,7	0,35	0,65	0,032			
Uranium	U_3O_8	4	0,3	< 0,05					
Scandium	Sc_2O_3	16							2 150[2]

Sources : [1]Mineral Info, [2]Panorama 2014 BRGM

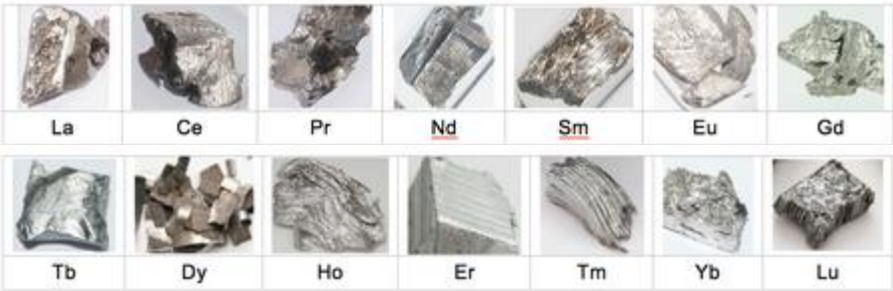
Rare-Earth elements are rare…in every mine

Element	Upper crust ppm	Middle crust	Lower crust	Total crust	Composition of the Earth's crust	Bulk composition of the Earth
Sc	14	19	31	21.9	20 ppm	10.1 ± 2 ppm
Y	21	20	16	19	31.5 ppm	2.4 ± 0.2 ppm
Cu	28	26	26	27	68 ppm	64.7 ± 5 ppm
La	31	24	8	20	35 ppm	415 ± 10 ppb
Ce	63	53	20	43	68 ppm	1088 ± 20 ppb
Pr	7.1	5.8	2.4	4.9	9.5 ppm	165 ± 5 ppb
Nd	27	25	11	20	40 ppm	814 ± 10 ppb
Sm	4.7	4.6	2.8	3.9	7.5 ppm	259 ± 3 ppb
Dy	3.9	3.8	3.1	3.6	6.2 ppm	424 ± 10 ppb
Tb	0.7	0.7	0.48	0.6	1.2 ppm	66.6 ± 5 ppb
Lu	0.31	0.4	0.25	0.3	0.81 ppm	42.5 ± 2 ppb
Pt	0.5	0.85	2.7	1.5	0.004 ppm	1562 ± 40 ppb
Au	1.5	0.66	1.6	1.3	0.0041 ppm	102 ± 20 ppb

Oxides



Metals



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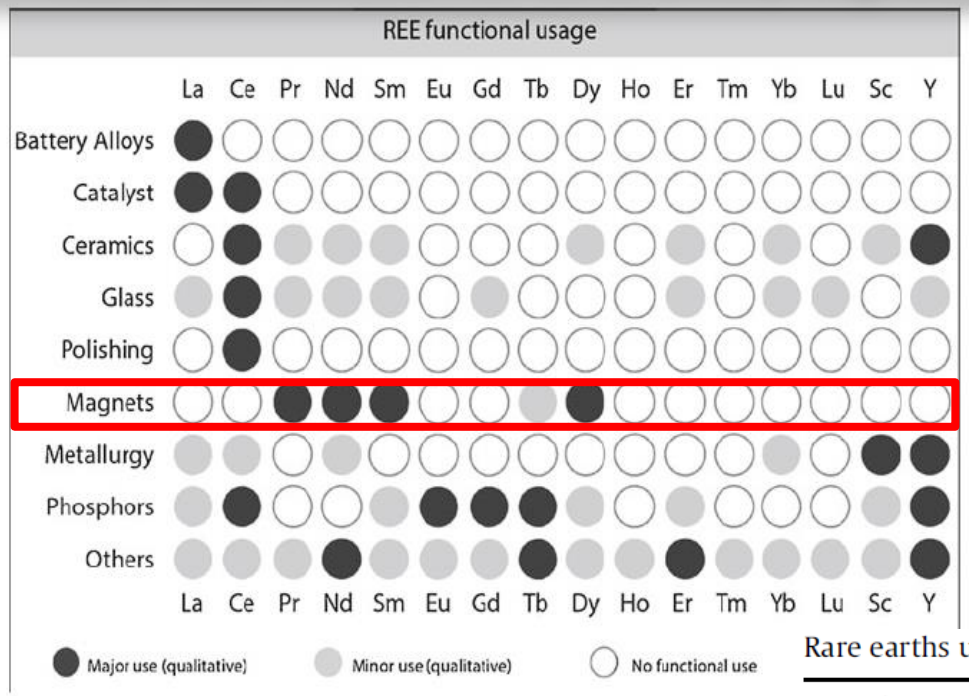
Rare-earth elements are key ingredients….



Rare earths usage by application, in % (Curtis, 2010).[a]

Application	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Y	Other
Magnets			23.4	69.4			2	0.2	5		
Battery alloys	50	33.4	3.3	10	3.3						
Metallurgy	26	52	5.5	16.5							
Auto catalysts	5	90	2	3							
FCC	90	10									
Polishing powders	31.5	65	3.5								
Glass additives	24	66	1	3						2	4
Phosphors	8.5	11				4.9	1.8	4.6		69.2	
Ceramics	17	12	6	12						53	
Others	19	39	4	15	2		1			19	

[a] The percentages are estimated average consumption distribution by application; the actual distribution varies from manufacturer to manufacturer.

Zepf, V., ***Rare Earth Elements***; Springer-Verlag Berlin Heidelberg, **2013**
Binnemans, K.; ***Journal of Cleaner Production*** **2013**, *51*, 1-22.

Rare-earth elements are key ingredients….

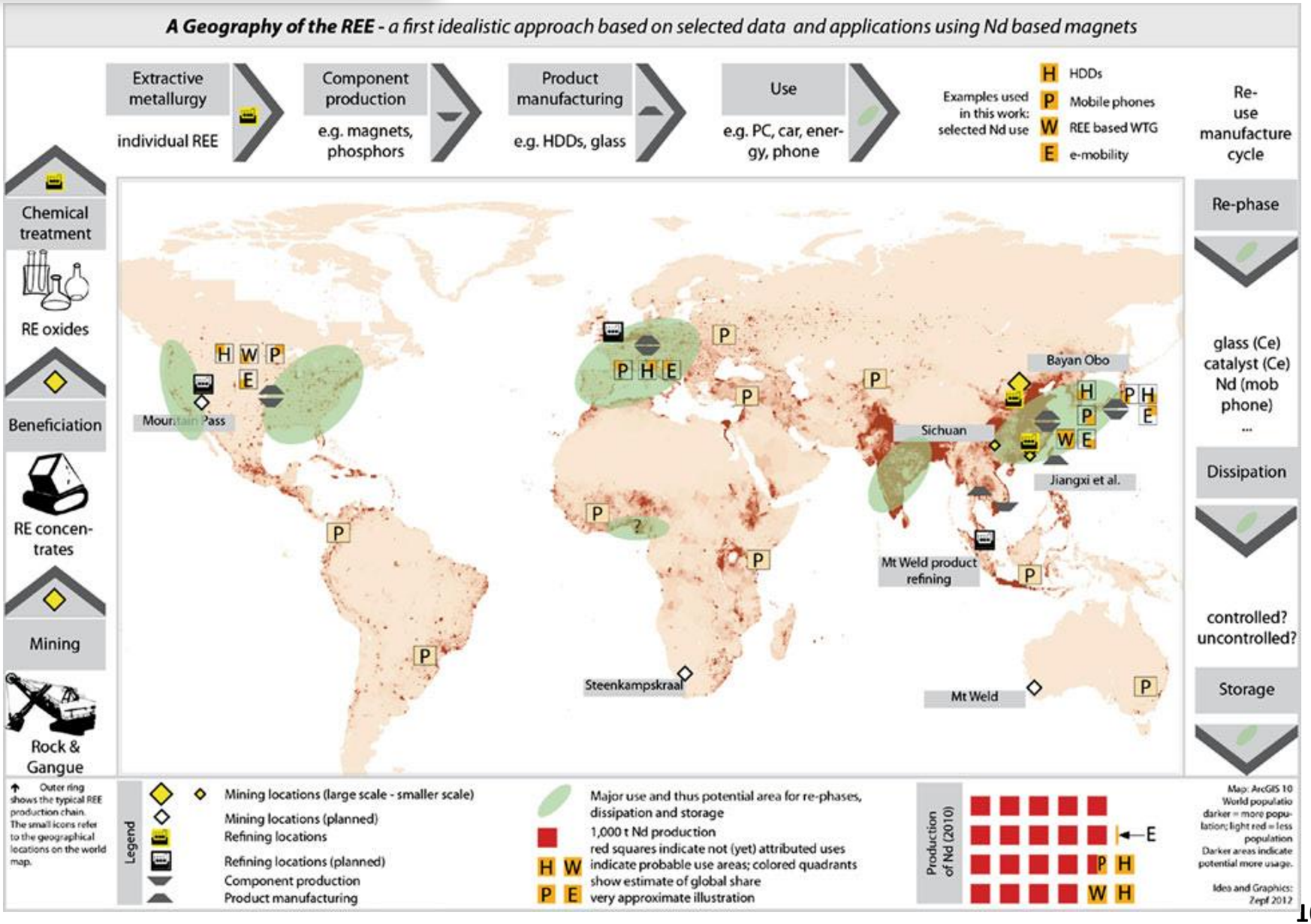
Typical dysprosium content in NdFeB magnets for different applications (Constantinides, 2011).

Application	Typical Dy content (%)[a]
Hybrid and electric cars	8.7
Generators	6.4
Wave guides: TWT, undulators, wigglers	6.4
Electric bikes	4.1
Electric storage systems	4.1
Magnetic brakes	4.1
Magnetically levitated transportation	4.1
Motors, industrial, cars, etc.	4.1
Pipe inspection systems	4.1
Relays and switches	4.1
Reprographics	4.1
Torque coupled drives	4.1
Wind turbines	4.1
Gauges	2.8
Hysteresis clutch	2.8
Magnetic separators	2.8
Magnetic refrigerators	1.4
MRI scanners	1.4
Sensors	1.4
HDDs, CDs, DVDs	0.0
Transducers and loudspeakers	0.0
Toys and gadgets	0.0

[a] % of Dy compared to the other rare earths.

Binnemans, K.; ***Journal of Cleaner Production* 2013**, *51*, 1-22.

Rare-Earth elements cycle



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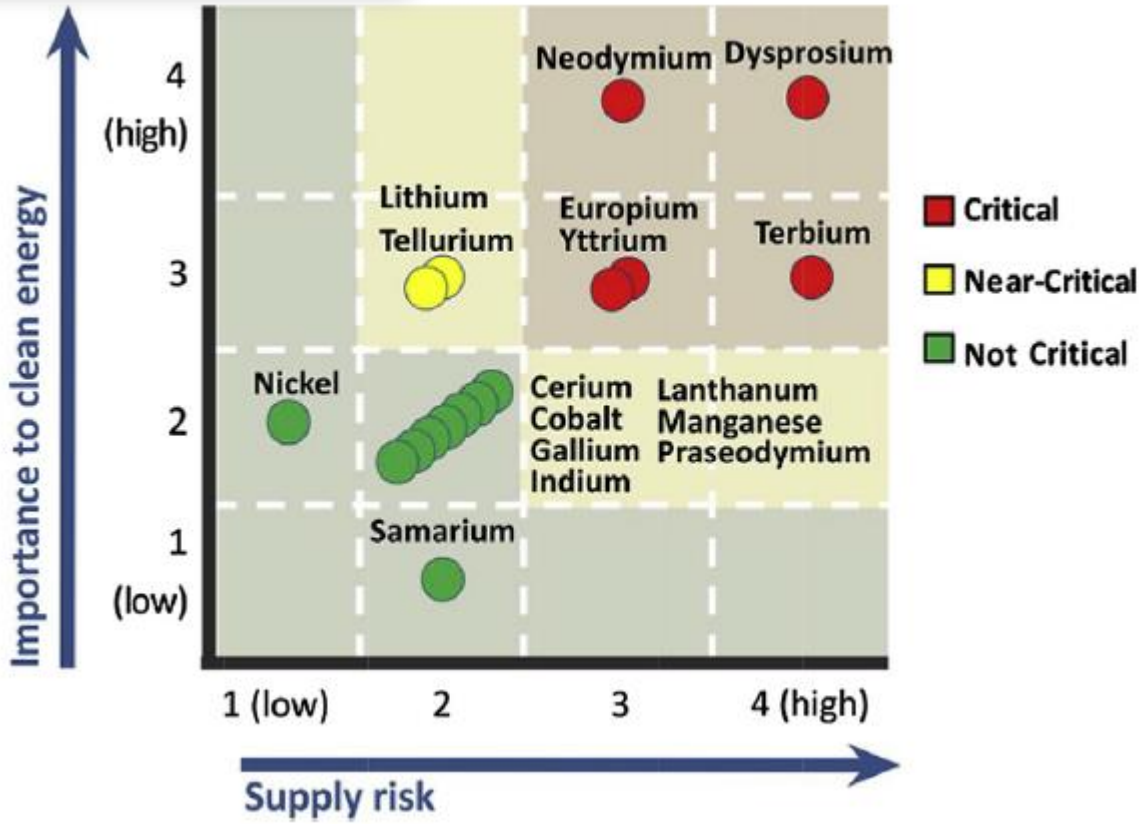
Rare-Earth elements (re)cycle



Recycling potentials for REE from magnets, nickel-metal-hydride batteries and phosphors.

REE application	Estimated REE stocks in 2020 (tons)	Estimated average lifetime (years)	Estimated REE old scrap in 2020 (tons)	Pessimistic scenario: recycled REE in 2020 (tons)	Optimistic scenario: recycled REE in 2020 (tons)
Magnets	300,000	15	20,000	3300	6600
Lamp Phosphors	25,000	6	4167	1333	2333
Nickel-metal-hydride batteries	50,000	10	5000	1000	1750
Total	375,000		29,167	5633	10,683

Binnemans, K.; ***Journal of Cleaner Production* 2013**, *51*, 1-22.

The chemists periodic table !

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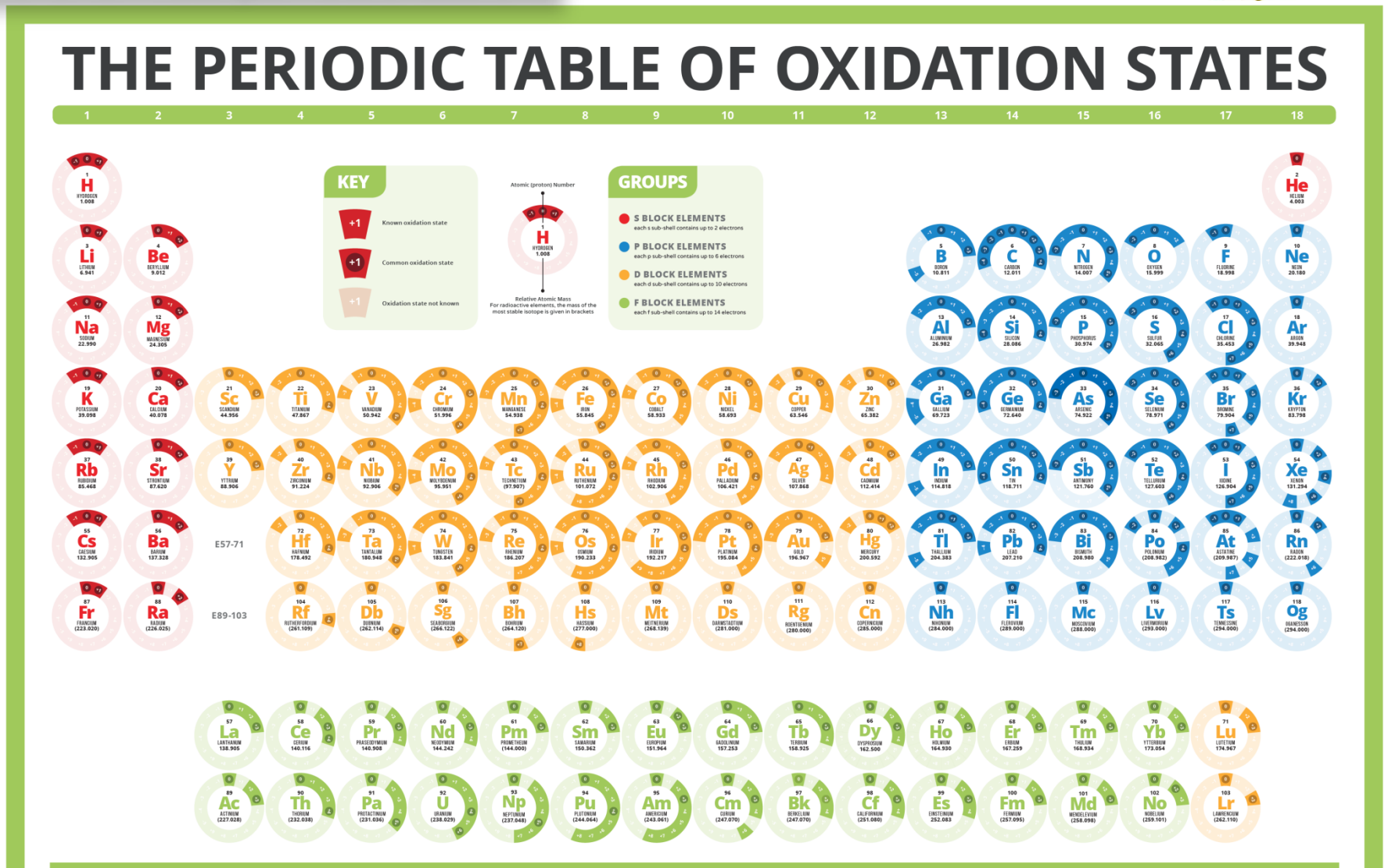

The chemists periodic table !

For trivalent lanthanides ions : [Xe] 4f^n

n= 0 1 2 3 4 5 6 7 8 9 10 11 12 13 14

Ln	χ_P	I_3	I_{1-3}	$E^0_{r,3-0}$	$E^0_{r,3-2}$
La	1.10	1850	3455	−2.379	−3.1
Ce	1.12	1949	3523	−2.336	−2.92(8)
Pr	1.13	2086	3627	−2.353	−2.84(6)
Nd	1.14	2130	3694	−2.323	−2.62(5)
Pm	1.13	2150	3738	−2.30	−2.44(5)
Sm	1.17	2260	3871	−2.304	−1.50(1)
Eu	1.2	2404	4035	−1.991	−0.34(1)
Gd	1.20	1990	3750	−2.279	−2.85(7)
Tb	1.1	2114	3790	−2.28	−2.83(7)
Dy	1.22	2200	3898	−2.295	−2.56(5)
Ho	1.23	2204	3924	−2.33	−2.79(6)
Er	1.24	2194	3934	−2.331	−2.87(8)
Tm	1.25	2285	4045	−2.319	−2.22(5)
Yb	1.1	2415	4194	−2.19	−1.18(1)
Lu	1.27	2033	3896	−2.28	n.a.
Y	1.22	1980	3777	−2.372	n.a.

Most stable oxidation state is +III

Rare-Earth main properties

Table 1. Selected properties of lanthanides, yttrium, and their trivalent ions.

Ln	χ_P	I_3	I_{1-3}	$E^0_{r,3-0}$	$E^0_{r,3-2}$	ΔH^0_h	$\log^* \beta_{11}$	pH	r_i (6)	r_i (9)	r_i (12)
La	1.10	1850	3455	−2.379	−3.1	−3326	−9.01	7.47	103	122	136
Ce	1.12	1949	3523	−2.336	−2.92(8)	−3380	−10.6	7.10	101	120	134
Pr	1.13	2086	3627	−2.353	−2.84(6)	−3421	−8.55	6.96	99	118	132
Nd	1.14	2130	3694	−2.323	−2.62(5)	−3454	−8.43	6.78	98	116	130
Pm	1.13	2150	3738	−2.30	−2.44(5)	−3482	n.a.	n.a.	97	114	128
Sm	1.17	2260	3871	−2.304	−1.50(1)	−3512	−8.34	6.65	96	113	127
Eu	1.2	2404	4035	−1.991	−0.34(1)	−3538	−8.31	6.61	95	112	125
Gd	1.20	1990	3750	−2.279	−2.85(7)	−3567	−8.35	6.58	94	111	124
Tb	1.1	2114	3790	−2.28	−2.83(7)	−3600	−8.16	6.47	92	110	123
Dy	1.22	2200	3898	−2.295	−2.56(5)	−3634	−8.10	6.24	91	108	122
Ho	1.23	2204	3924	−2.33	−2.79(6)	−3663	−8.04	6.20	90	107	121
Er	1.24	2194	3934	−2.331	−2.87(8)	−3692	−7.99	6.14	89	106	119
Tm	1.25	2285	4045	−2.319	−2.22(5)	−3717	−7.95	5.98	88	105	118
Yb	1.1	2415	4194	−2.19	−1.18(1)	−3740	−7.92	5.87	87	104	117
Lu	1.27	2033	3896	−2.28	n.a.	−3759	−7.90	5.74	86	103	116
Y	1.22	1980	3777	−2.372	n.a.	−3640	−8.36	n.a.	90	108	n.a.

Notes: Key: χ_P = Pauling's electronegativity; I_3 = third ionization energy (rounded to 1 kJ mol^{-1}) [8]; I_{1-3} = sum of the first three ionization energies (rounded to 1 kJ mol^{-1}) [8]; $E^0_{r,3-0}$ = standard redox potential Ln^{+3}/Ln^0 in V at pH 0 [12]; $E^0_{r,3-2}$ = redox potential Ln^{+3}/Ln^{+2} in V [13], value for La is calculated; ΔH^0_h = standard hydration enthalpies in kJ mol^{-1} calculated by semi-empirical methods (Born–Haber cycles) [14]; $*\beta_{11} = [(LnOH)^{2+}][H^+]/[Ln^{3+}]$, ionic strength = 0.3 M [15]; pH = pH at which hydroxide precipitation starts in $Ln(NO_3)_3$ solutions 0.1 M in water [16]; $r_i(n)$ = ionic radii for coordination numbers n = 6, 9, and 12 in pm [17].

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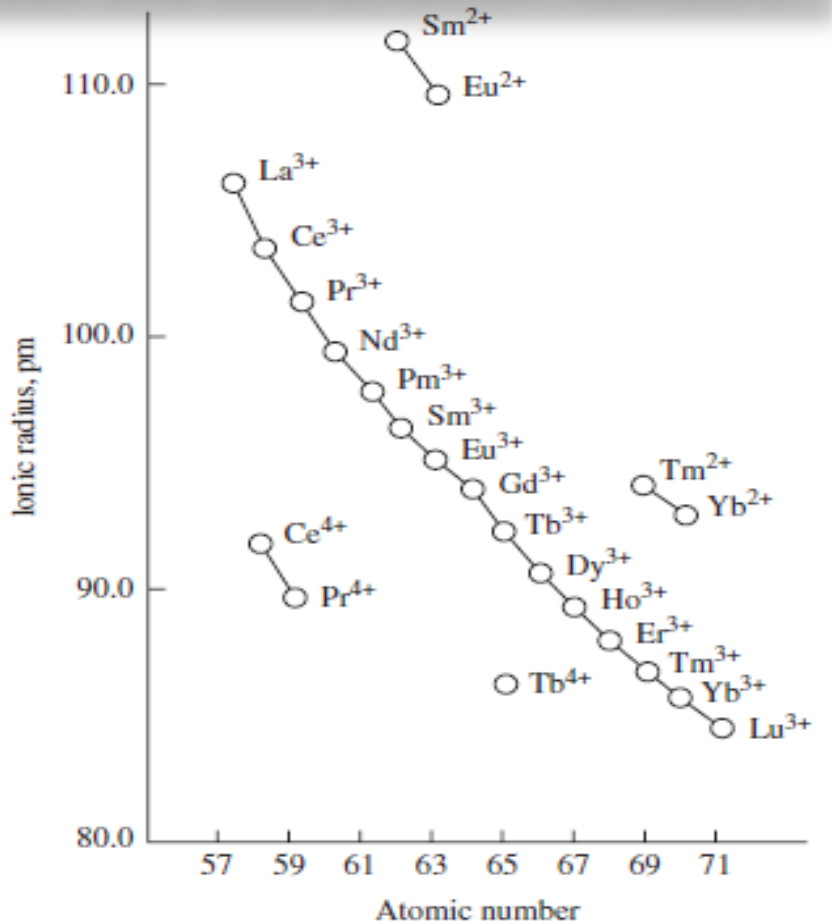
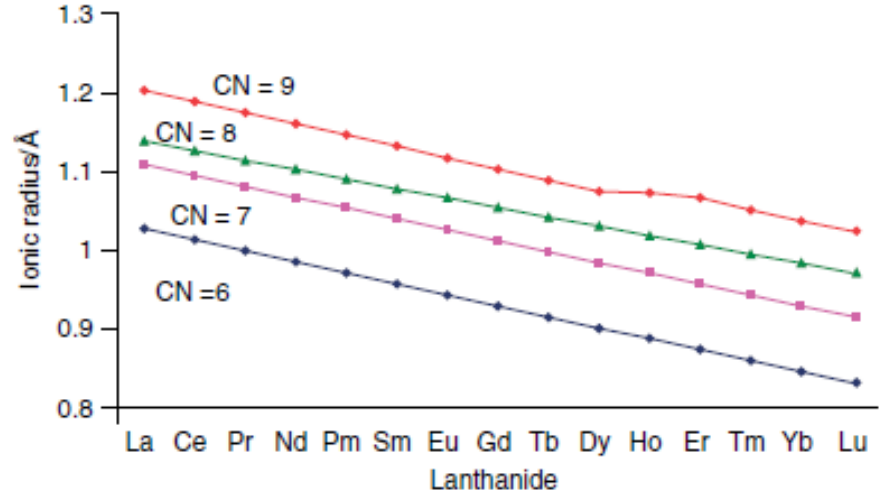
Ionic radii and coordination numbers





When C.N. is increased → increase of r_i

The relationship between ionic radius and atomic number of lanthanide ions

- **Trend on the series,**
- **Decrease of r_i by 0.2 Å from La to Lu→ lanthanide contraction**
- **"gadolinium break"**

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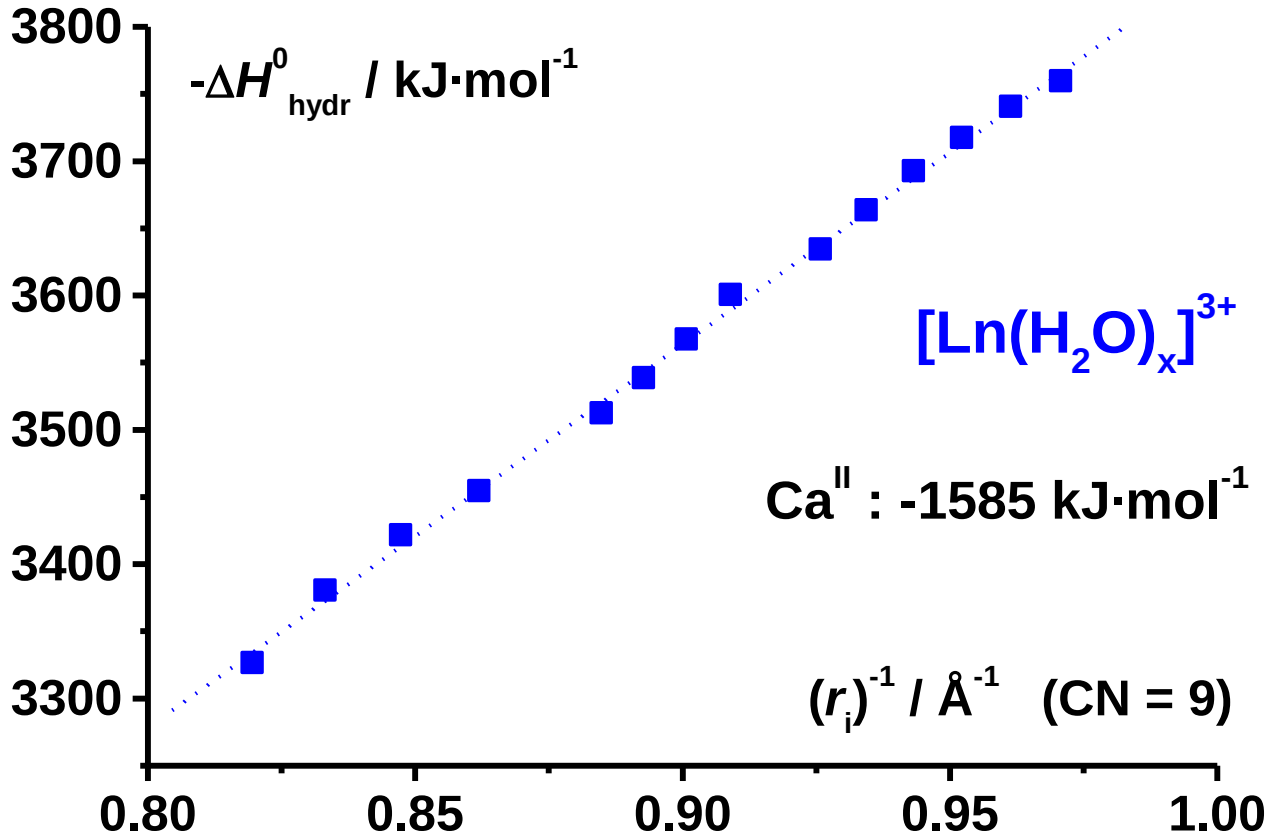
Hydratation enthalpies

Ln	ΔH_h^0
La	−3326
Ce	−3380
Pr	−3421
Nd	−3454
Pm	−3482
Sm	−3512
Eu	−3538
Gd	−3567
Tb	−3600
Dy	−3634
Ho	−3663
Er	−3692
Tm	−3717
Yb	−3740
Lu	−3759
Y	−3640



- **Very large hydratation enthalpies** (most of Ln salts are hygroscopic)
- **Trend along the series**
- **Ligands have to substitute water molecules**
- **Ln^{III} ions have hard Lewis character → hard bases for ligands such as carboxylates, etc…**

Electronegativity

Table 1. Selected properties of lanthanides, yttrium, and their trivalent ions.

Ln	χ_P	I_3	I_{1-3}	$E^0_{r,3-0}$	$E^0_{r,3-2}$	ΔH^0_h	$\log^* \beta_{11}$	pH	r_i (6)	r_i (9)	r_i (12)
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Pm	1.13	2150	3738	−2.30	−2.44(5)	−3482	n.a.	n.a.	97	114	128
Sm	1.17	2260	3871	−2.304	−1.50(1)	−3512	−8.34	6.65	96	113	127
Eu	1.2	2404	4035	−1.991	−0.34(1)	−3538	−8.31	6.61	95	112	125
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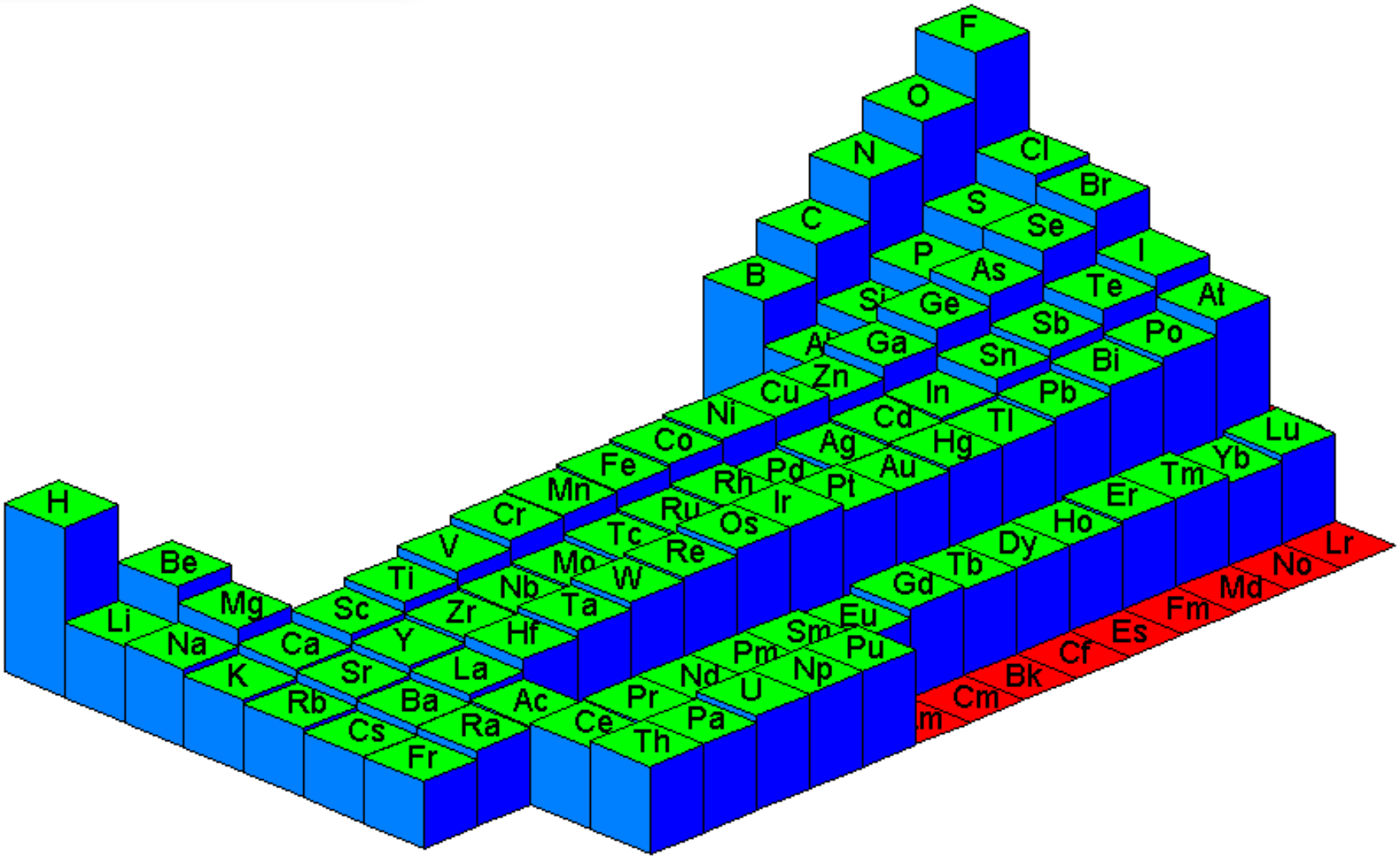
Tb	1.1	2114	3790	−2.28	−2.83(7)	−3600	−8.16	6.47	92	110	123
Dy	1.22	2200	3898	−2.295	−2.56(5)	−3634	−8.10	6.24	91	108	122
Ho	1.23	2204	3924	−2.33	−2.79(6)	−3663	−8.04	6.20	90	107	121
Er	1.24	2194	3934	−2.331	−2.87(8)	−3692	−7.99	6.14	89	106	119
Tm	1.25	2285	4045	−2.319	−2.22(5)	−3717	−7.95	5.98	88	105	118
Yb	1.1	2415	4194	−2.19	−1.18(1)	−3740	−7.92	5.87	87	104	117
Lu	1.27	2033	3896	−2.28	n.a.	−3759	−7.90	5.74	86	103	116
Y	1.22	1980	3777	−2.372	n.a.	−3640	−8.36	n.a.	90	108	n.a.

Notes: Key: χ_P = Pauling's electronegativity; I_3 = third ionization energy (rounded to 1 kJ mol^{-1}) [8]; I_{1-3} = sum of the first three ionization energies (rounded to 1 kJ mol^{-1}) [8]; $E^0_{r,3-0}$ = standard redox potential Ln^{+3}/Ln^0 in V at pH 0 [12]; $E^0_{r,3-2}$ = redox potential Ln^{+3}/Ln^{+2} in V [13], value for La is calculated; ΔH^0_h = standard hydration enthalpies in kJ mol^{-1} calculated by semi-empirical methods (Born–Haber cycles) [14]; $*\beta_{11} = [(LnOH)^{2+}][H^+]/[Ln^{3+}]$, ionic strength = 0.3 M [15]; pH = pH at which hydroxide precipitation starts in $Ln(NO_3)_3$ solutions 0.1 M in water [16]; $r_i(n)$ = ionic radii for coordination numbers n = 6, 9, and 12 in pm [17].

J.-C. G. Bünzli ***J. Coord. Chem.*** **2014**, *67*.

Electronegativity



Similar electronegativities → difficult separation of each RE in RE ore.

Electronegativity

Institut des Sciences Chimiques de Rennes UMR CNRS 6226

Stability toward hydroxides ($Ln(OH)_2^-$, $Ln(OH)_3$) and oxo-hydroxides is different

Table 1. Selected properties of lanthanides, yttrium, and their trivalent ions.

Ln	χ_P	I_3	I_{1-3}	$E^0_{r,3-0}$	$E^0_{r,3-2}$	ΔH^0_h	$\log^* \beta_{11}$	pH	r_i (6)	r_i (9)	r_i (12)
La	1.10	1850	3455	−2.379	−3.1	−3326	−9.01	7.47	103	122	136
Ce	1.12	1949	3523	−2.336	−2.92(8)	−3380	−10.6	7.10	101	120	134
Pr	1.13	2086	3627	−2.353	−2.84(6)	−3421	−8.55	6.96	99	118	132
Nd	1.14	2130	3694	−2.323	−2.62(5)	−3454	−8.43	6.78	98	116	130
Pm	1.13	2150	3738	−2.30	−2.44(5)	−3482	n.a.	n.a.	97	114	128
Sm	1.17	2260	3871	−2.304	−1.50(1)	−3512	−8.34	6.65	96	113	127
Eu	1.2	2404	4035	−1.991	−0.34(1)	−3538	−8.31	6.61	95	112	125
Gd	1.20	1990	3750	−2.279	−2.85(7)	−3567	−8.35	6.58	94	111	124
Tb	1.1	2114	3790	−2.28	−2.83(7)	−3600	−8.16	6.47	92	110	123
Dy	1.22	2200	3898	−2.295	−2.56(5)	−3634	−8.10	6.24	91	108	122
Ho	1.23	2204	3924	−2.33	−2.79(6)	−3663	−8.04	6.20	90	107	121
Er	1.24	2194	3934	−2.331	−2.87(8)	−3692	−7.99	6.14	89	106	119
Tm	1.25	2285	4045	−2.319	−2.22(5)	−3717	−7.95	5.98	88	105	118
Yb	1.1	2415	4194	−2.19	−1.18(1)	−3740	−7.92	5.87	87	104	117
Lu	1.27	2033	3896	−2.28	n.a.	−3759	−7.90	5.74	86	103	116
Y	1.22	1980	3777	−2.372	n.a.	−3640	−8.36	n.a.	90	108	n.a.

Notes: Key: χ_P = Pauling's electronegativity; I_3 = third ionization energy (rounded to 1 kJ mol^{-1}) [8]; I_{1-3} = sum of the first three ionization energies (rounded to 1 kJ mol^{-1}) [8]; $E^0_{r,3-0}$ = standard redox potential Ln^{+3}/Ln^0 in V at pH 0 [12]; $E^0_{r,3-2}$ = redox potential Ln^{+3}/Ln^{+2} in V [13], value for La is calculated; ΔH^0_h = standard hydration enthalpies in kJ mol^{-1} calculated by semi-empirical methods (Born–Haber cycles) [14]; $^*\beta_{11} = [(LnOH)^{2+}][H^+]/[Ln^{3+}]$, ionic strength = 0.3 M [15]; pH = pH at which hydroxide precipitation starts in $Ln(NO_3)_3$ solutions 0.1 M in water [16]; $r_i(n)$ = ionic radii for coordination numbers n = 6, 9, and 12 in pm [17].

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Coordination numbers

Main CN are 8 and 9

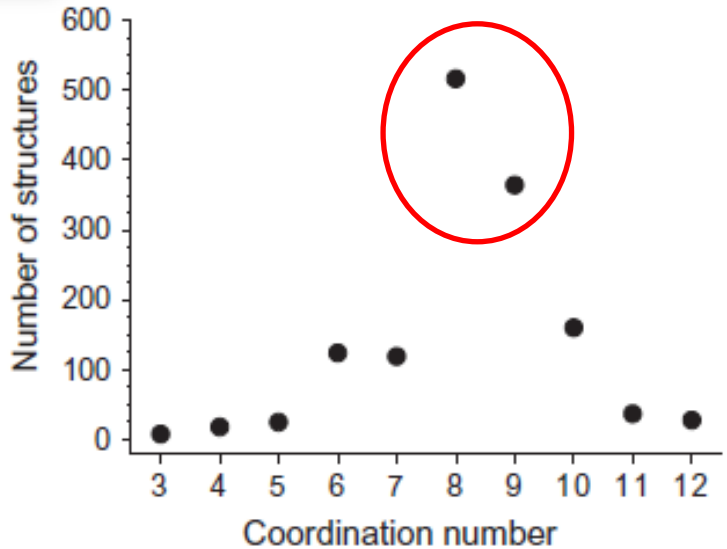
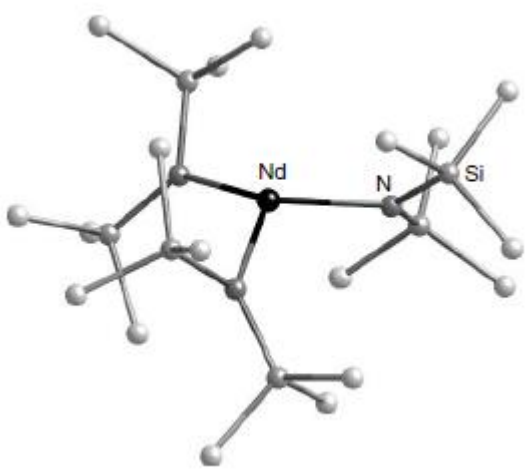


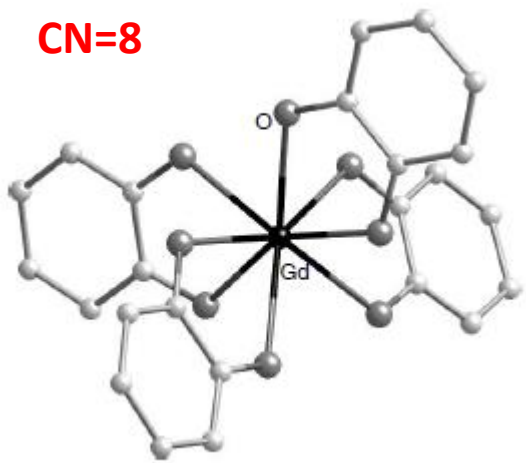
Figure 1. Distribution of coordination numbers among rare earth complexes from 1389 crystal structures published between 1935 and 1995 [9].

CN=3



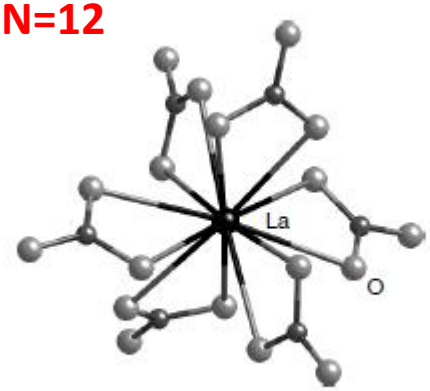
$[Nd(N(SiMe_3)_2)_3]$

CN=8



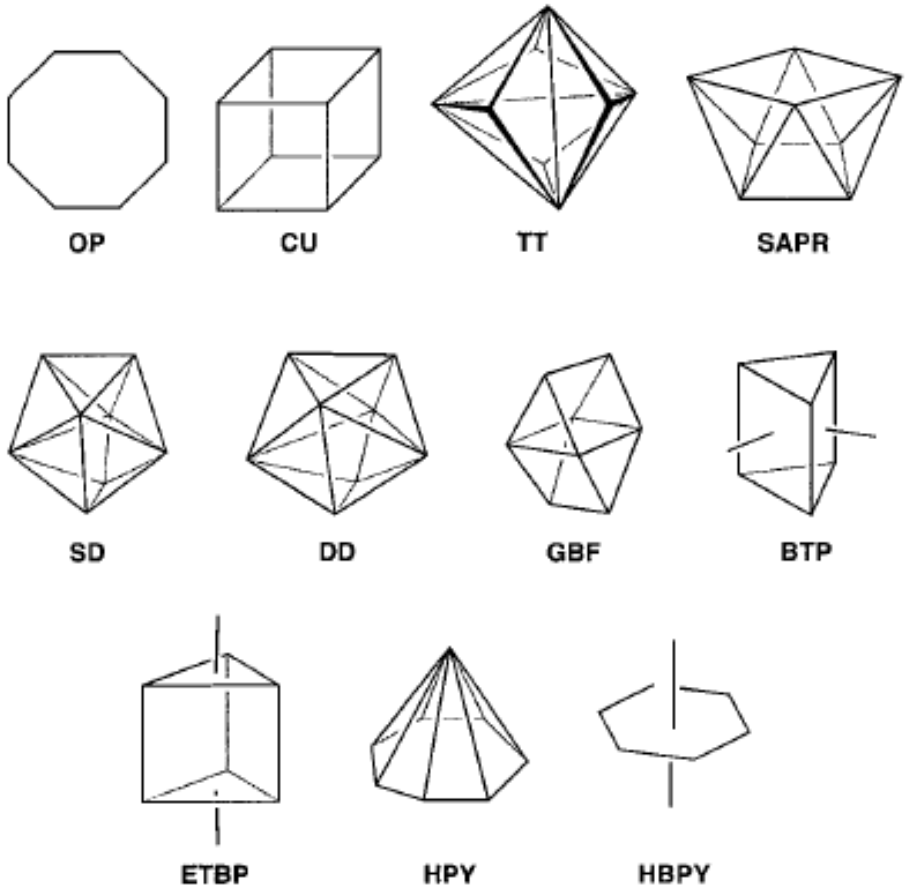
$[Gd(catecholate)_4]^{5-}$

CN=12



$[La(NO_3)_6]^{3-}$

Coordination polyhedra for CN=8



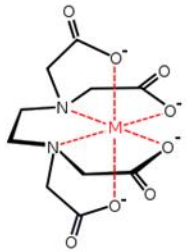
Ideal shape	Abbreviation	Symmetry
octagon	**OP**	D_{8h}
cube	**CU**	O_h
triakis-tetrahedron	**TT**	T_d
square antiprism	**SAPR**	D_{4d}
snub disphenoid	**J-SD**	T_d
triangular dodecahedron	**DD**	D_{2d}
gyrobifastigium	**J-GBF**	D_{2d}
biaugmented trigonal prism	**J-BTP**	C_{2v}
	s-BTP	C_{2v}
elongated trigonal bipyramid	**J-ETBP**	D_{3h}
	s-ETBP	D_{3h}
heptagonal pyramid	**HPY**	D_{7h}
hexagonal bipyramid	**HBPY**	D_{6h}

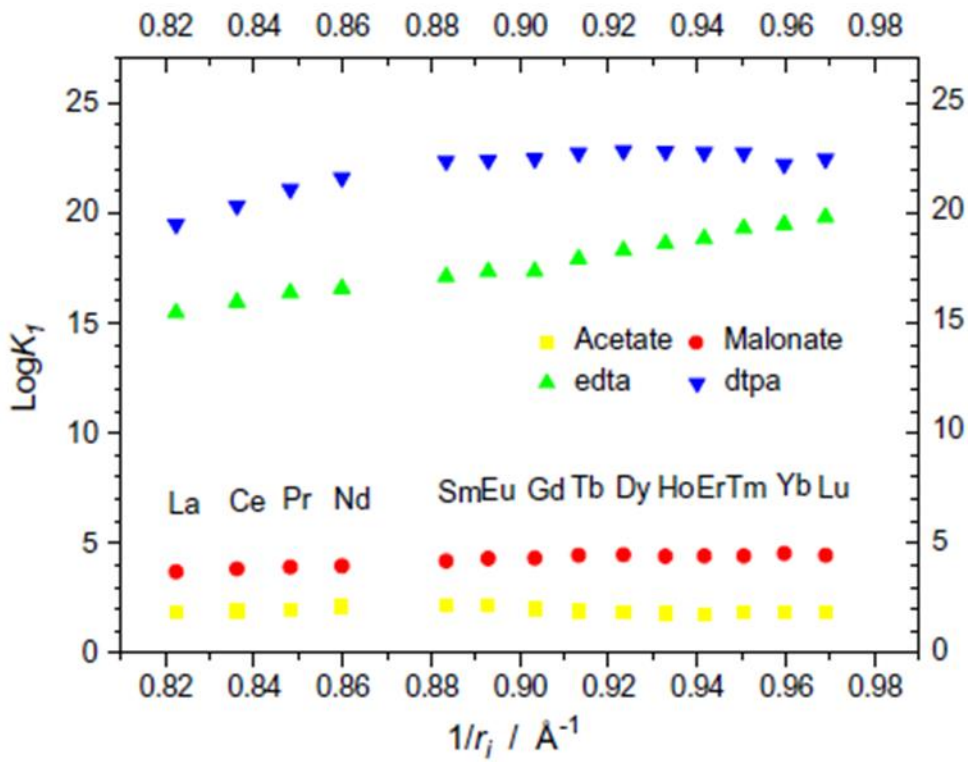
See also SHAPE program from Univ Barcelona

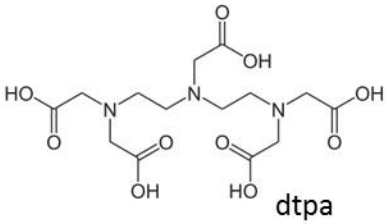
S. Alvarez, P. Alemany, M. Llunel

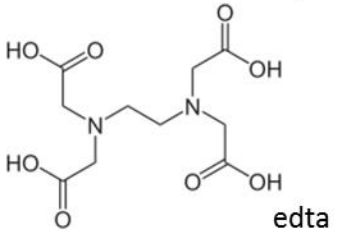
D. Casanova *et al.*, ***Chem. Eur. J.*** **2005**, *11*

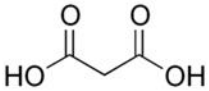
Stability



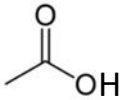








Malonic acid



Acetic acid

Stability constants for the formation of 1:1 complexes in water at 298 K *vs.* reciprocal ionic radii for coordination number 9.

- **Polydentate ligands vs monodetate ligands:**
  dtpa complexes are 20 orders of magnitude more stable than acetates
  → Entropic stabilization

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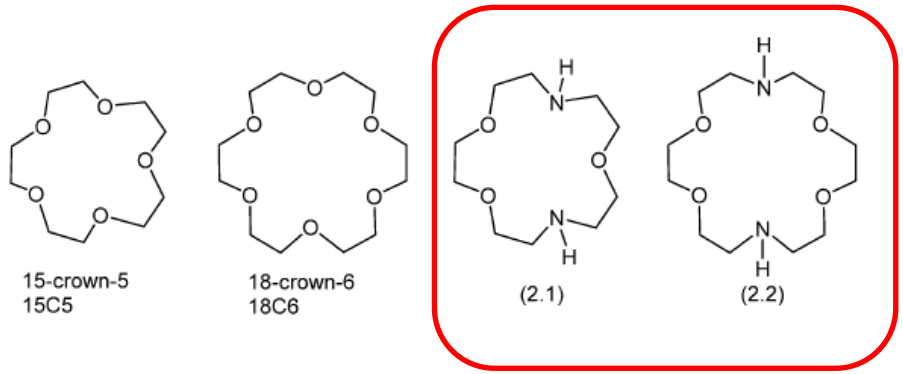
Macrocyclic Lanthanide Chemistry

15-crown-5 d = 1.7-2.2 Å
18-crown-6 d = 2.6-3.2 Å



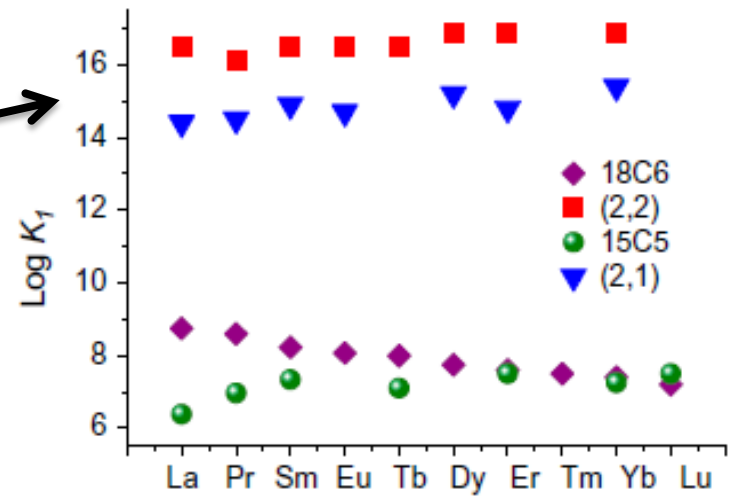


Figure 4. Stability constants of 1:1 coronates in propylene carbonate at 298 K and μ = 0.1 M Et_4NClO_4; drawn from data reported in Ref. [41].

- **Variation in cavity dimension (1.7 to 3.2 Å) do not change stability that much (no « lock-and-key » discrimination as with alcaline or 3d ions)**

- **Variation in the coordinating atoms affords tremendous changes in stability:**
  → Enthalpic stabilization

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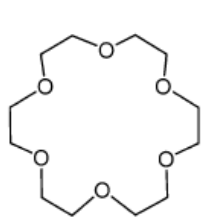
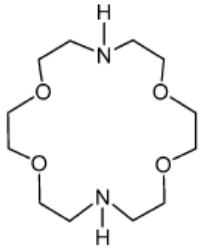
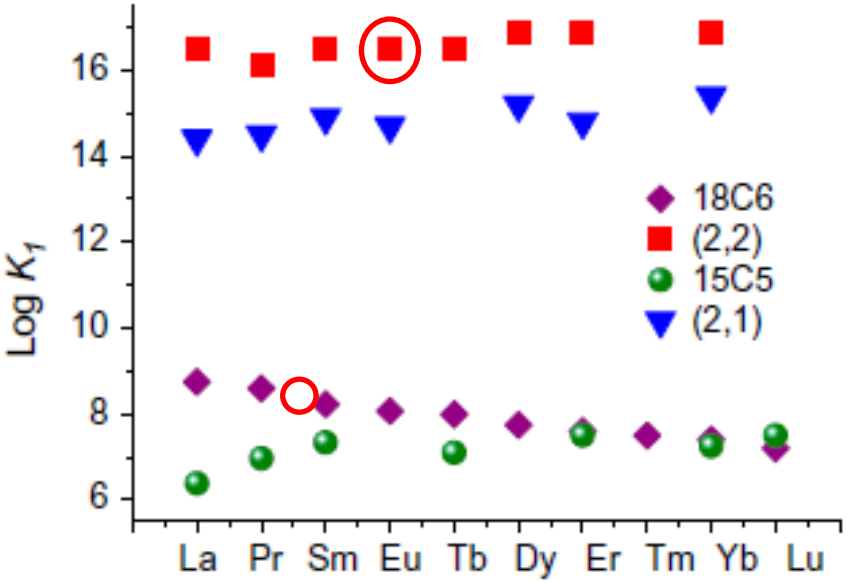
Macrocyclic Lanthanide Chemistry



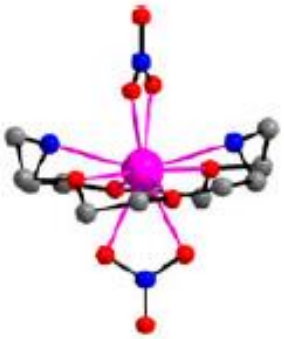
18-crown-6
18C6



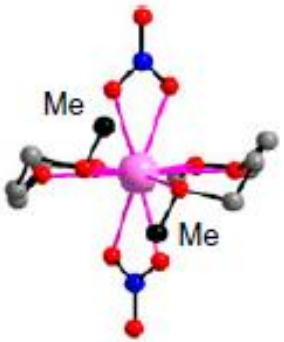
(2.2)



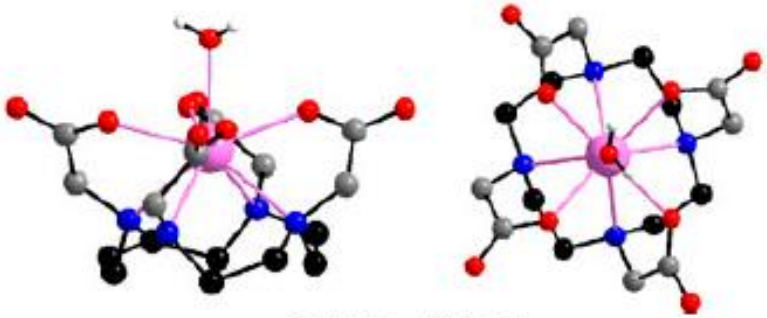
$[Nd(NO_3)_2(18C6)]^+$



$[Eu(NO_3)_2(2,2)]^+$



$[La(NO_3)_2(18P6)]^+$



$[Gd(dota)(H_2O)]^-$

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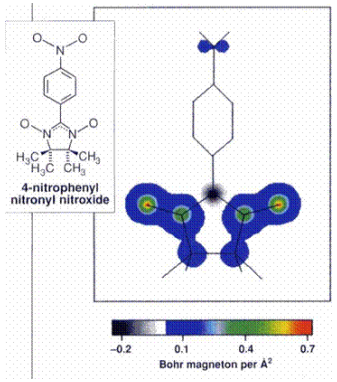
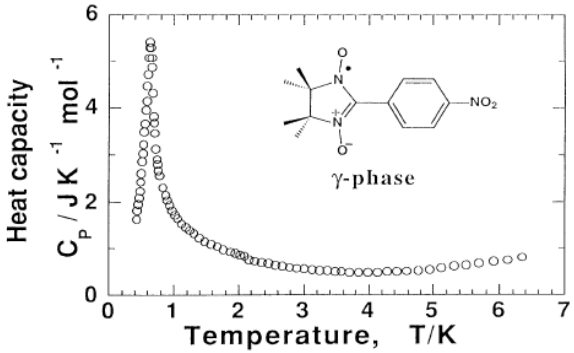
UMR CNRS 6226

From Magnetochemistry to Molecular Magnetism : The role of lanthanide ions

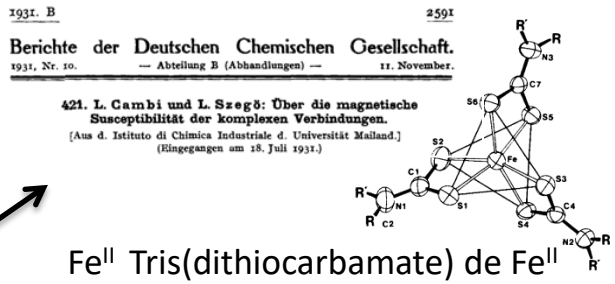
The heritage





NIT-PhNO$_2$ → **First organic magnet** T_c =0.6 K

Takahashi, M. *et al.* ***Phys. Rev. Lett.*** **1991**, *67*, 746-748


1931. B 2591

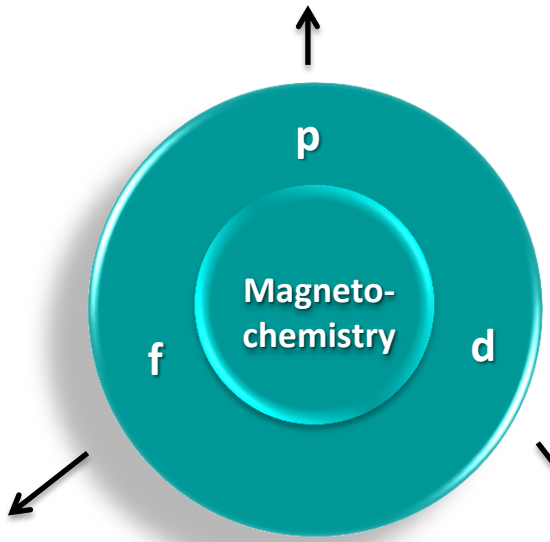
Berichte der Deutschen Chemischen Gesellschaft.

1931, Nr. 10. — Abteilung B (Abhandlungen) — 11. November.

421. L. Cambi und L. Szegö: Über die magnetische Susceptibilität der komplexen Verbindungen.

[Aus d. Istituto di Chimica Industriale d. Universität Mailand.]

(Eingegangen am 18. Juli 1931.)



Fe^{II} Tris(dithiocarbamate) de Fe^{II}

→ **Spin Cross Over**

Cambi, L. *et al.*, ***Ber. Dtsch. Chem. Ges.*** **1931**, 64, 2591

Stahl K. *et al.*, ***Acta Chem. Scand.*** **1983**, A37, 729.

On the Theory of Spin–Lattice Relaxation in Paramagnetic Salts

By R. ORBACH

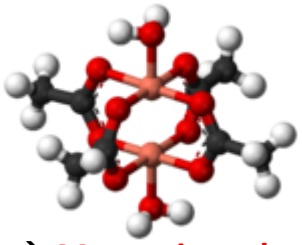
Clarendon Laboratory, Oxford

MS. received 4th November 1960

Trivalent rare-earth ions

→ **Magnetic relaxation theory**

Orbach, R. ***Proc. R. Soc. London, Ser. A*** **1961**, *264*, 458-484.



Copper acetate → **Magnetic exchange**

Guha, B.C. **Proc. Roy. Soc (London) 1951**, 206, 353.

Bleaney, B. *et al,* **Proc. Roy. Soc (London) 1952**, 214, 451

Carlin, R. J. ***Magnetochemistry***; Springer: Berlin, **1986**

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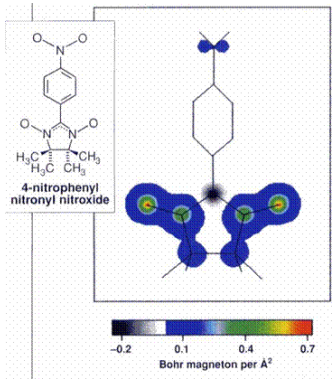

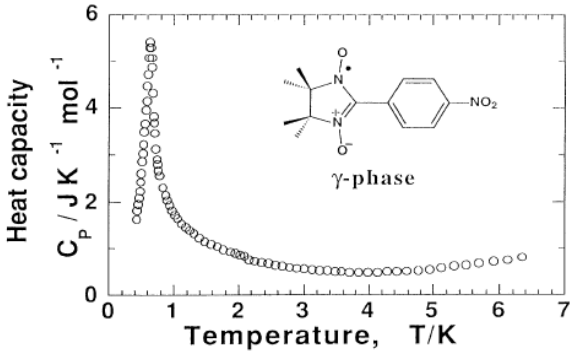

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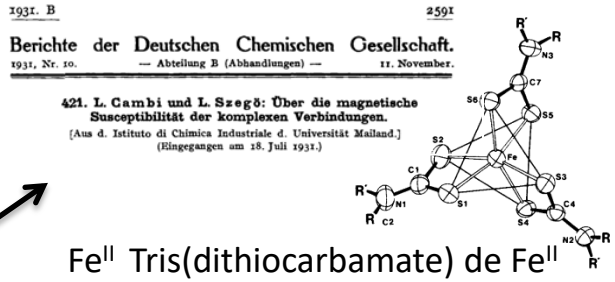
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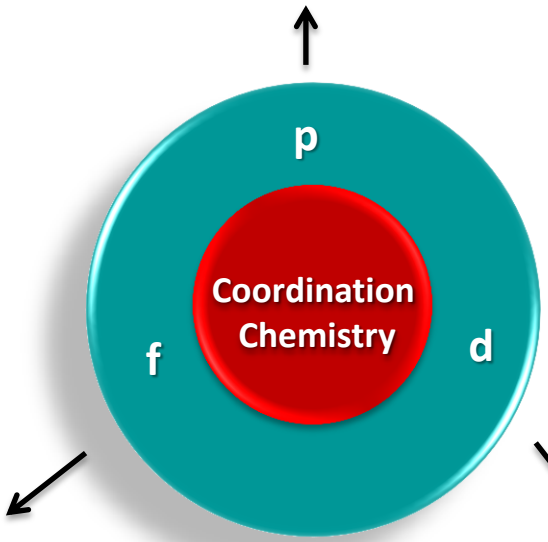

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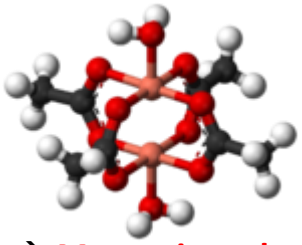

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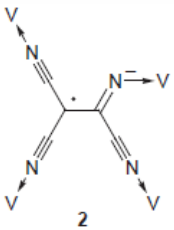
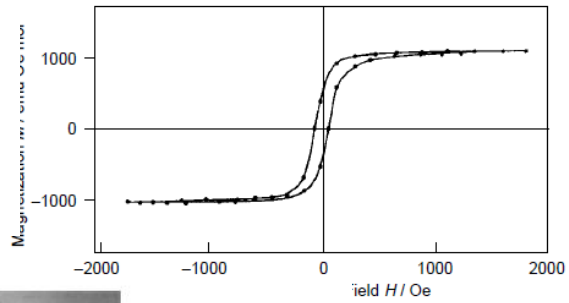
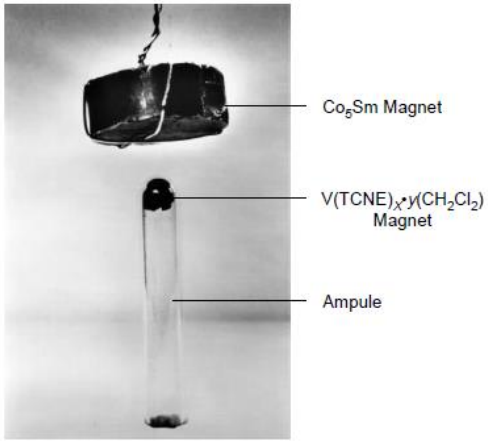
The heritage

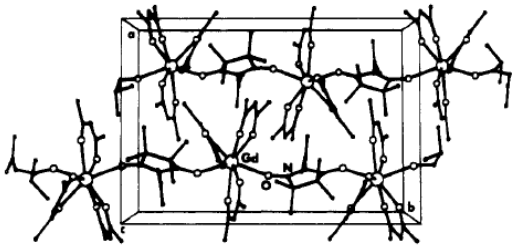






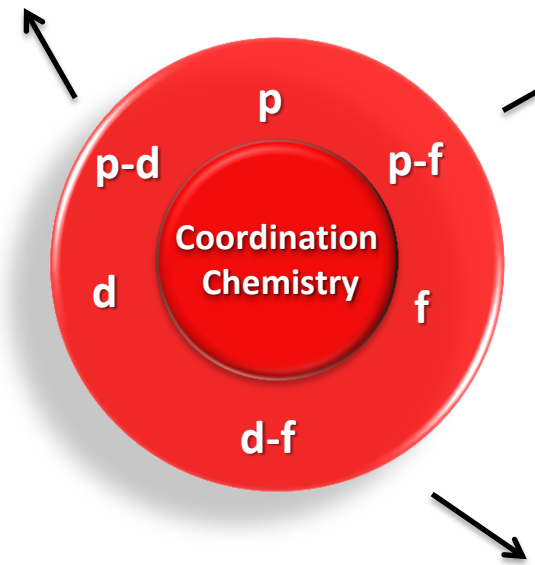
V(TCNE) → **Hight Tc permanent magnets**

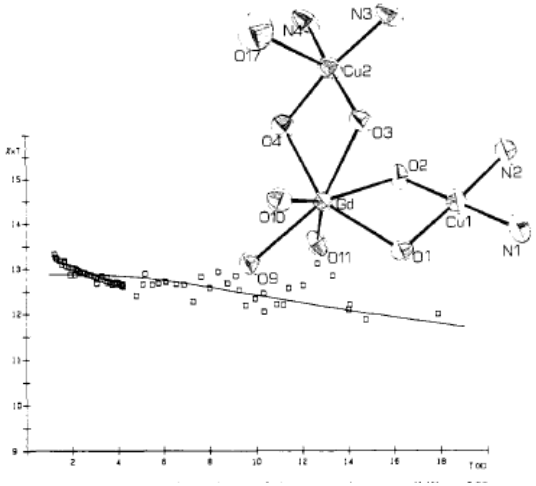
S. Miller, J. *et al.*, ***Chem. Commun.*** **1998**, 1319-1325



GdNITiPr → **Next-nearest neigbor interactions**

Benelli, C. *et al.* ***Inorg. Chem.*** **1990**, 29, 4223



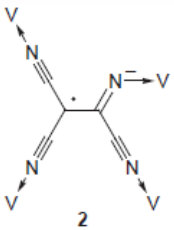


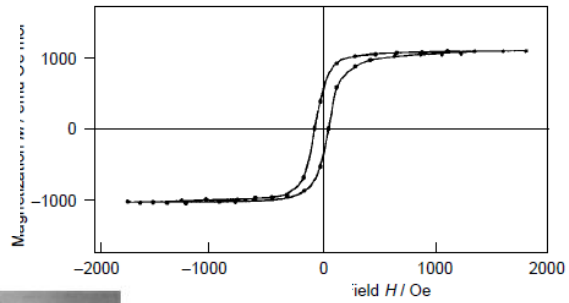
$(CuSalen)_2Gd(H_2O)_3]^{3+}$ → **3d-4f ferromagnetic coupling**

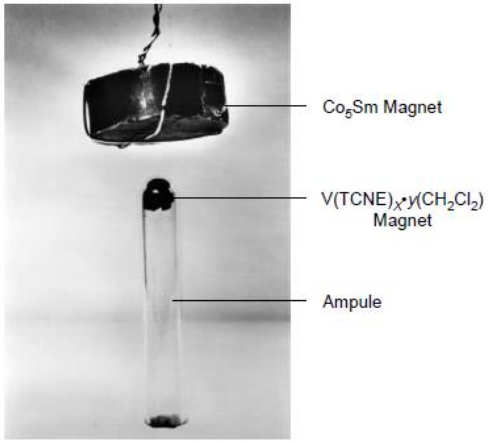
Bencini, A. *et al.*, ***J. Am. Chem. Soc.*** **1985**, *107*, 8128

Ribas, J. ***Coordination Chemistry***; Wiley-vch: Weinheim, **2008**

The heritage

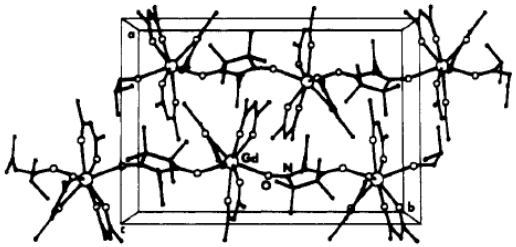






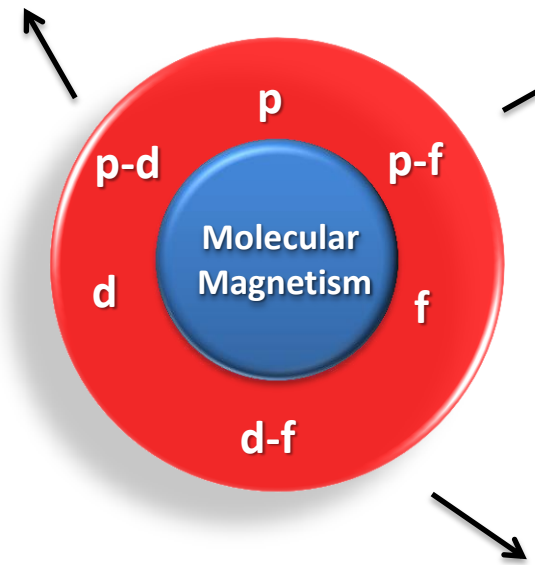
V(TCNE) → **Hight Tc permanent magnets**

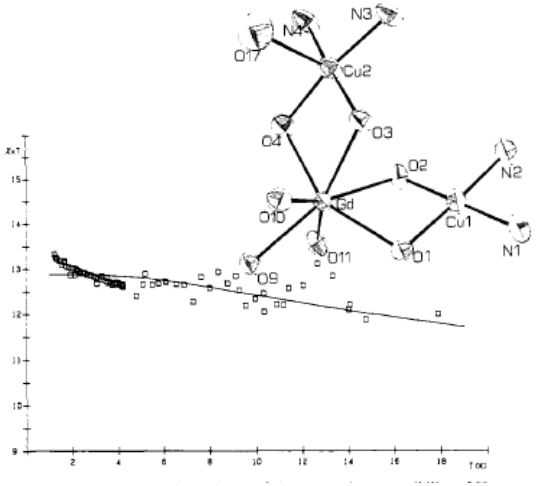
S. Miller, J. *et al.*, ***Chem. Commun.*** **1998**, 1319-1325



GdNITiPr → **Next-nearest neigbor interactions**

Benelli, C. *et al.* ***Inorg. Chem.*** **1990**, 29, 4223



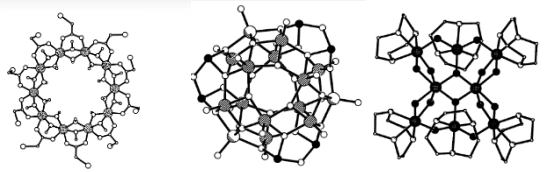


$(CuSalen)_2Gd(H_2O)_3]^{3+}$ → **3d-4f ferromagnetic coupling**

Bencini, A. *et al.*, ***J. Am. Chem. Soc.*** **1985**, *107*, 8128

Ribas, J. ***Coordination Chemistry***; Wiley-vch: Weinheim, **2008**

Molecular Magnetism

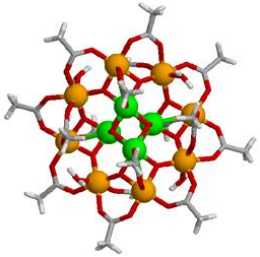


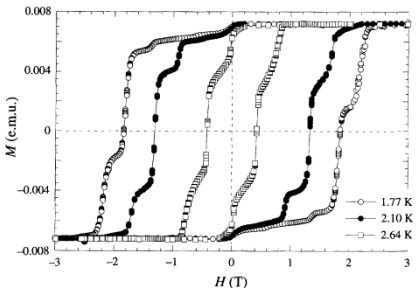
ARTICLE

Large Clusters of Metal Ions: The Transition from Molecular to Bulk Magnets

→ **Toward Single-Molecule Magnet (SMM)**

Gatteschi, D. *et al.*, *Science* **1994**, *265*, 1054



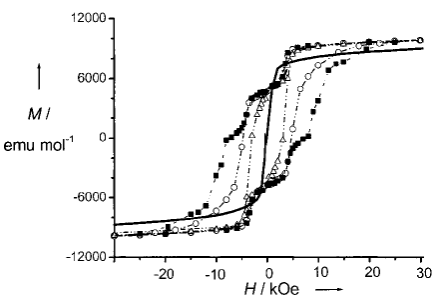


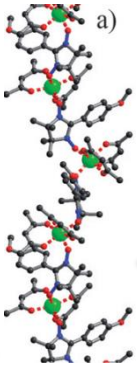
→ **Quantum effects on SMM**

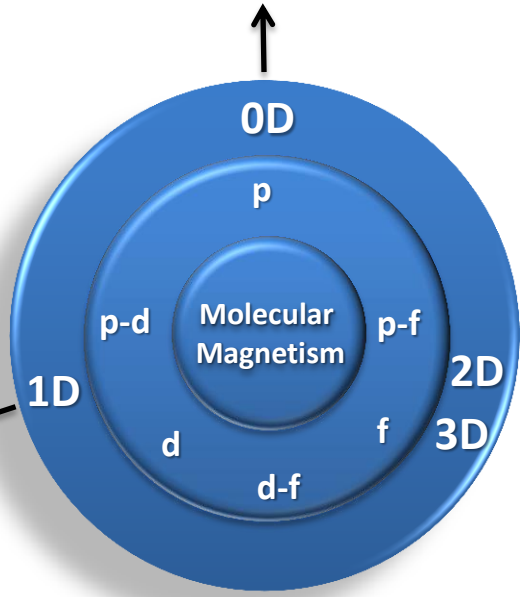
Thomas, L. et al, *Nature* **1996**, *383*, 145

Mn_{12} → **Molecular magnetic bistability**

Sessoli, R. *et al., Nature* **1993**, *365*, 141

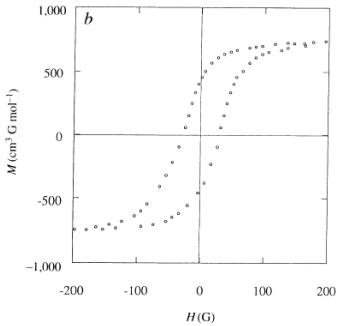






LETTERS TO NATURE

A room-temperature organometallic magnet based on Prussian blue



CoPhOMe → **Single-Chain Magnets (SCM)**

Caneschi *et al, Angew. Chem.*, **2001**, *40, 1760*

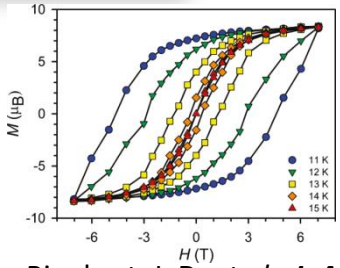
Prussian Blue

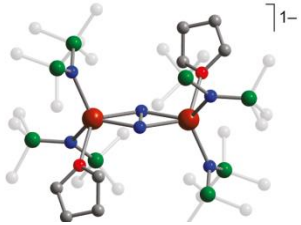
→ **high Tc permanent magnets**

Ferlay, S. *et al., Nature* **1995**, 378, 701-703.

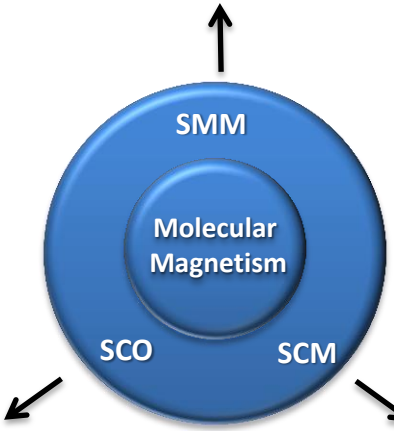
Kahn, O. ***Molecular Magnetism***; Wiley-VCH: Weinheim, **1993**

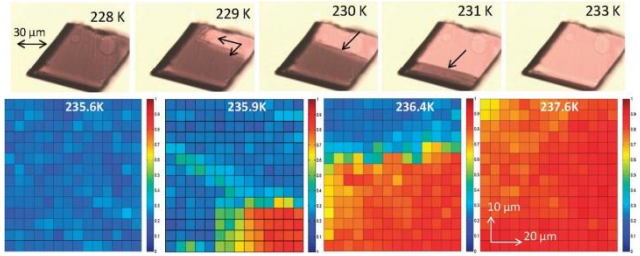
Molecular Magnetism



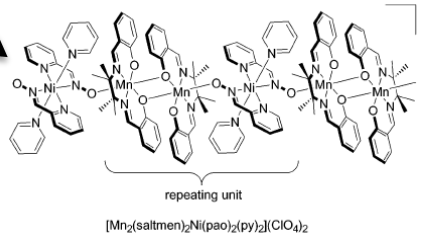


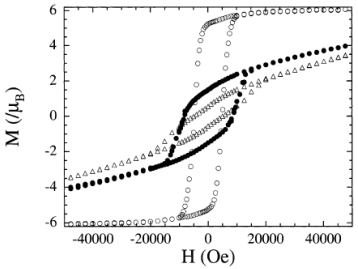
Rinehart, J. D. *et al.*, ***J. Am. Chem. Soc.*** **2011**, *133*, 14236





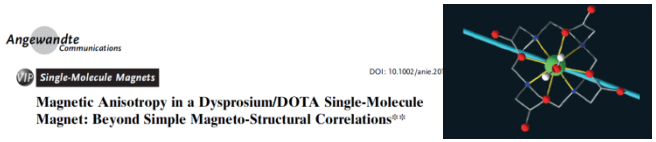
Bedoui, S., ***Chem. Phys. Lett.*** **2010**, *499*, 94.



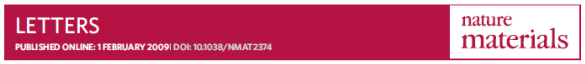


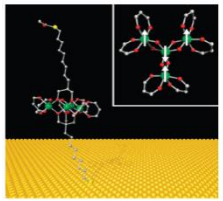
Clérac, R.; *et al.*, ***J. Am. Chem. Soc.*** **2002**, *124*, 12837

Molecular Magnetism



Magnetic activity of MRI agents
Cucinotta *et al.*, ***Angew. Chem. Int. Ed.*** **2012**, 51, 1606

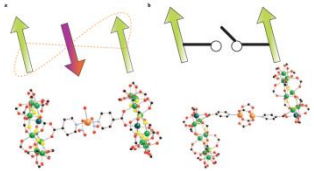




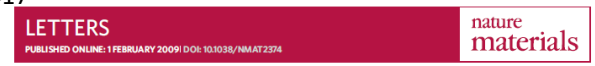
Magnetic memory of a single-molecule quantum magnet wired to a gold surface

SMM on surfaces
Mannini, M, *et al.*, ***Nat. Mater.*** **2009**, *8*, 194
Mannini, M. *et al*, ***Nature*** **2010**, *468*, 417

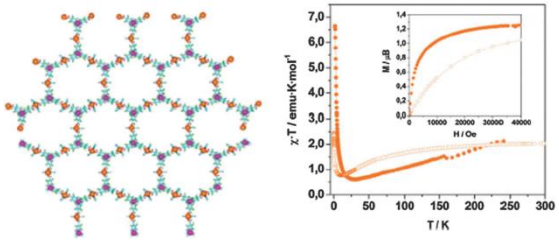
Engineering the coupling between molecular spin qubits by coordination chemistry



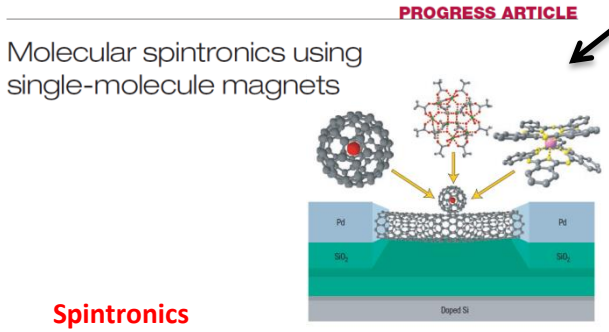
Quantum computing
Timco, G. A. *et al.*, ***Nat Nano*** **2009**, *4*, 173



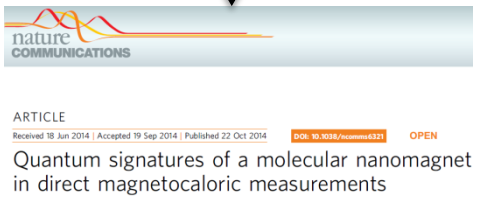
A nanoporous molecular magnet with reversible solvent-induced mechanical and magnetic properties



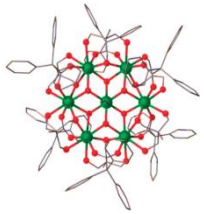
Nanoporous magnets / host-guest systems
Maspoch, D., et al. ***Nat. Mater.*** **2003**, *2*, 190

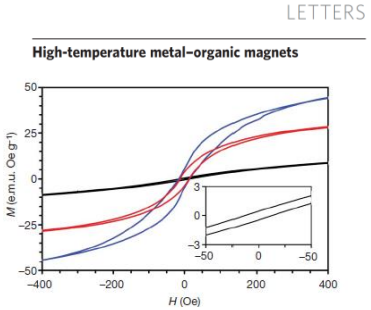


Spintronics
Bogani, L., *et al.*, *Nat. Mater.* **2008**, *7*, 179-186.

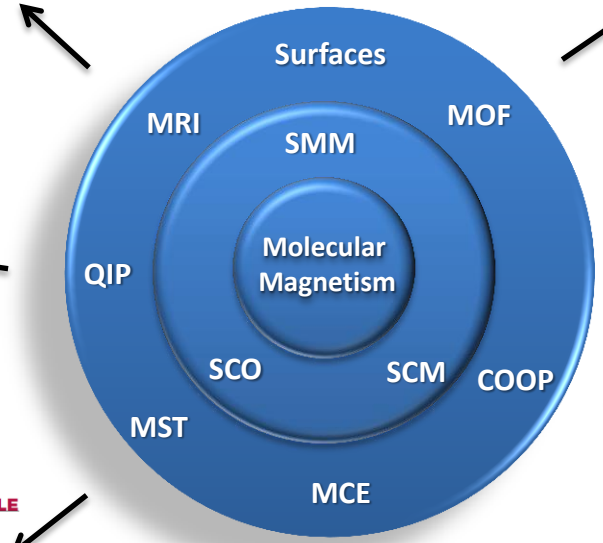


Sub-Kelvin nano-coolers
Sharples, J. W. et al., ***Nat Commun*** **2014**, *5*





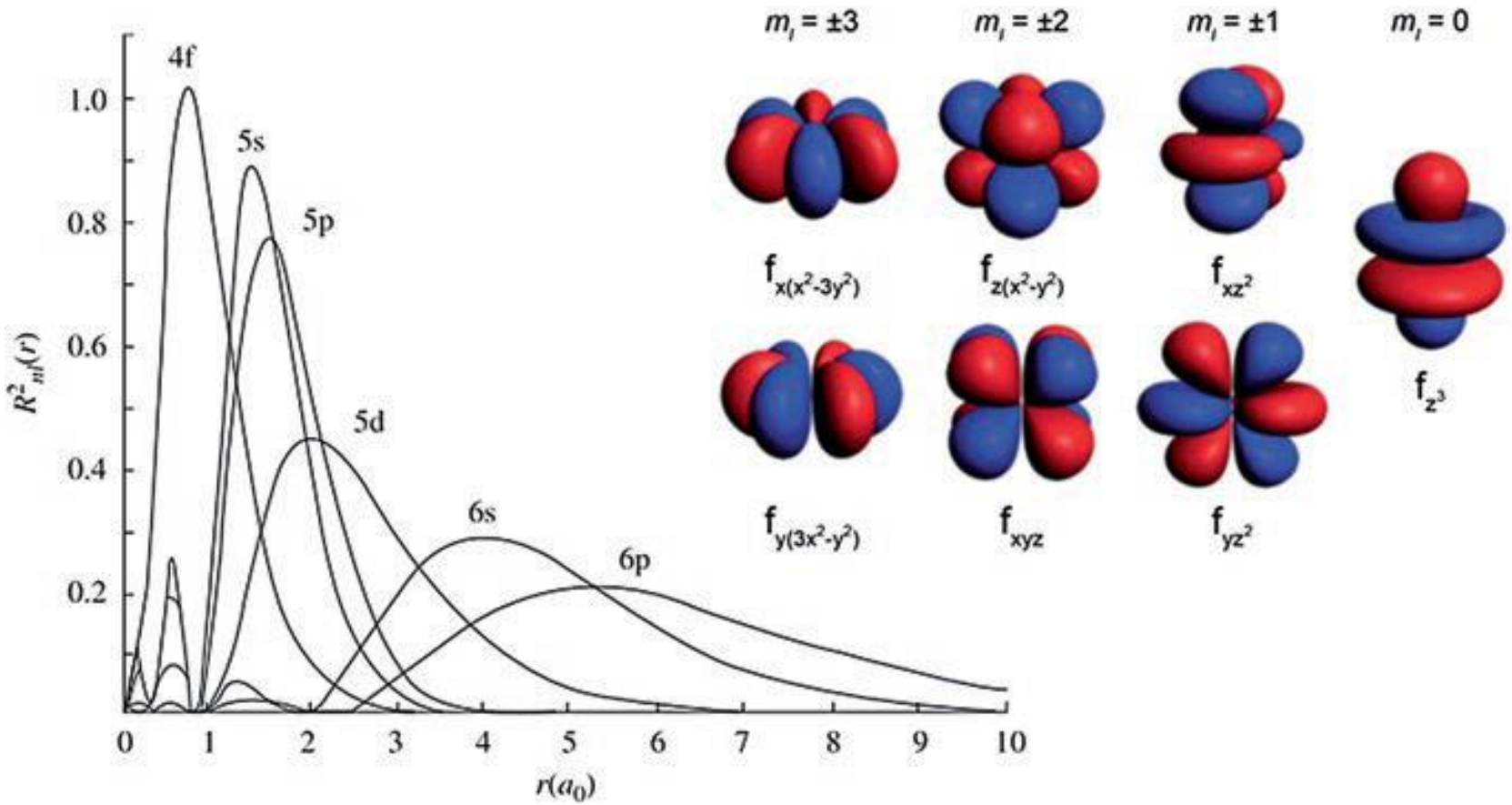
Tc > 400 K (Ni_2TCNE, TCNQ, BenzoQ)
Jain, R. *et al.* ***Nature*** **2007**, *445*, 291



Benelli, C.; Gatteschi, D.
Introduction to Molecular Magnetism: From Transition Metals to Lanthanides, **2015**

Basics of Magnetism of Trivalent Lanthanide ions

4*f* free ion electronic structure



- **Radial dependence of 4*f* orbitals: shielding by 5s, 5p**
- **Angular dependence of 4*f* orbitals: changes with m_L states → strong Spin-Orbit coupling**

- **Russel-Saunders coupling scheme: interelectronic repulsion > SO coupling**

J. Tang, P. Zhang, **Lanthanide Single Molecule Magnets,** Springer, **2015**

4*f* free ion electronic structure

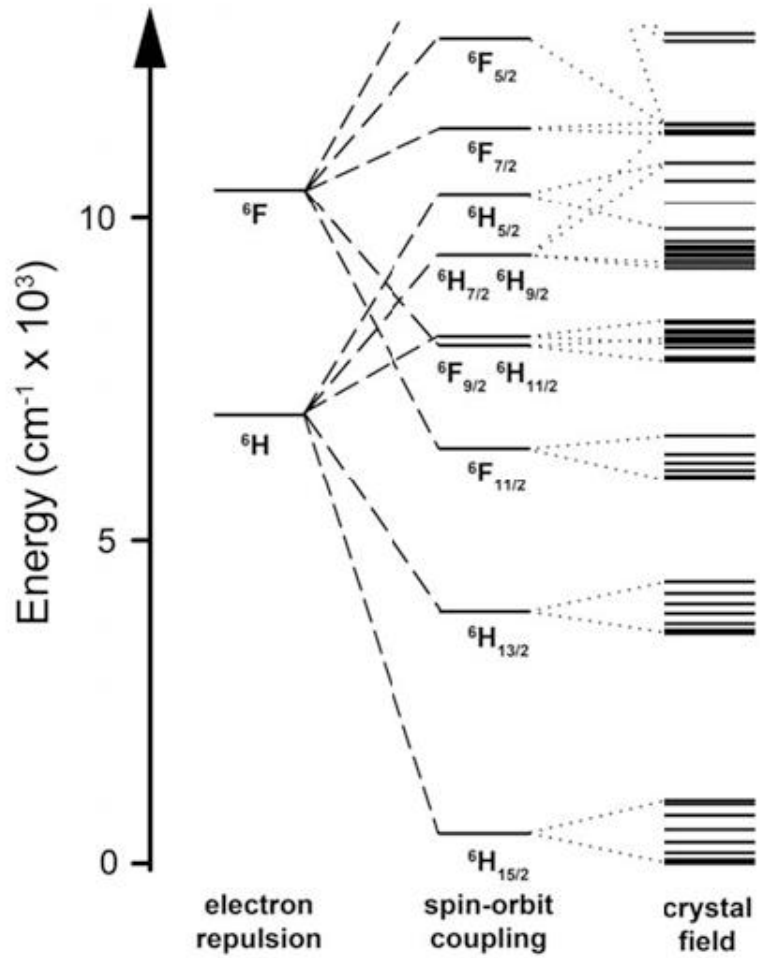
- **Spins of all electrons are coupled:** $\vec{S}=\sum_i \vec{s}_i$
- **Angular momenta are coupled:** $\vec{L}=\sum_i \vec{l}_i$
- ***L* = 0, 1, 2, 3,….provides S, P, D, F,…**
- **The total momentum *J* is:**

$$\boxed{(|L-S| \leq J \leq |L+S|)}$$

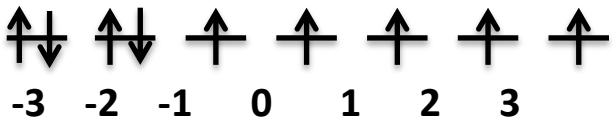
- **A multiplet noted $^{2S+1}L_J$ is obtained whose energy is:**

$$\boxed{E\left(^{2S+1}L_J\right) = (\lambda/2)[J(J+1) - L(L+1) - S(S+1)]}$$

where λ is the spin-orbit coupling constant of the ion



- **Ex: Dy^{III}, $4f^9$**



***S*=5/2;**
***L*=5; → H**
***J*=*S*+*L*=15/2**

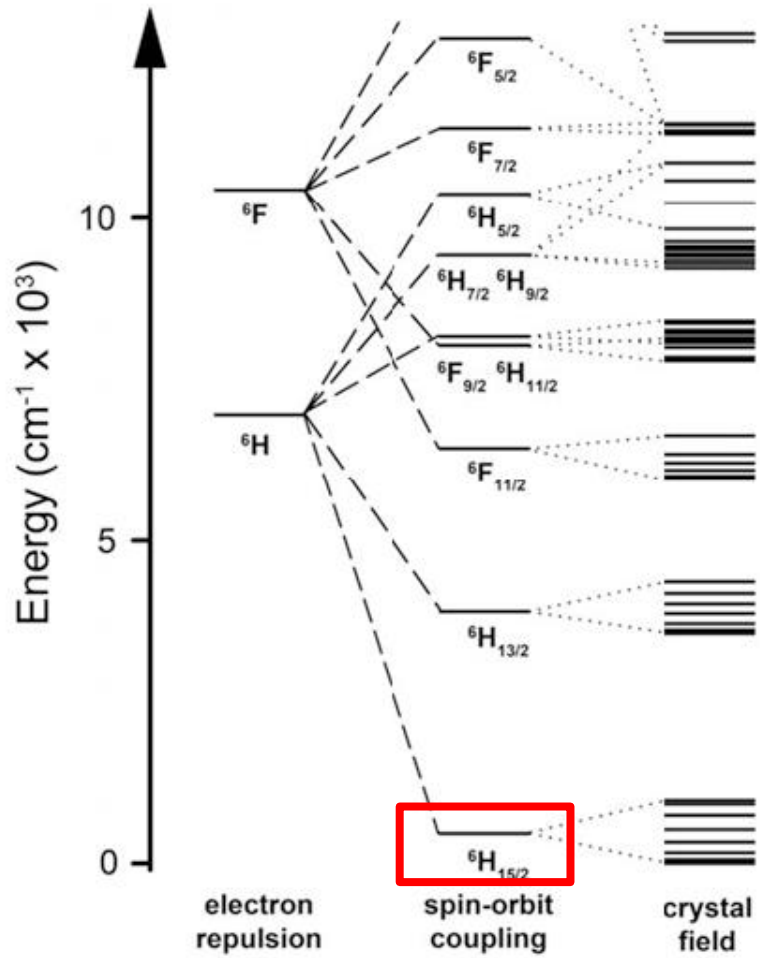
$^{2S+1}L_J = {}^6H_{15/2}$

4*f* free ion electronic structure

- **SO coupling split the terms with same L and S and different *J* → the lowest lying *J* multiplet is the "ground state"**

- **Except for Eu^{III} and Sm^{III}, S.O. is large so magnetic properties of the ion → magnetic properties of the ground state**

Ln^{3+}	$4f^n$	Ground state	g_J	χT (emu mol^{-1} K)	First excited state	Energy separation (cm^{-1})
Ce	f^1	$^2F_{5/2}$	6/7	0.8	$^2F_{7/2}$	2200
Pr	f^2	$^3H_4$	4/5	1.6	$^3H_5$	2100
Nd	f^3	$^4I_{9/2}$	8/11	1.64	$^4I_{11/2}$	1900
Pm	f^4	$^5I_4$	3/5	0.9	$^5I_5$	1600
Sm	f^5	$^6H_{5/2}$	2/7	0.09	$^6H_{7/2}$	1000
Eu	f^6	$^7F_0$	0		$^7F_1$	300
Gd	f^7	$^8S_{7/2}$	2	7.88	$^6P_{7/2}$	30,000
Tb	f^8	$^7F_6$	3/2	11.82	$^7F_5$	2000
Dy	f^9	$^6H_{15/2}$	4/3	14.17	$^6H_{13/2}$	–
Ho	f^{10}	$^5I_8$	5/4	14.07	$^5I_7$	–
Er	f^{11}	$^4I_{15/2}$	6/5	11.48	$^4I_{13/2}$	6500
Tm	f^{12}	$^3H_6$	7/6	7.15	$^3H_5$	–
Yb	f^{13}	$^2F_{7/2}$	8/7	2.57	$^2F_{5/2}$	10,000



J. Tang, P. Zhang, **Lanthanide Single Molecule Magnets,** Springer, **2015**

4*f* free ion magnetism

- By applying a magnetic field, the degeneracy of the 2*J*+1 levels in each $^{2S+1}L_J$ is removed

→ it provides a series of M_J levels : $-J \leq M_J \leq +J$

- The corresponding magnetic moments are:

$$\mu_J = \mu_B g_J \boldsymbol{J}$$

- With the Landé factor that is :

$$g_J = \frac{3}{2} + \frac{S(S+1) - L(L+1)}{2J(J+1)}$$

- And the magnetic susceptibility that follows the Curie law: (except Eu^{3+} and Sm^{3+})

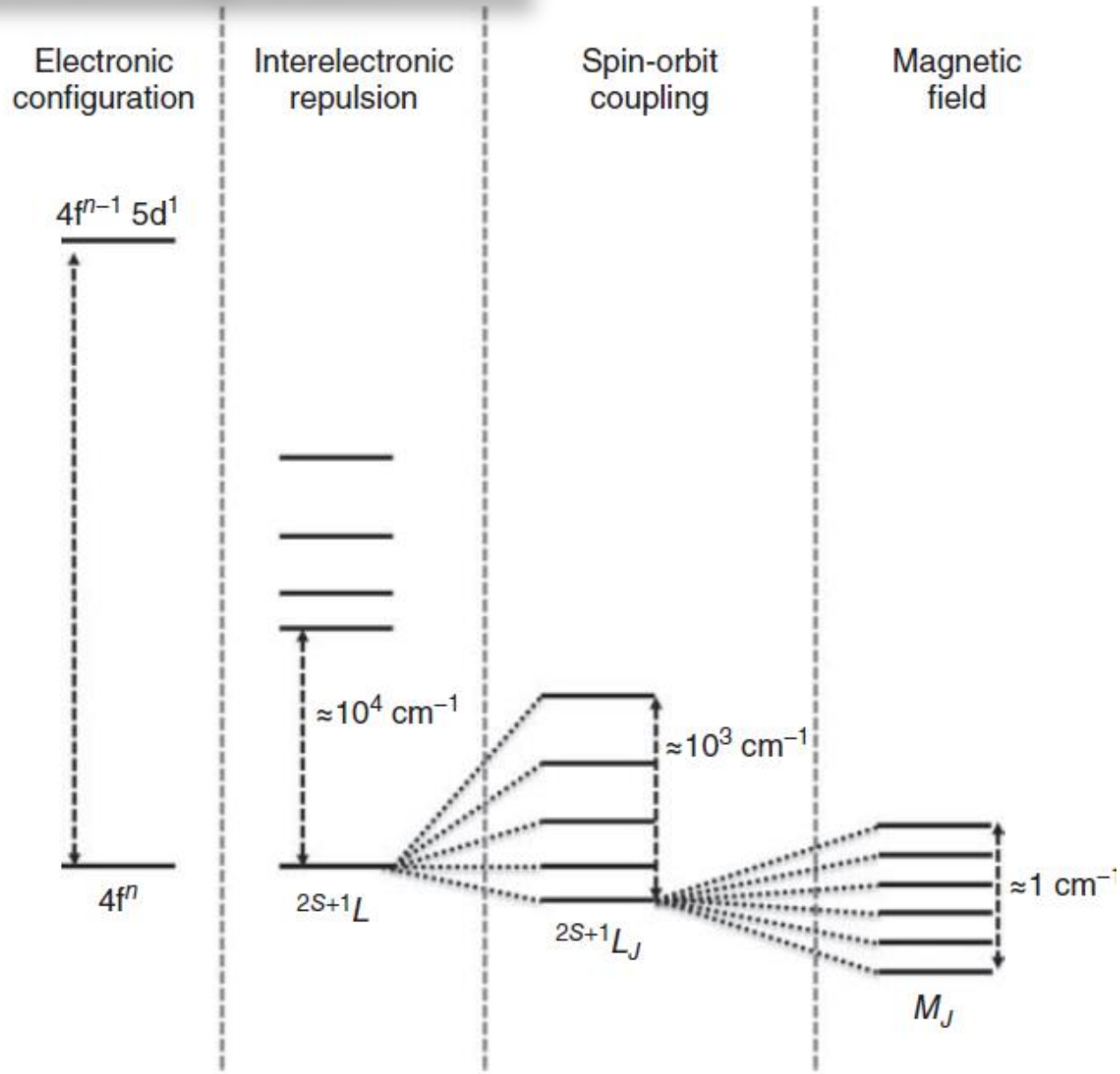
$$\chi^M = \frac{N_A g_J^2 \mu_B^2}{3kT} J(J+1)$$

with $N_A \mu_B^2 / 3k_B T = 1/8$

- Ex: for Dy^{3+} (S=5/2, L= 5, J=15/2), the $^6H_{15/2}$ multiplet is split in 2J+1 M_J states= 16

g_J= 4/3 and $\chi_M T_{(300K)}$ = 14.17 emu.mol^{-1}

4*f* free ion magnetism



Lanthanides and Actinides in Molecular Magnetism; Ed. R.A. Layfield, M. Murugesu, Wiley-VCH, **2015**

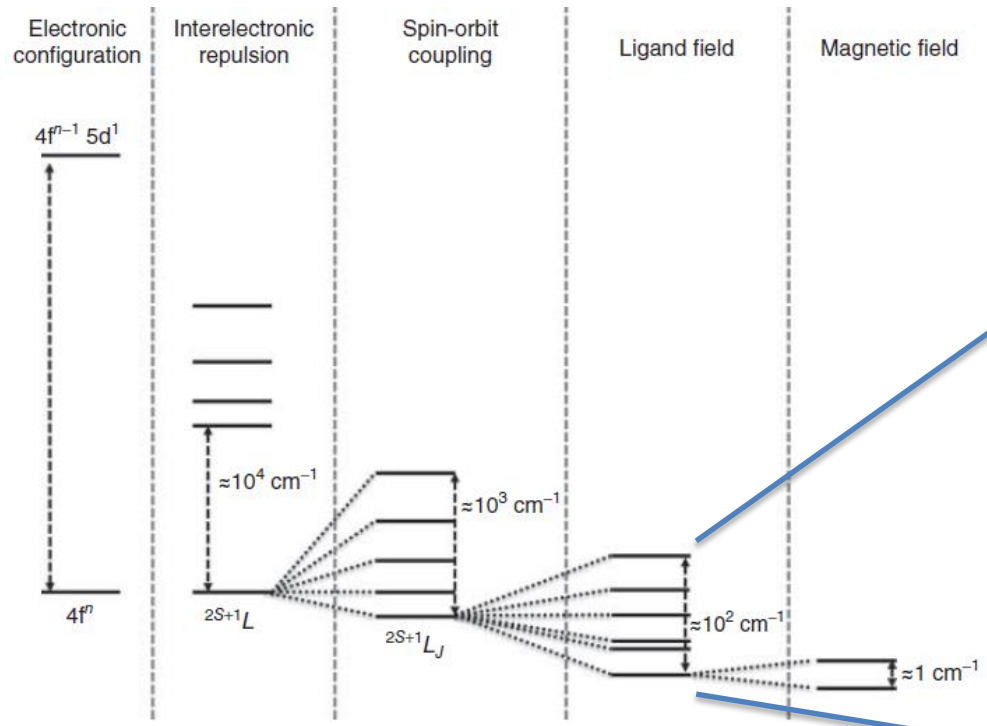
4*f* anisotropy in a crystal field

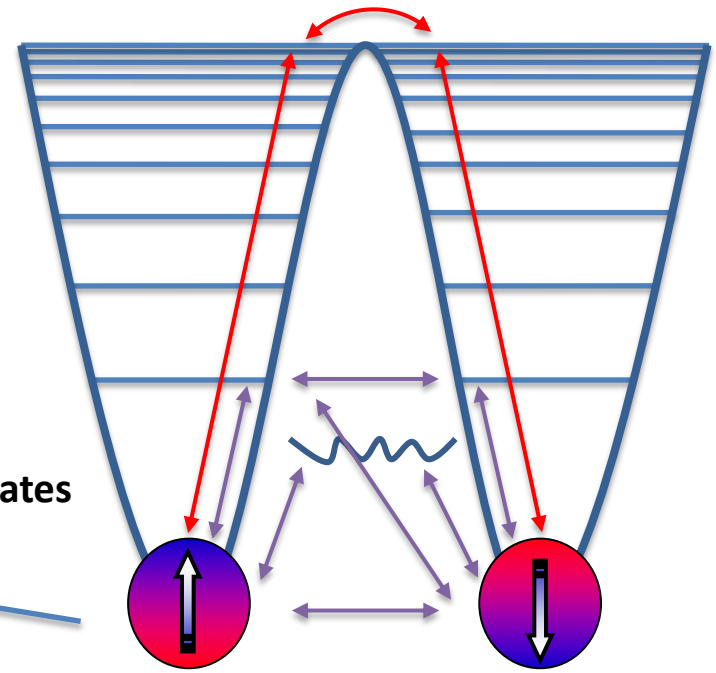
- **Spin is isotropic but orbital component reflects the symmetry of the system and can be anisotropic**
- **Magnetic anisotropy → depends of Spin Orbit coupling (SO or LS coupling) and Crystal field (CF)**
- **For 3d ions: orbital moments are quenched because LS << CF**
- **For 4f ions : orbital moments are unquenched because LS >> CF**
  → the total angular momentum *J* is a good quantum number

Group	Shell	Electronic repulsion	LS coupling	CF splitting
Fe	$3d$	10^5	10	10^3
Pd, Pt	$4d$, $5d$	10^4	10^2	10^4
RE	$4f$	10^5	10^3	10^2

J. Tang, P. Zhang, **Lanthanide Single Molecule Magnets,** Springer, **2015**

4*f* anisotropy in a crystal field





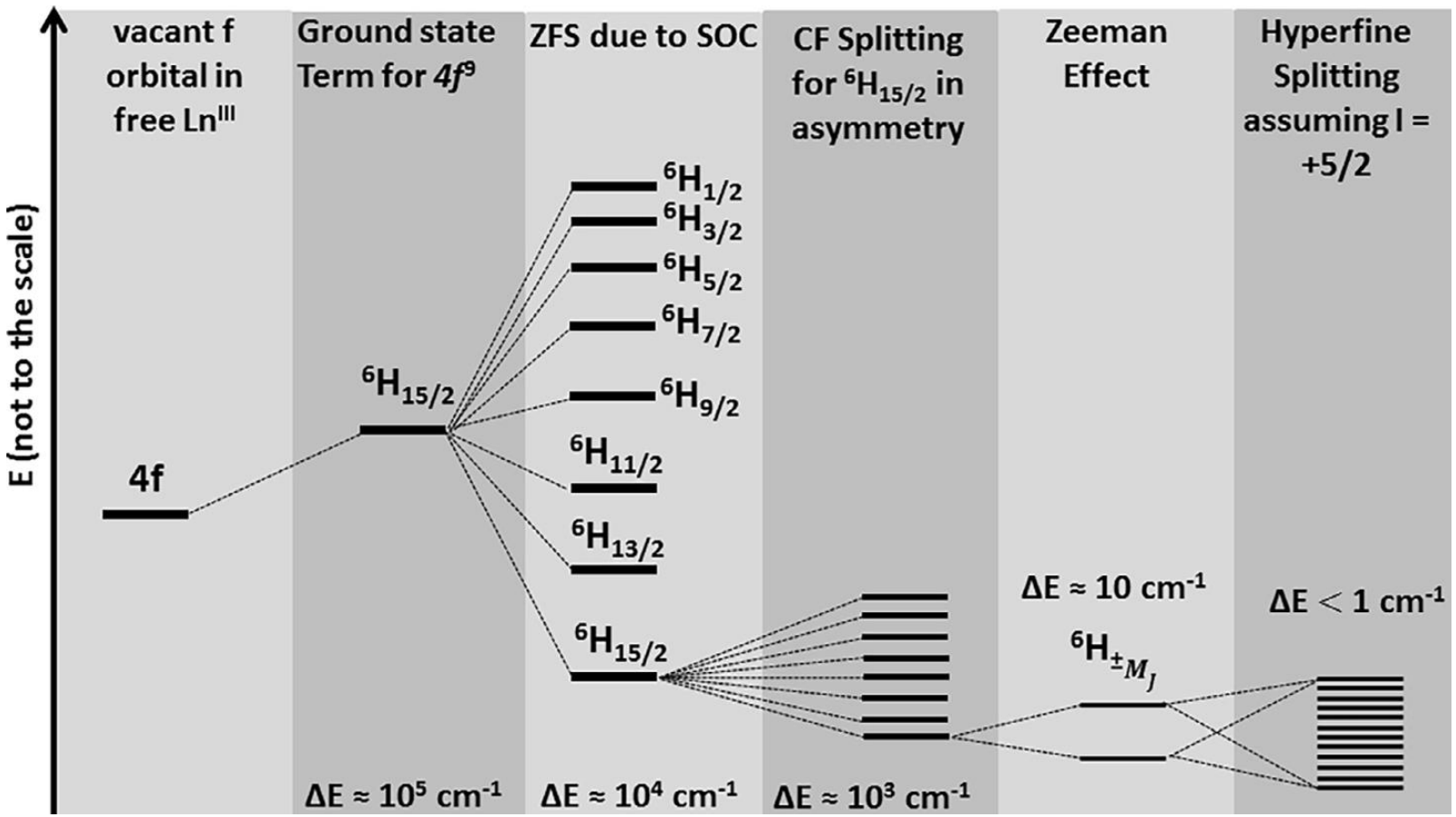
Orbach

Under-barrier relaxation mecanisms (QTM, T-assisted QTM, Raman, Direct)

Lanthanides and Actinides in Molecular Magnetism; Ed. R.A. Layfield, M. Murugesu, Wiley-VCH, **2015**

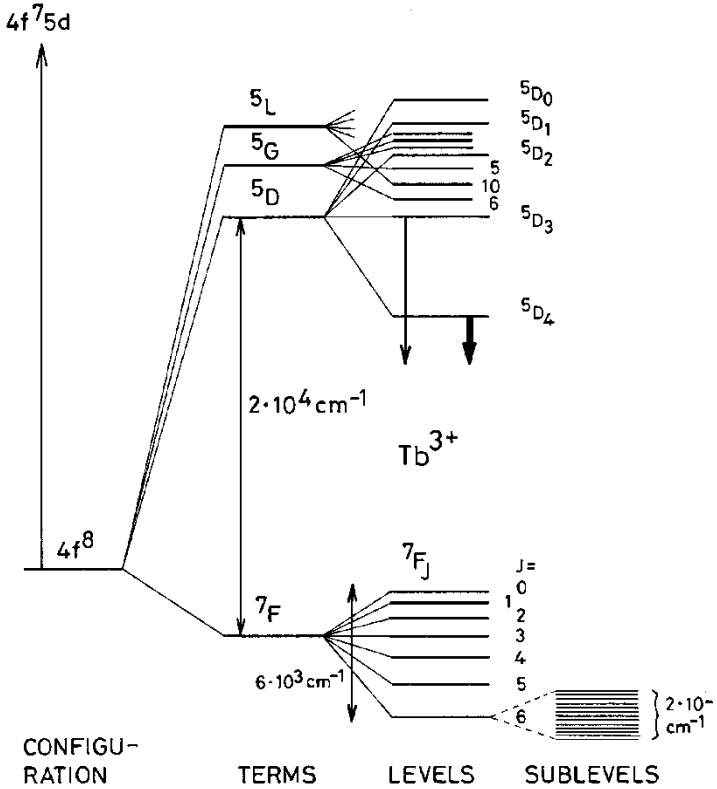
4*f* anisotropy in a crystal field

- **For $^{161}Dy^{III}$:**

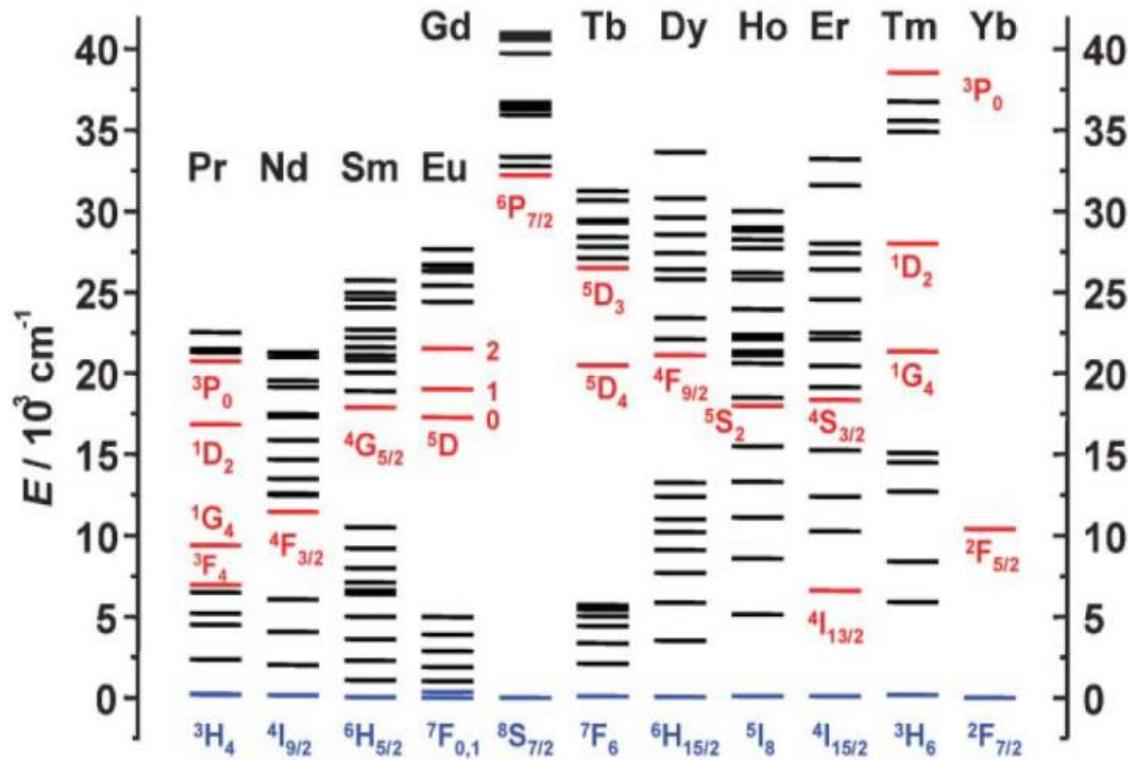


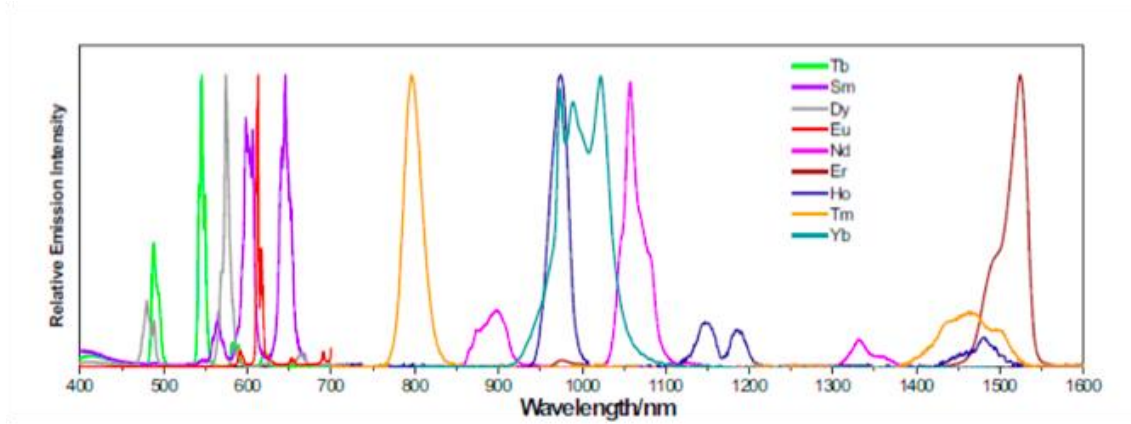
A.K. Bar *et al.*, ***Coord. Chem. Rev.* 2018**, 367, 163

Basics of Lanthanides luminescence



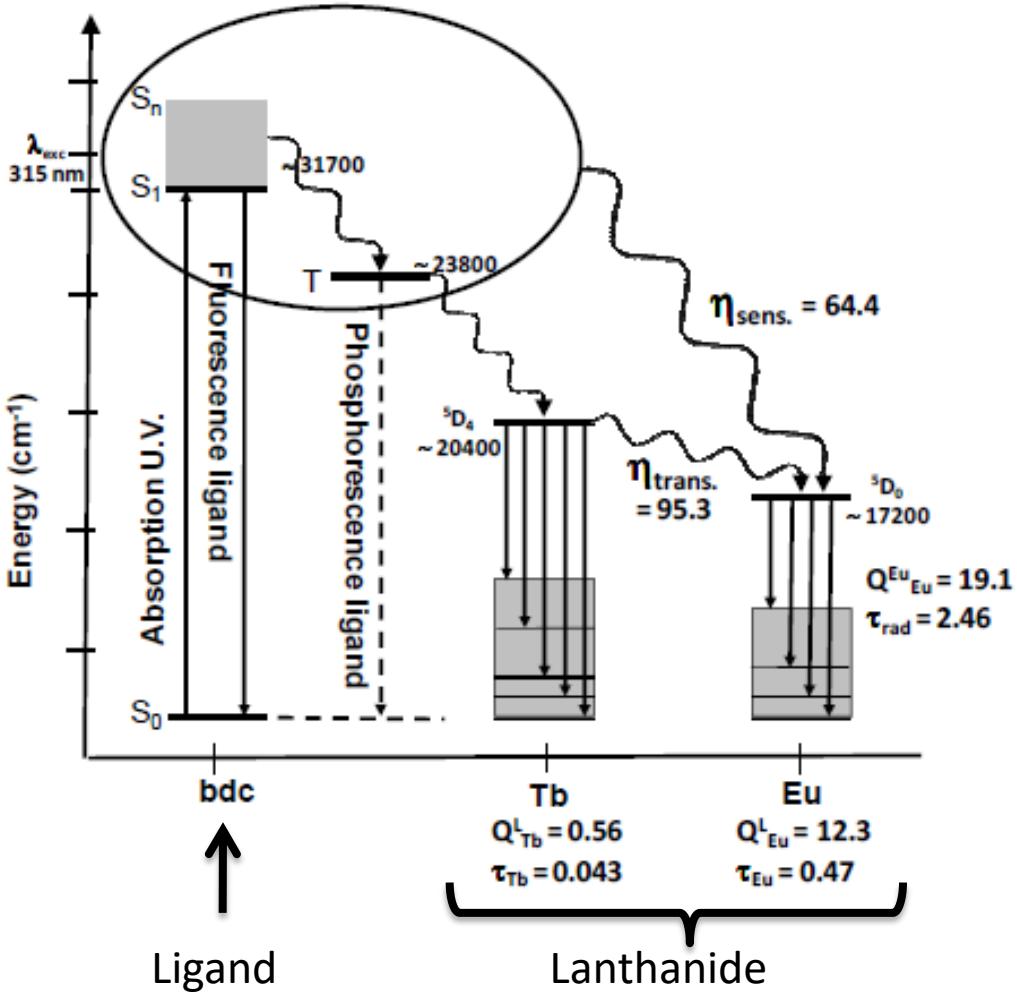
From J.-C. Bünzli

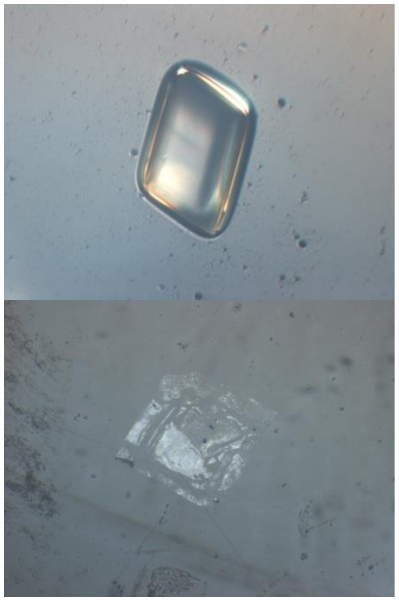




Basics of Lanthanides luminescence

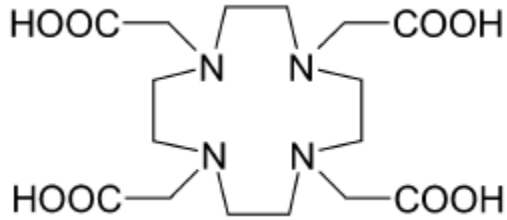
- *f-f* transitions are Laporte forbidden so emissions are weak
- Ln^{III} emissive level can be fed using an organic ligand as energy absorber (UV). If the triplet(s) state(s) of the ligand is (are) at an appropriate energy → transfer toward the Ln^{III} →antenna effect
- Antenna effect enhance Ln^{III} emissions by several orders of magnitude

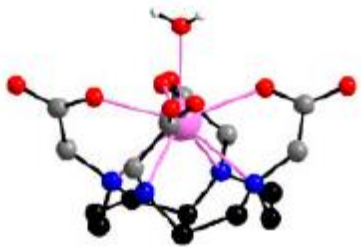


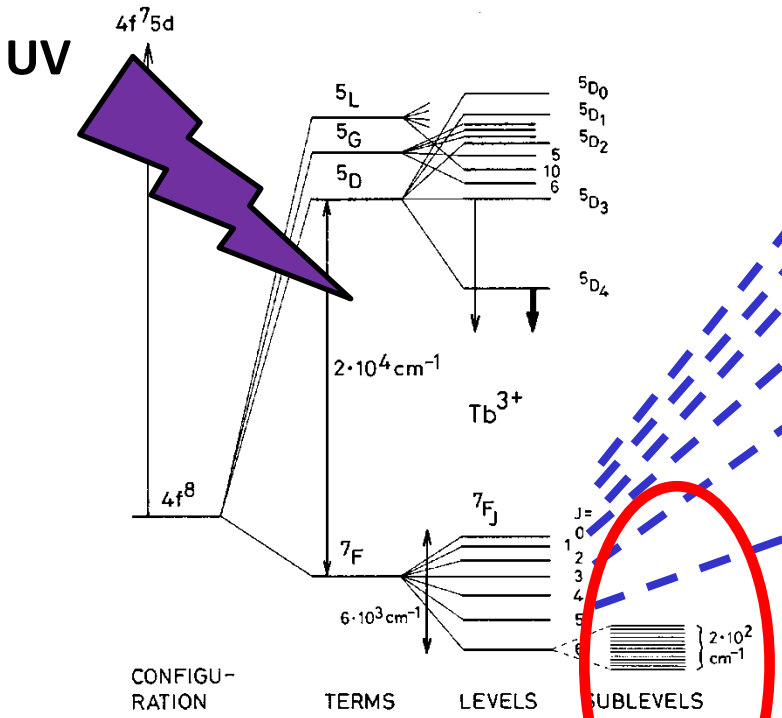


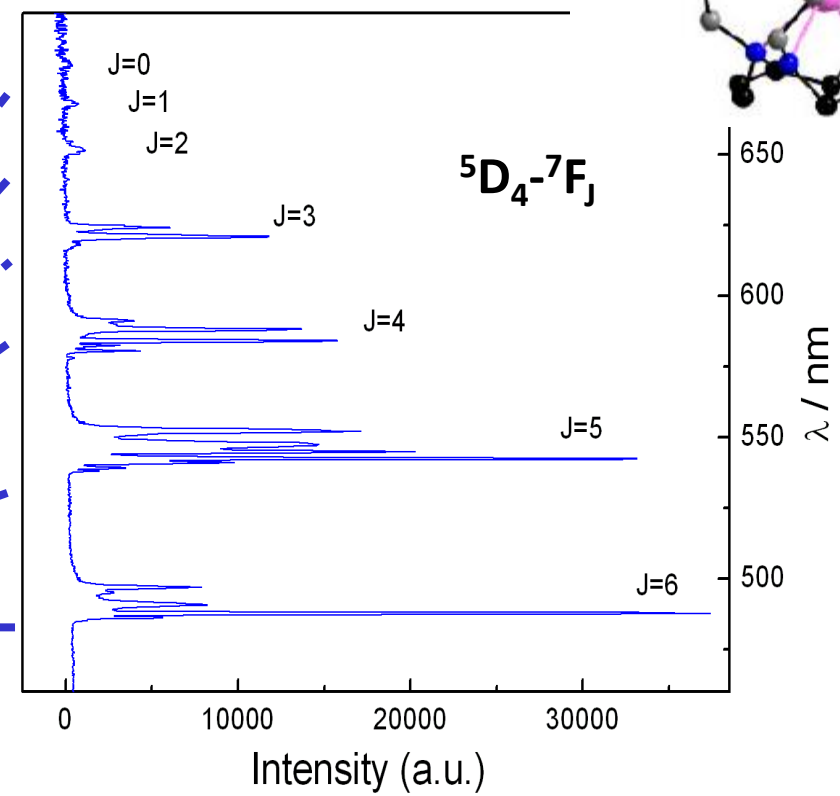
Lanthanides Spectroscopy

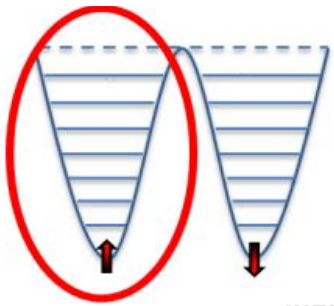
TbDOTA







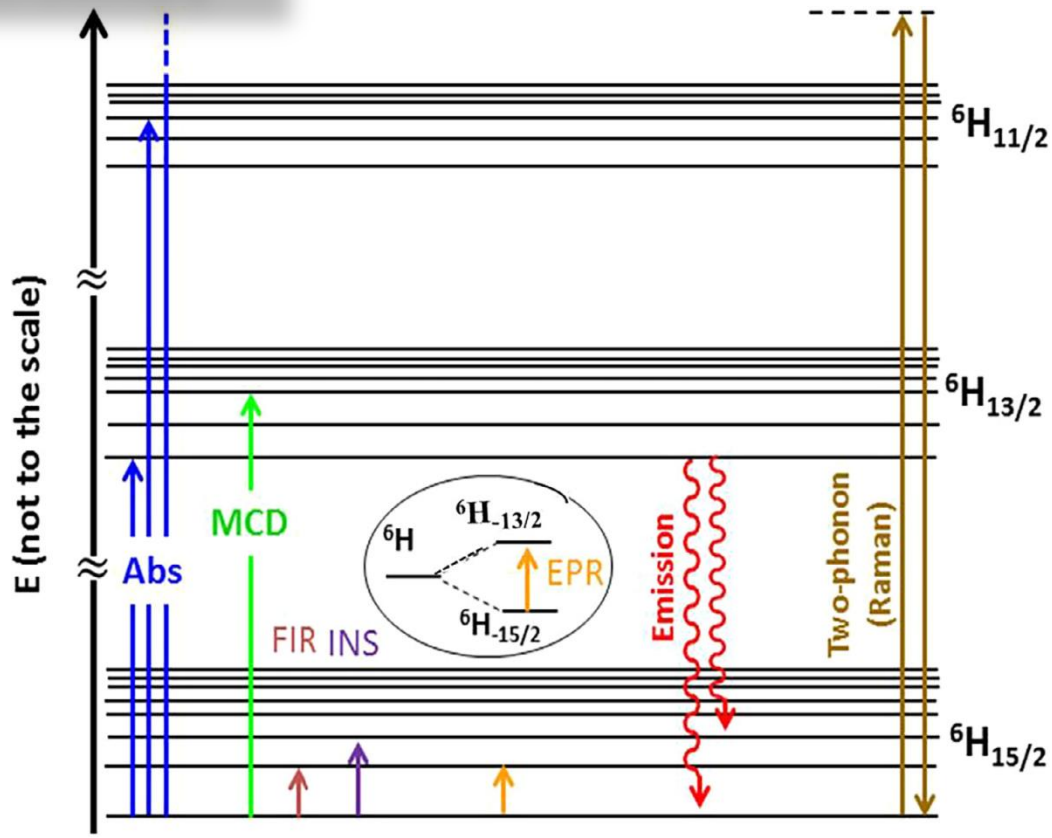




Emission spectroscopy → access to Tb^{III} 's M_J

G. Cucinnotta *et al*, ***Angew. Chem. Int. Ed*. 2012**, *51, 1606-1610*
M.-E Boulon *et al*, ***Angew. Chem. Int. Ed*. 2013**, *52, 350-354*
J. Long et al. ***Coord. Chem. Rev***. 2018, *363, 57*

Lanthanides Spectroscopy



Landscape of Dy(III) ion portraying the energy levels associated in:

- **Optical absorption (Abs)**
- **Magnetic circular dichroism (MCD)**
- **Far infra-red (FIR)**
- **Inelastic neutron scattering (INS)**
- **Electron paramagnetic resonance (EPR)**
- **Emission**
- **and Raman spectroscopy**

A.K. Bar *et al.*, ***Coord. Chem. Rev.*** **2018**, 367, 163

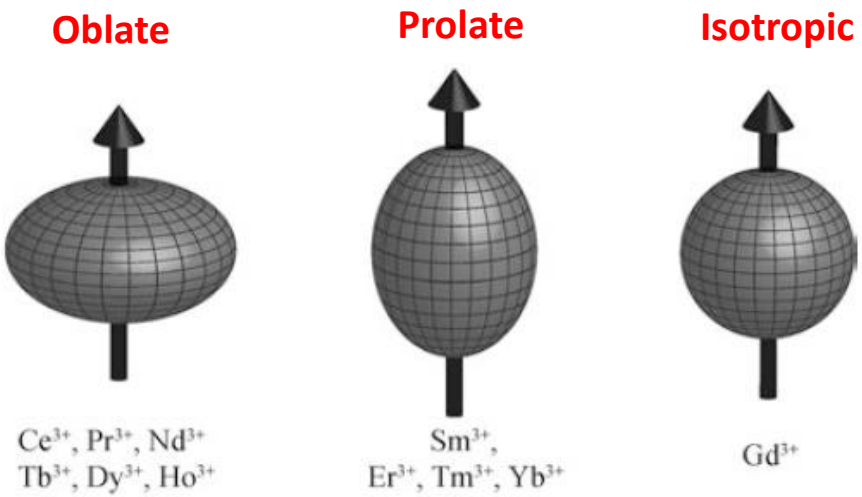
Single ion anisotropy

- **Single ion anisotropy of lanthanide ions is linked to the charge distribution on the lowest *J* states whose shape is based on the quadrupole moment:**

$$Q_2 = \alpha_J \left\langle r^2 \right\rangle_{4f} \left(2J^2 - J\right)$$

r: 4*f* shell radius
α_J: second order Stevens coefficient

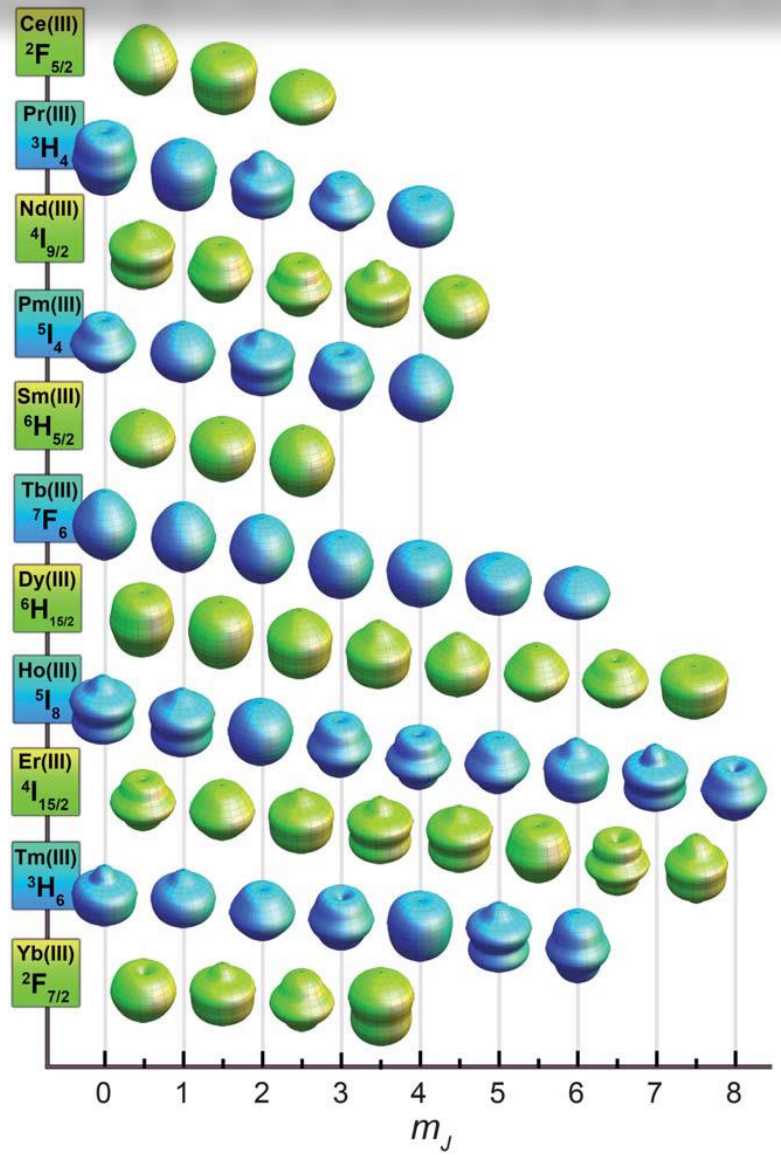
Ln^{3+}	Ground state	α_J	β_J	γ_J	Q_2
Ce	$^2F_{5/2}$	$\frac{-2}{5\cdot 7}$	$\frac{2}{3^2\cdot 5\cdot 7}$	0	−0.686
Pr	$^3H_4$	$\frac{-2^2\cdot 13}{3^2\cdot 5^2\cdot 11}$	$\frac{-2^2}{3^2\cdot 5\cdot 11^2}$	$\frac{2^4\cdot 17}{3^4\cdot 5\cdot 7\cdot 11^2\cdot 13}$	−0.639
Nd	$^4I_{9/2}$	$\frac{-7}{3^2\cdot 11^2}$	$\frac{-2^3\cdot 17}{3^3\cdot 11^3\cdot 13}$	$\frac{-5\cdot 17\cdot 19}{3^3\cdot 7\cdot 11^3\cdot 13^2}$	−0.232
Pm	$^5I_4$	$\frac{2\cdot 7}{3\cdot 5\cdot 11^2}$	$\frac{2^3\cdot 7\cdot 17}{3^3\cdot 5\cdot 11^3\cdot 13}$	$\frac{2^3\cdot 17\cdot 19}{3^3\cdot 7\cdot 11^2\cdot 13^2}$	0.202
Sm	$^6H_{5/2}$	$\frac{13}{3^2\cdot 5\cdot 7}$	$\frac{2\cdot 13}{3^3\cdot 5\cdot 7\cdot 11}$	0	0.364
Eu	$^7F_0$	0	0	0	–
Gd	$^8S_{7/2}$	0	0	0	0
Tb	$^7F_6$	$\frac{-1}{3^2\cdot 11}$	$\frac{2}{3^3\cdot 5\cdot 11^2}$	$\frac{-1}{3^4\cdot 7\cdot 11^2\cdot 13}$	−0.505
Dy	$^6H_{15/2}$	$\frac{-2}{3^2\cdot 5\cdot 7}$	$\frac{-2^3}{3^3\cdot 5\cdot 7\cdot 11\cdot 13}$	$\frac{2^2}{3^3\cdot 7\cdot 11^2\cdot 13^2}$	−0.484
Ho	$^5I_8$	$\frac{-1}{2\cdot 3^2\cdot 5^2}$	$\frac{-1}{2\cdot 3\cdot 5\cdot 7\cdot 11\cdot 13}$	$\frac{-5}{3^3\cdot 7\cdot 11^2\cdot 13^2}$	−0.185
Er	$^4I_{15/2}$	$\frac{2^2}{3^2\cdot 5^2\cdot 7}$	$\frac{5}{3^2\cdot 5\cdot 7\cdot 11\cdot 13}$	$\frac{2^3}{3^3\cdot 7\cdot 11^2\cdot 13^2}$	0.178
Tm	$^3H_6$	$\frac{1}{3^2\cdot 11}$	$\frac{2^3}{3^4\cdot 5\cdot 11^2}$	$\frac{-5}{3^4\cdot 7\cdot 11^2\cdot 13}$	0.427
Yb	$^2F_{7/2}$	$\frac{2}{3^2\cdot 7}$	$\frac{-2}{3\cdot 5\cdot 7\cdot 11}$	$\frac{2^2}{3^3\cdot 7\cdot 11\cdot 13}$	0.409



Q_2>0, prolate electron distribution
Q_2<0, oblate electron distribution

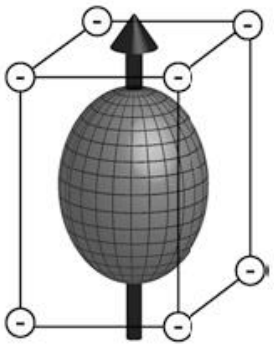
J. Tang, P. Zhang, **Lanthanide Single Molecule Magnets,** Springer, **2015**

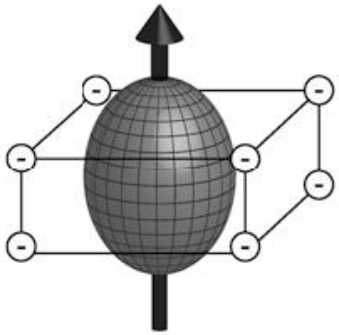
Single ion anisotropy and CF



- **Example of a prolate ion (Yb^{III}):**

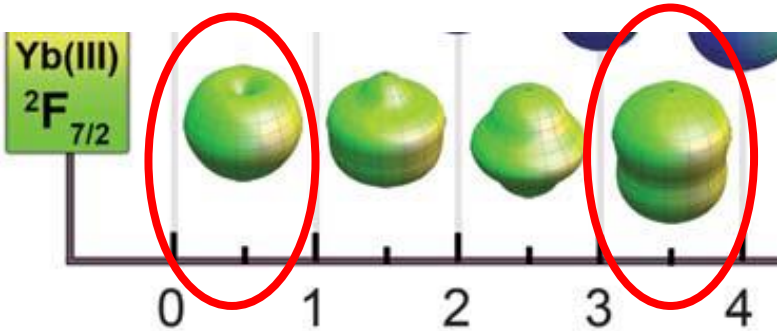
  A given CF orient the electronic charge cloud in a energetically favorable direction





Planar Anisotropy
Stabilization of the highest M_J

Axial Anisotropy
Stab. of the lowest M_J



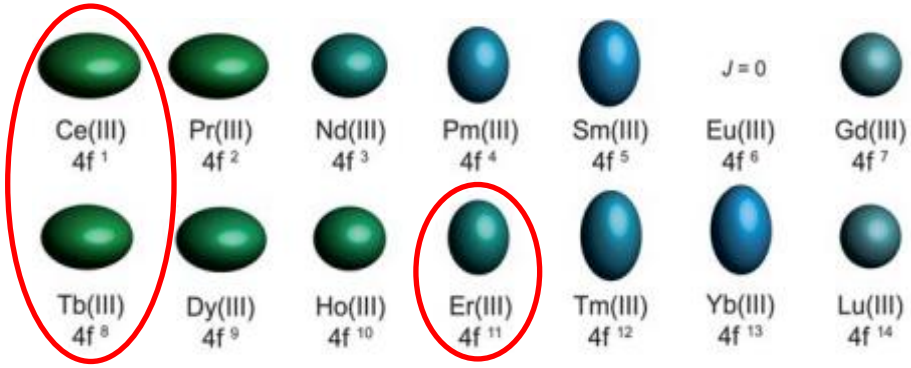
Carlin, R. J. ***Magnetochemistry*;** Springer: Berlin, **1986**

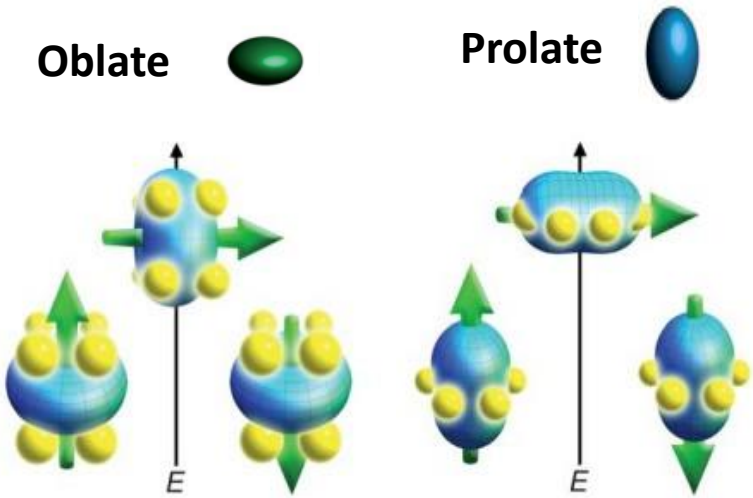
J. D. Rinehart., et al. ***Chem. Sci.***, **2011**, 2, 2078

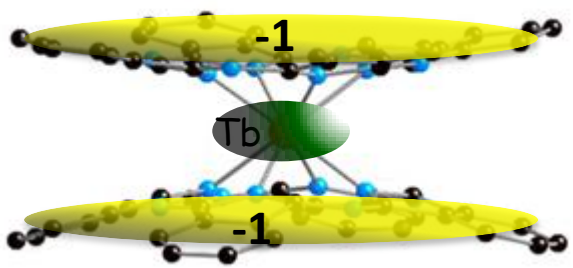
J. Tang, P. Zhang, **Lanthanide Single Molecule Magnets,** Springer, **2015**

Single ion anisotropy and CF

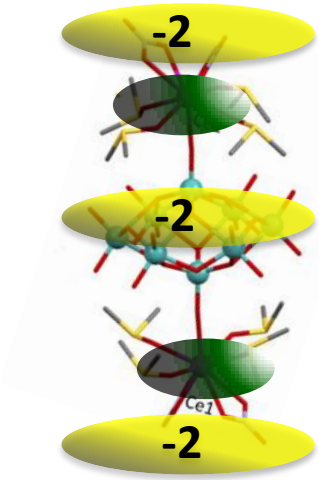
- **"Oblate/Prolate model"**

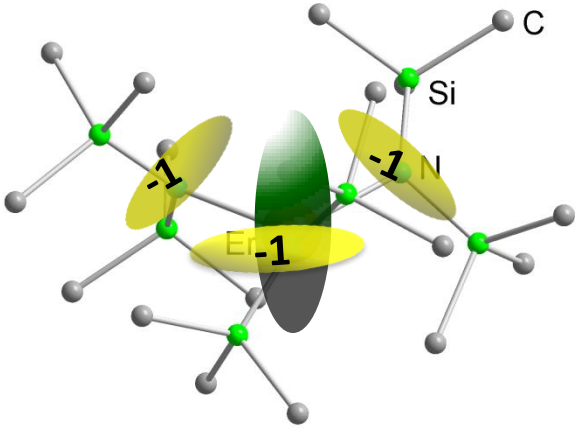






N. Ishikawa., et al. ***J. Am. Chem. Soc.*** **2003**, 125, 8694





P. Zhang., et al. ***J. Am. Chem. Soc***. **2014**, 136, 4484

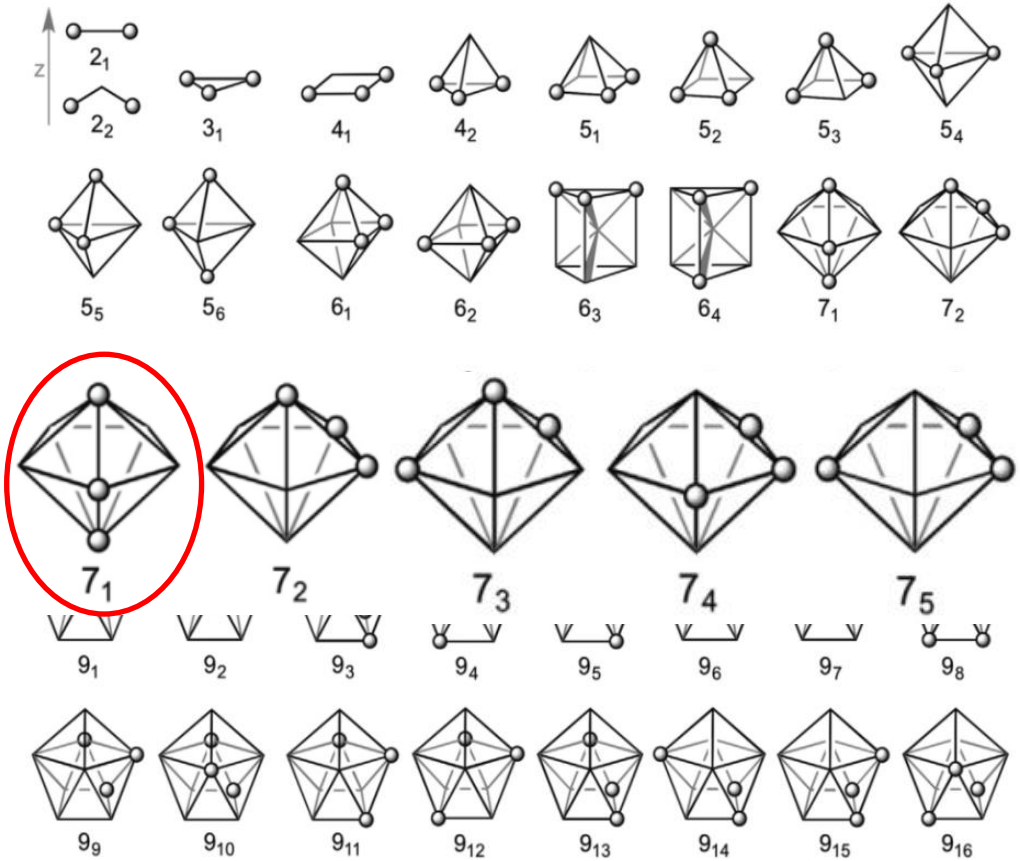
A. Ben Khélifa., et al. ***Dalton Trans***., **2015**, 44, 16458

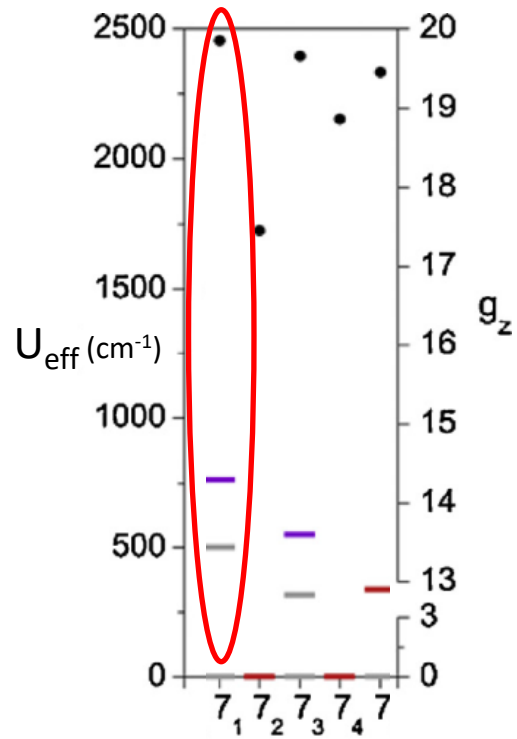
J. D. Rinehart., et al. ***Chem. Sci***., **2011**, 2, 078

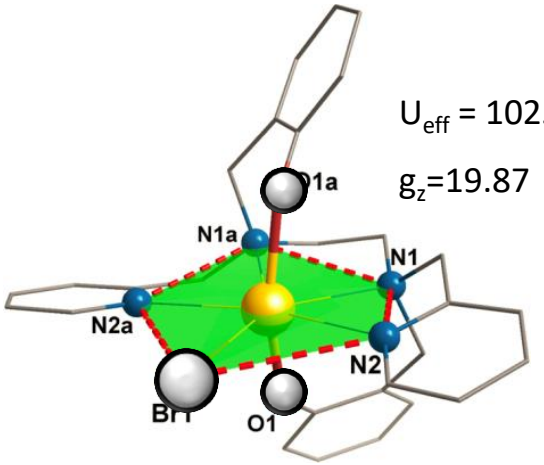
Single ion anisotropy and CF

- **Localized charges electrostatic model**

  Neutral Dy^{III} complexes







U_{eff} = 1025 K (711 cm^{-1})

g_z=19.87

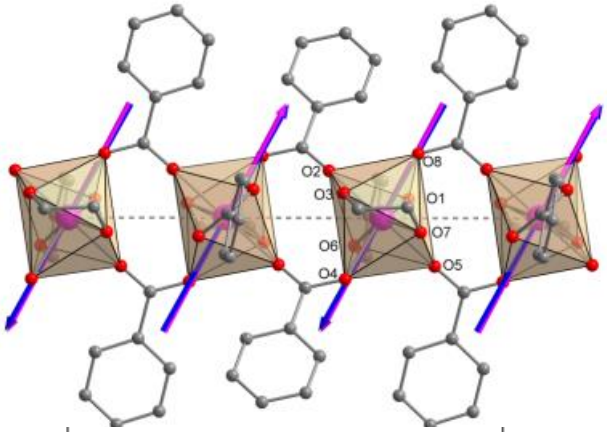
S. Gómez-Coca., et al. ***Coord. Chem. Rev***. 289-290, **2015**, 379

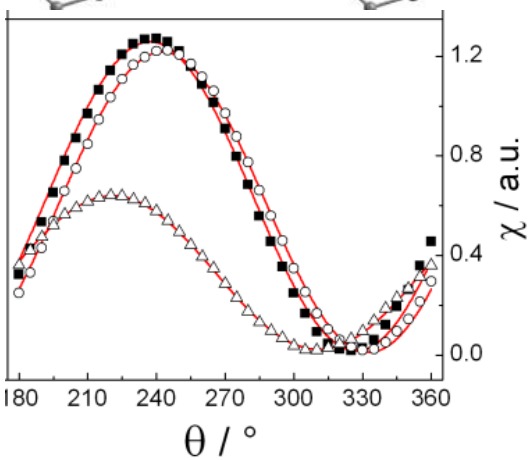
J. Liu ., et al. ***J. Am. Chem. Soc.*** **2016**, 138, 5441

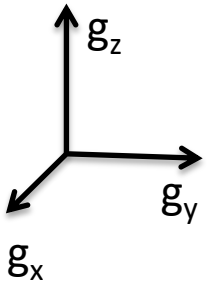
Quantification of Lanthanide(III) anisotropy in mononuclear molecules

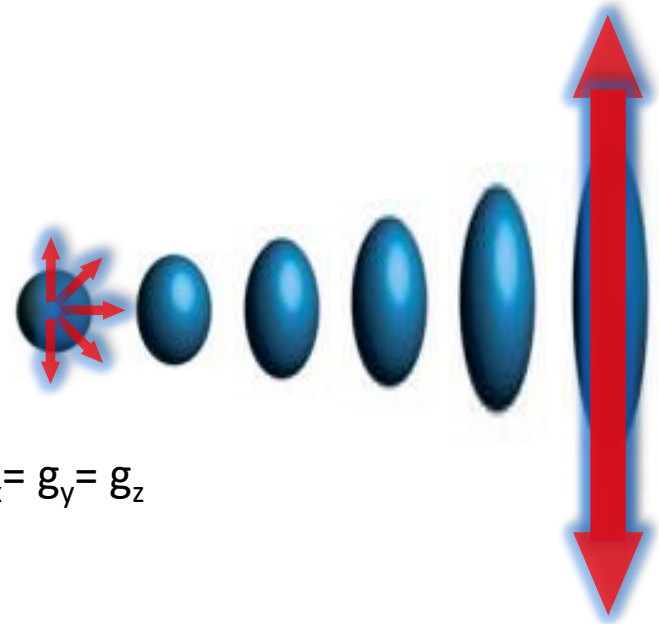
Quantification of the anisotropy

- **EPR**
- **Polarized neutron diffraction (PND)**
- **Single crystal magnetic measurements**
  - **→Cantilever magnetometry**
  - **→ Angle–resolved magnetometry**







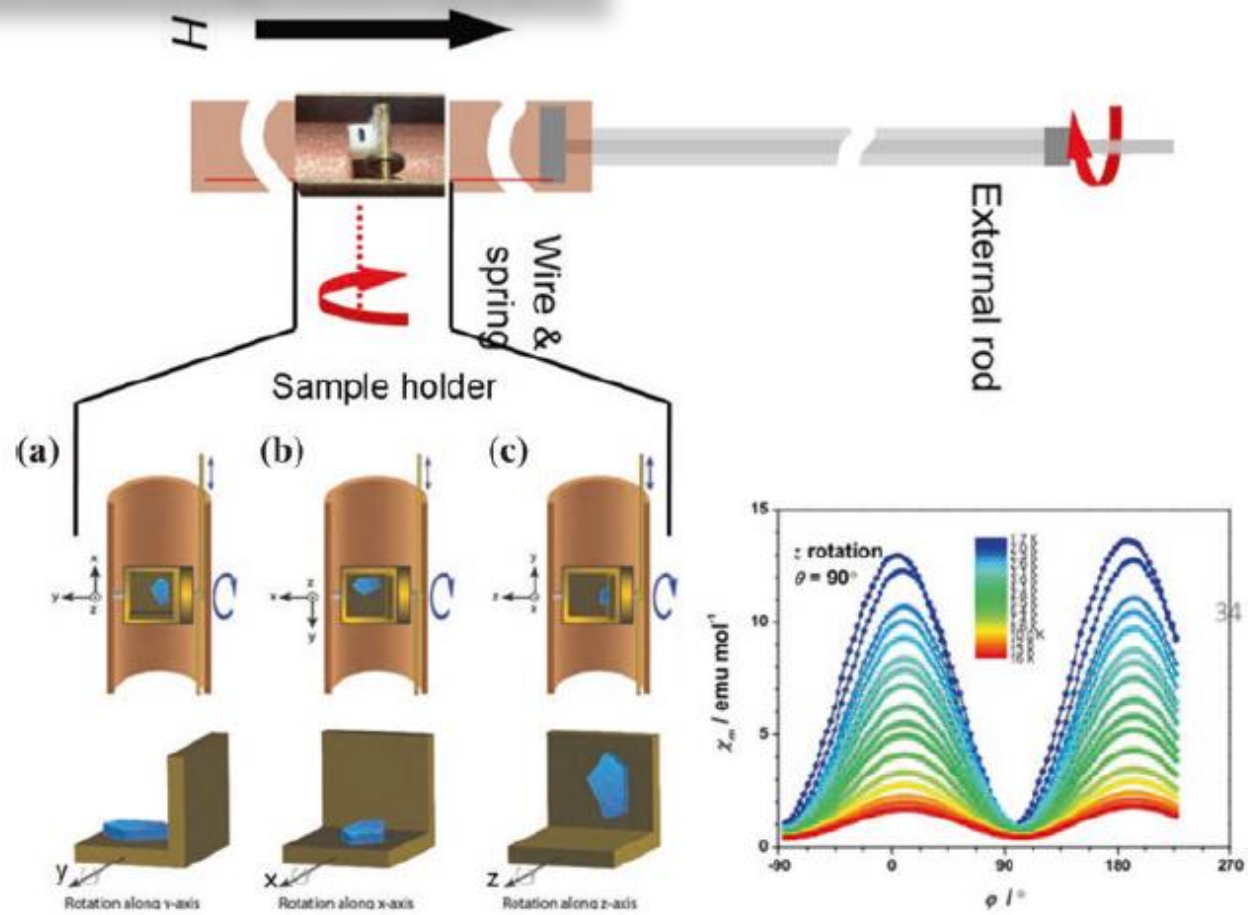


$g_x = g_y = g_z$

$g_x = g_y <<< g_z$

J. Jung, *et al.*, ***Chem. Commun* 2014**, 50, 13346

Angle-resolved magnetometry



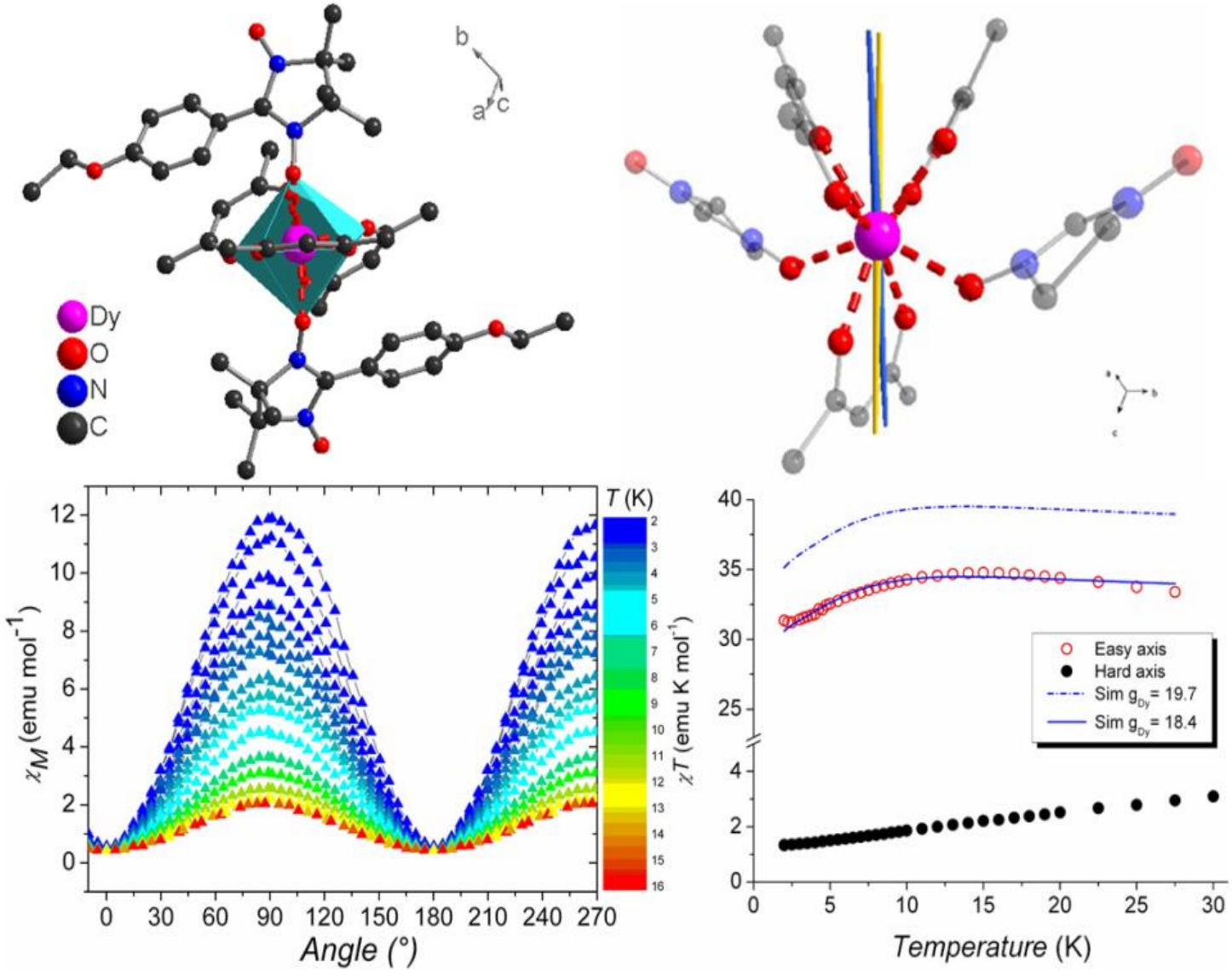
$$\chi^{\mathrm{rot}\gamma}(\theta) = \chi_{\alpha\alpha}\cos^2(\theta) + \chi_{\beta\beta}\cos^2(\theta) + 2\chi_{\alpha\beta}\cos^2(\theta)$$

$$\chi = \begin{pmatrix} \chi_{\alpha\alpha} & \chi_{\alpha\beta} & \chi_{\alpha\gamma} \\ \chi_{\beta\alpha} & \chi_{\beta\beta} & \chi_{\beta\gamma} \\ \chi_{\gamma\alpha} & \chi_{\gamma\beta} & \chi_{\gamma\gamma} \end{pmatrix} \rightarrow \begin{pmatrix} \chi_x & 0 & 0 \\ 0 & \chi_y & 0 \\ 0 & 0 & \chi_z \end{pmatrix}$$

K . Bernot, *et al.*, ***J. Am. Chem. Soc.*** **2009**, *131*, 5573

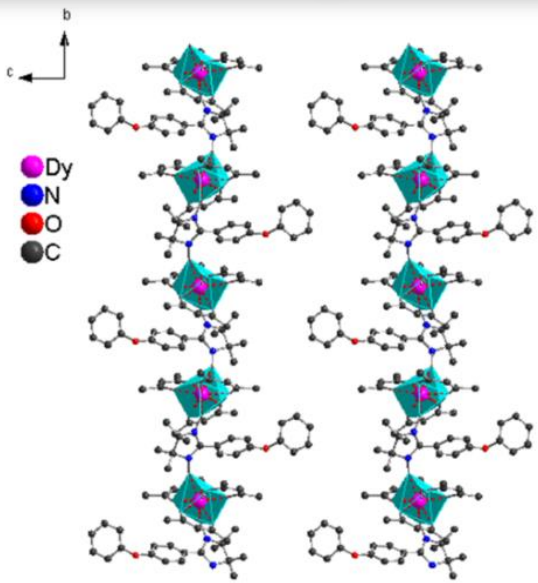
J. Tang, P. Zhang, **Lanthanide Single Molecule Magnets,** Springer, **2015**

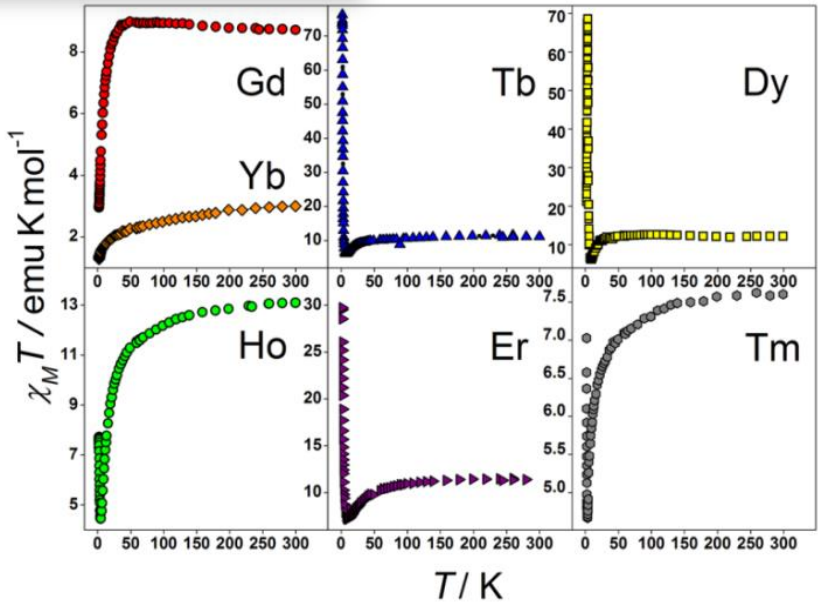
Angle-resolved magnetometry on SMM

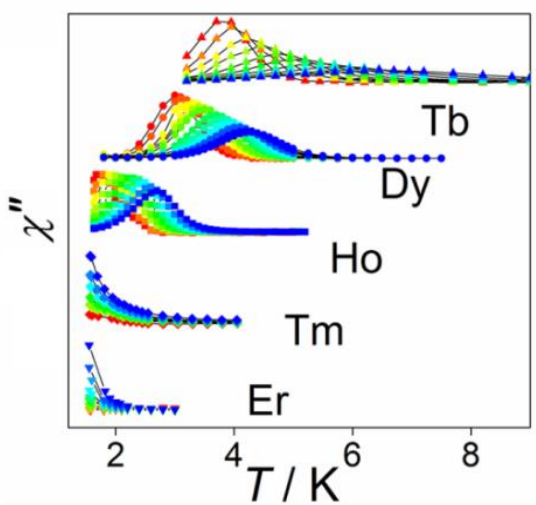


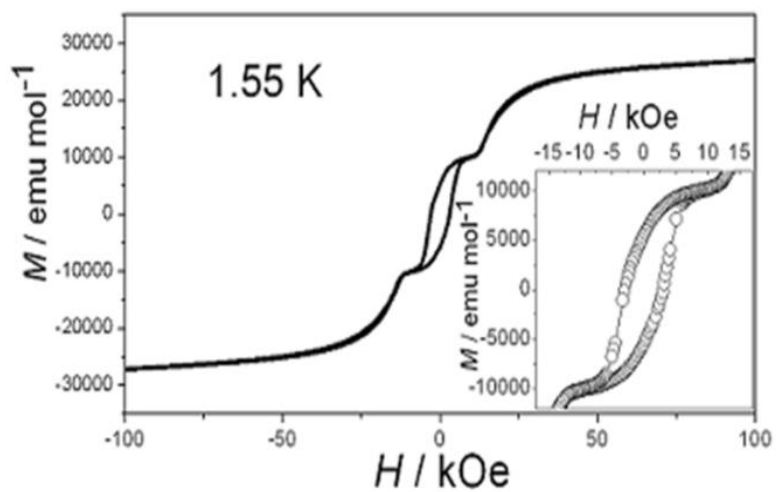
K. Bernot, *et al.*, ***J. Am. Chem. Soc.*** **2009**, *131*, 5573

Angle-resolved magnetometry on SCM





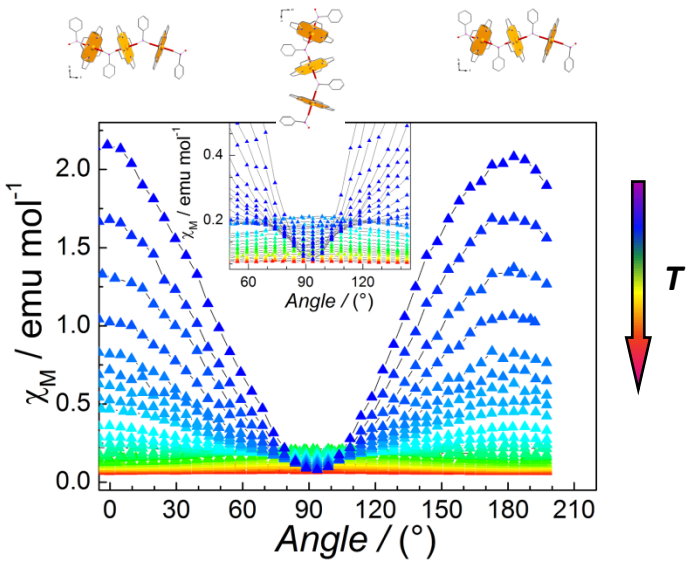


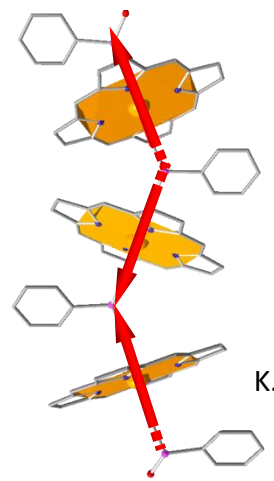


L. Bogani, *et al.*, ***Angew. Chem.* 2005,** 44, 5817
K. Bernot, *et al.*, ***J. Am. Chem. Soc.* 2006,** 128, (24), 7947
K. Bernot, *et al.*, ***Inorg. Chim. Acta*, 2007**, *360, (13), 3807*

Angle-resolved magnetometry on SCM

- **Temperature dependance of the chain anisotropy**

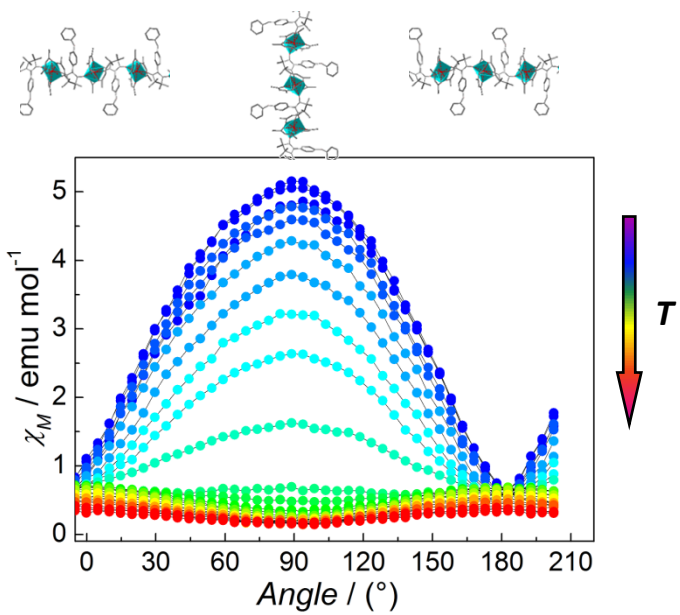


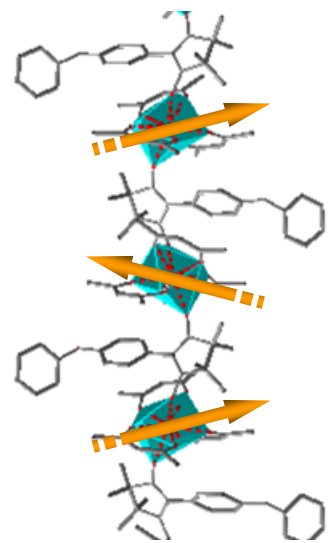


Mn^{III}-based SCM

→Antiferromagnetic SCM with weak canting

K. Bernot, *et al.*, ***J. Am. Chem. Soc., 2008***, *130, 1619*





Dy^{III}-based SCM

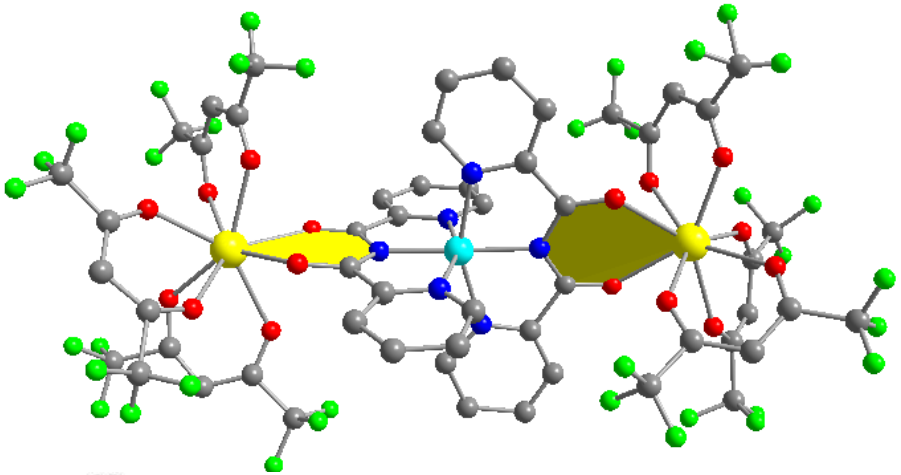
→ Antiferromagnetic SCM with strong canting

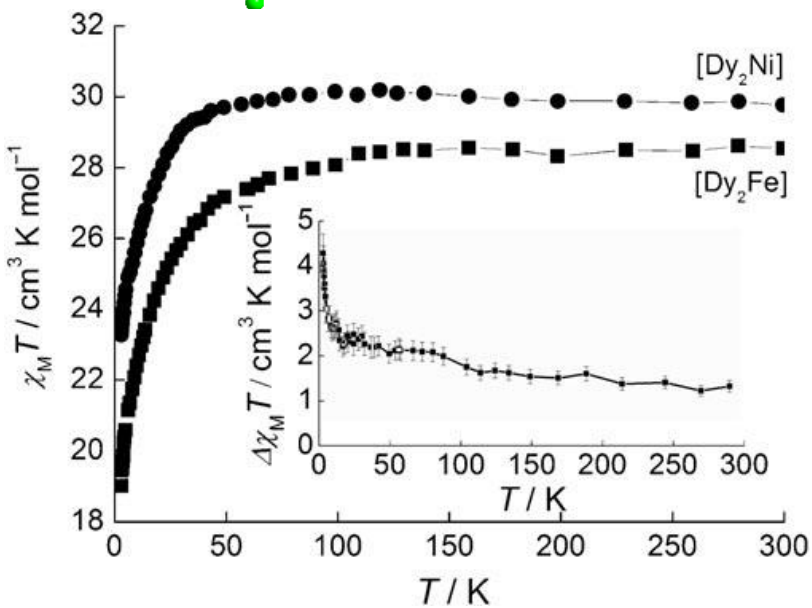
K. Bernot, *et al.*, ***Phys. Rev. B,*** 79, 134419 (**2009**).

Lanthanide anisotropy in polynuclear molecules

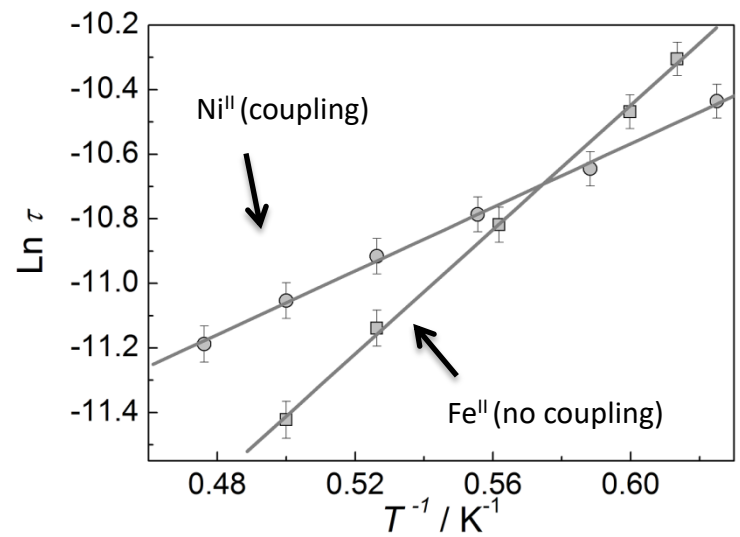
Lanthanide anisotropy in polynuclear molecules

- Dy^{III}-Fe^{II}-Dy^{III} and Dy^{III}-Ni^{II}-Dy^{III} SMMs
  - → Fe^{II} diamagnetic
  - → Ni^{II} paramagnetic





- Ferromagnetic Dy-Dy coupling (dipolar) via $\Delta\chi_M T$ method
- Anisotropy axes are orthogonal
  - → coupling reduces SMM properties

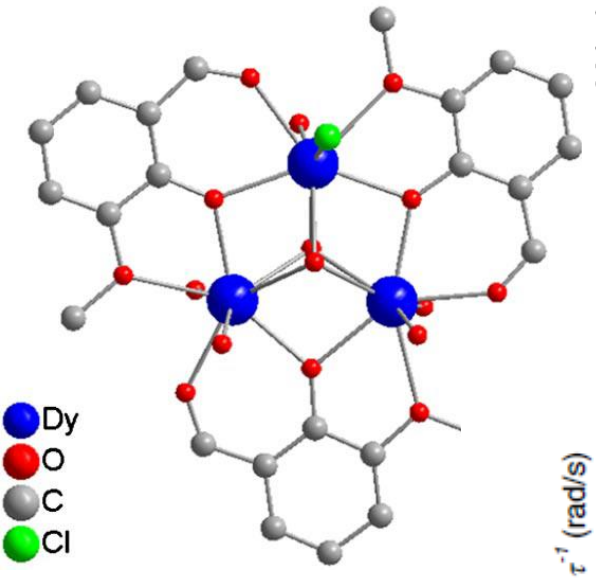


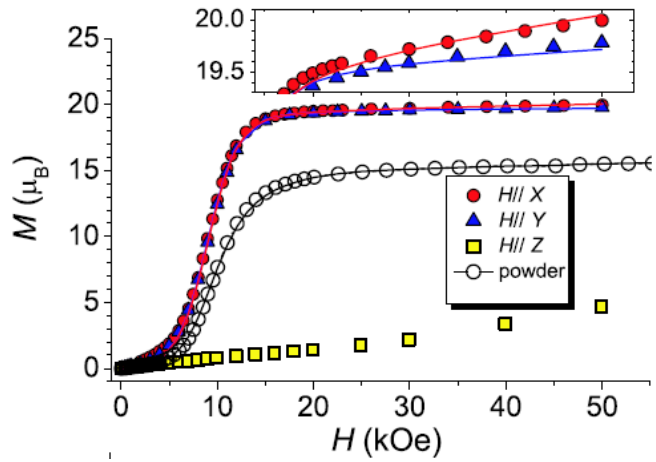
→ Relative orientation of anisotropy axes is a key parameter

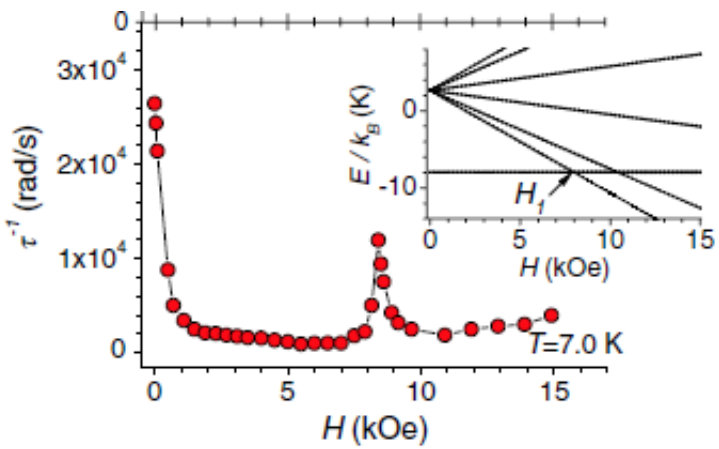
F. Pointillart, *et al.*, ***Chem. Eur. J.*** **2007**, *13*, 1602

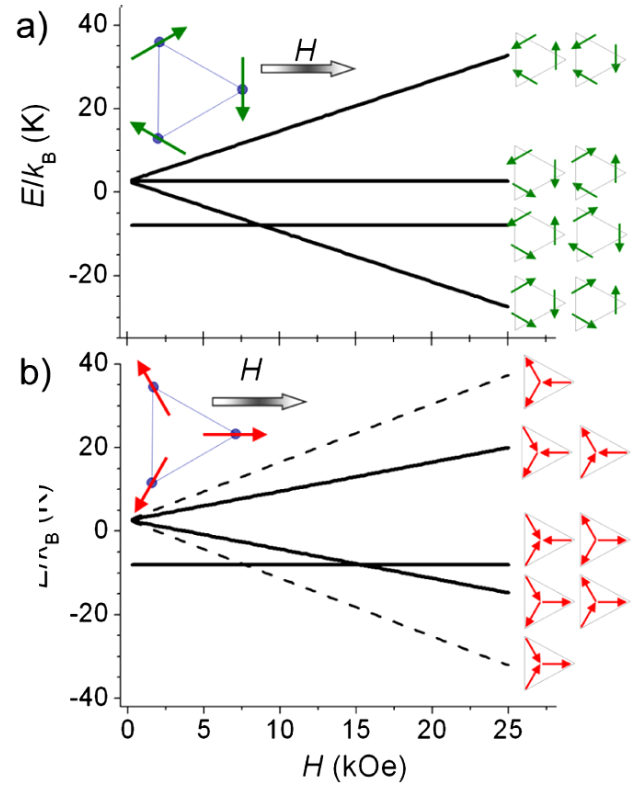
Lanthanide anisotropy in polynuclear molecules

- **Dy^{III} triangle with non-magnetic ground state**









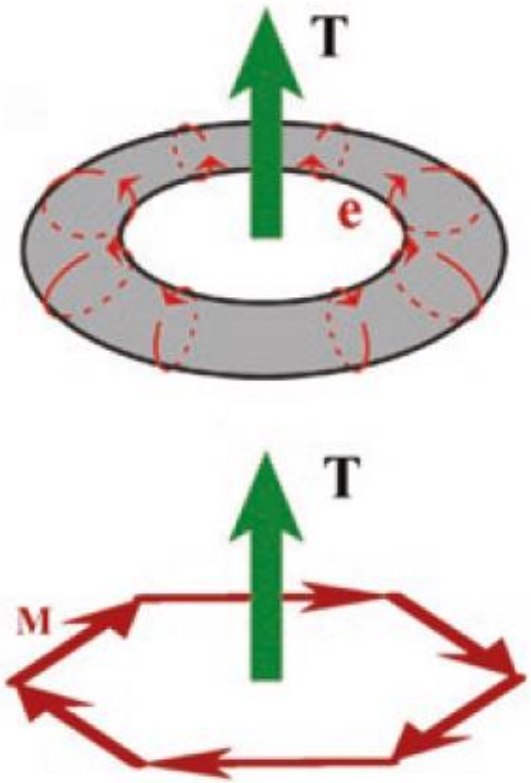
J. K. Tang, *et al.*, ***Angew. Chem.-Int. Edit.*** **2006**, *45*, 1729

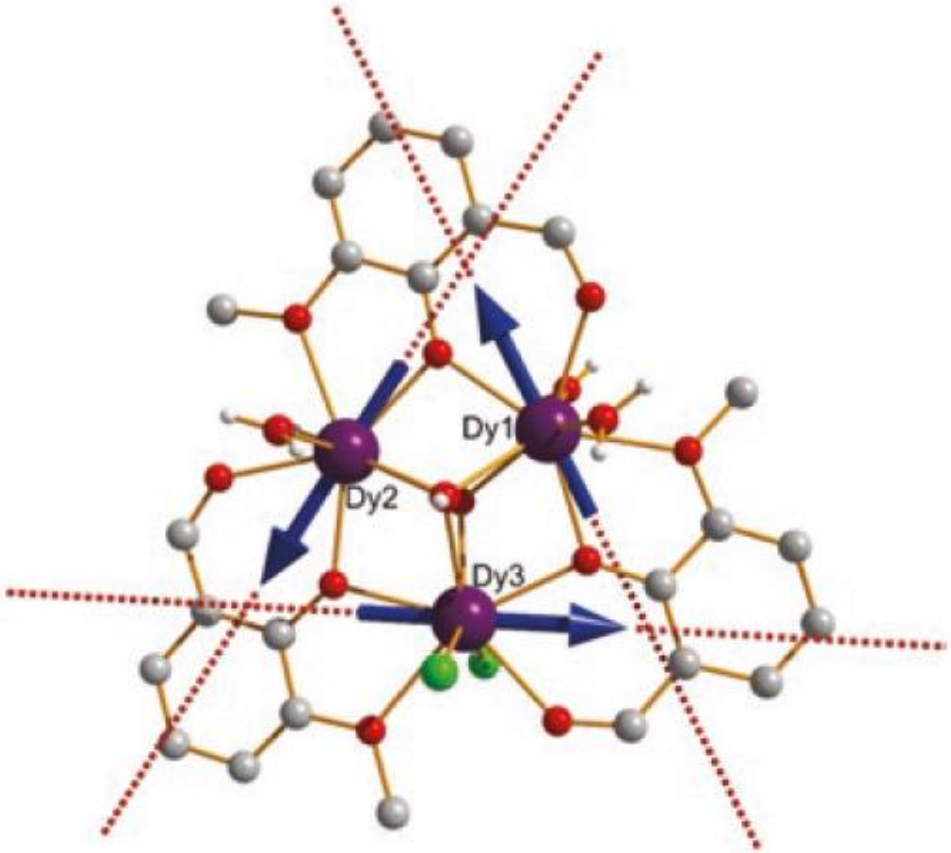
L. F. Chibotaru, *et al*. ***Angew. Chem. Int. Ed.*** **2008**, 47, 4126

J. Luzon, *et al*, ; ***Phys. Rev. Lett.*** **2008**, *100*, 247205.

Lanthanide anisotropy in polynuclear molecules

- **New class of molecules → toroics SMM**

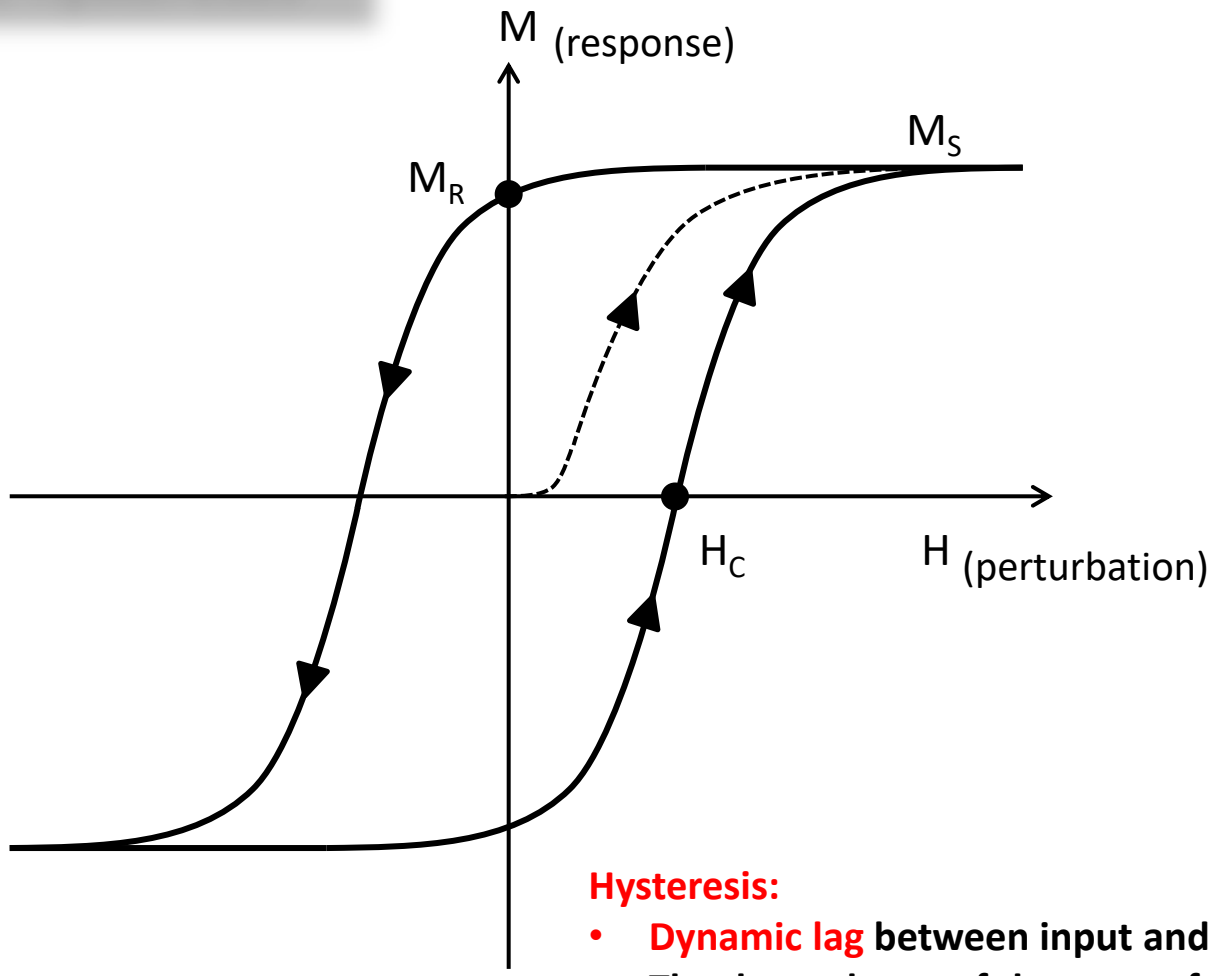




B.B. Van Aken, *et al*. **Nature**, **2007**, 449, 7163
L. Ungur, et. al. **Chem. Soc. Rev., 2014**, 42 (20), 6894

Molecular Magnetism : from 3d to 4f single-molecule magnets

Magnetic hystereses

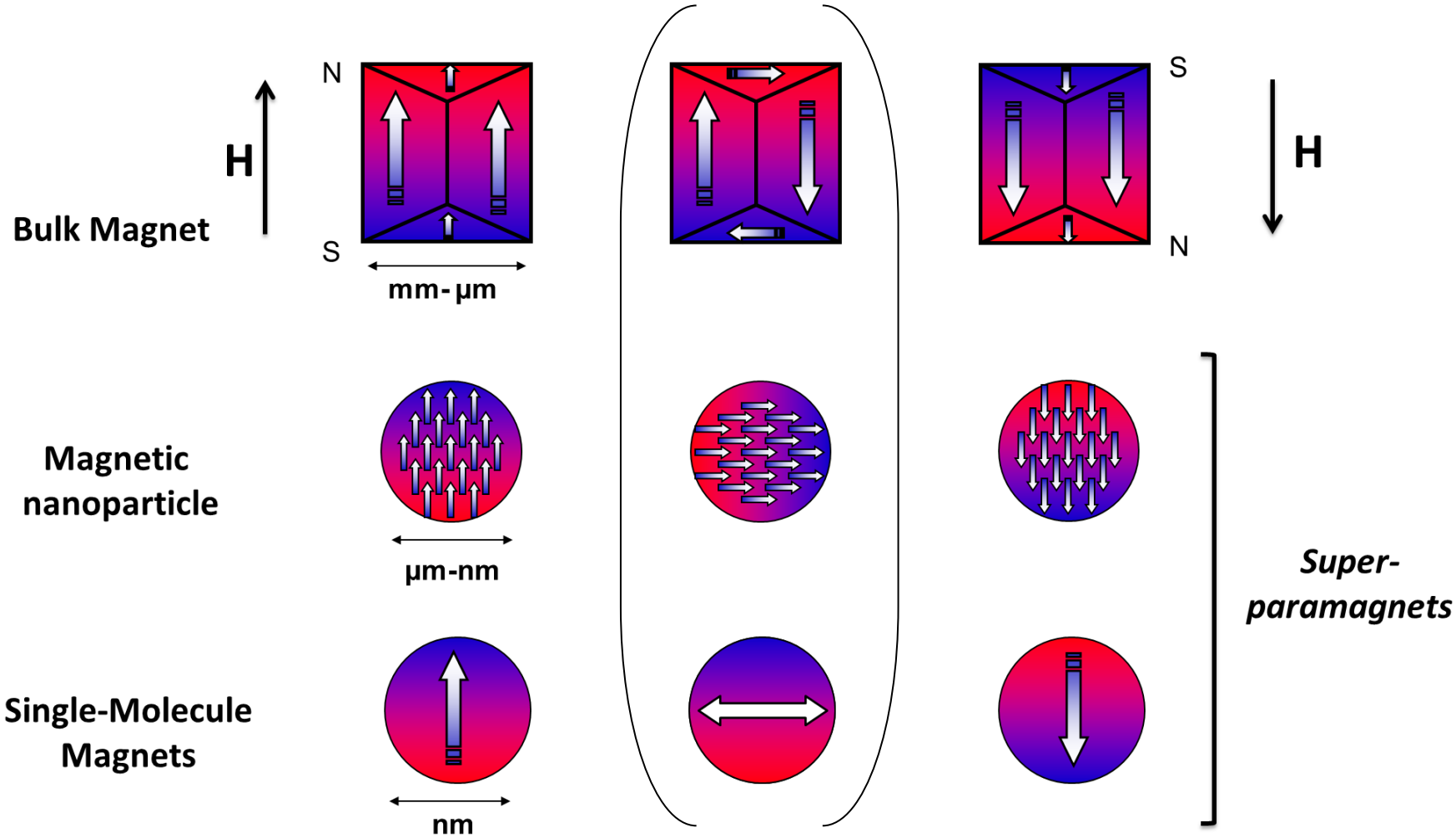


Hysteresis:

- **Dynamic lag between input and output**
- **The dependance of the state of a system on its history**
- **Rate-dependant (disapear if perturbation is slow)**
- **Rate-independant**

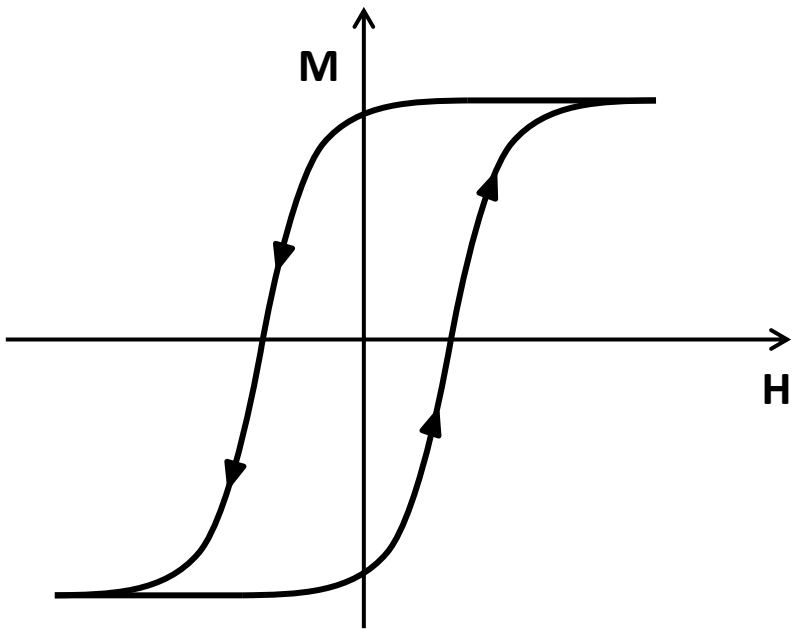
- **M_S : Magnetization @ saturation**
- **M_R : Remanent magnetization M@(H=0)**
- **H_C : Coercitive field H@(M=0)**

Magnetic hystereses

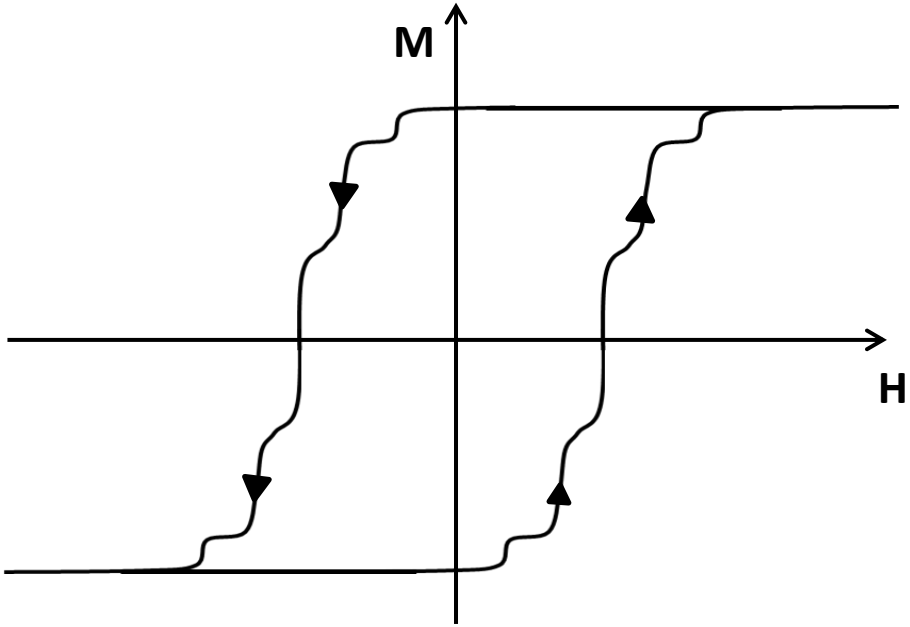


Magnetic hystereses

Nanoparticle



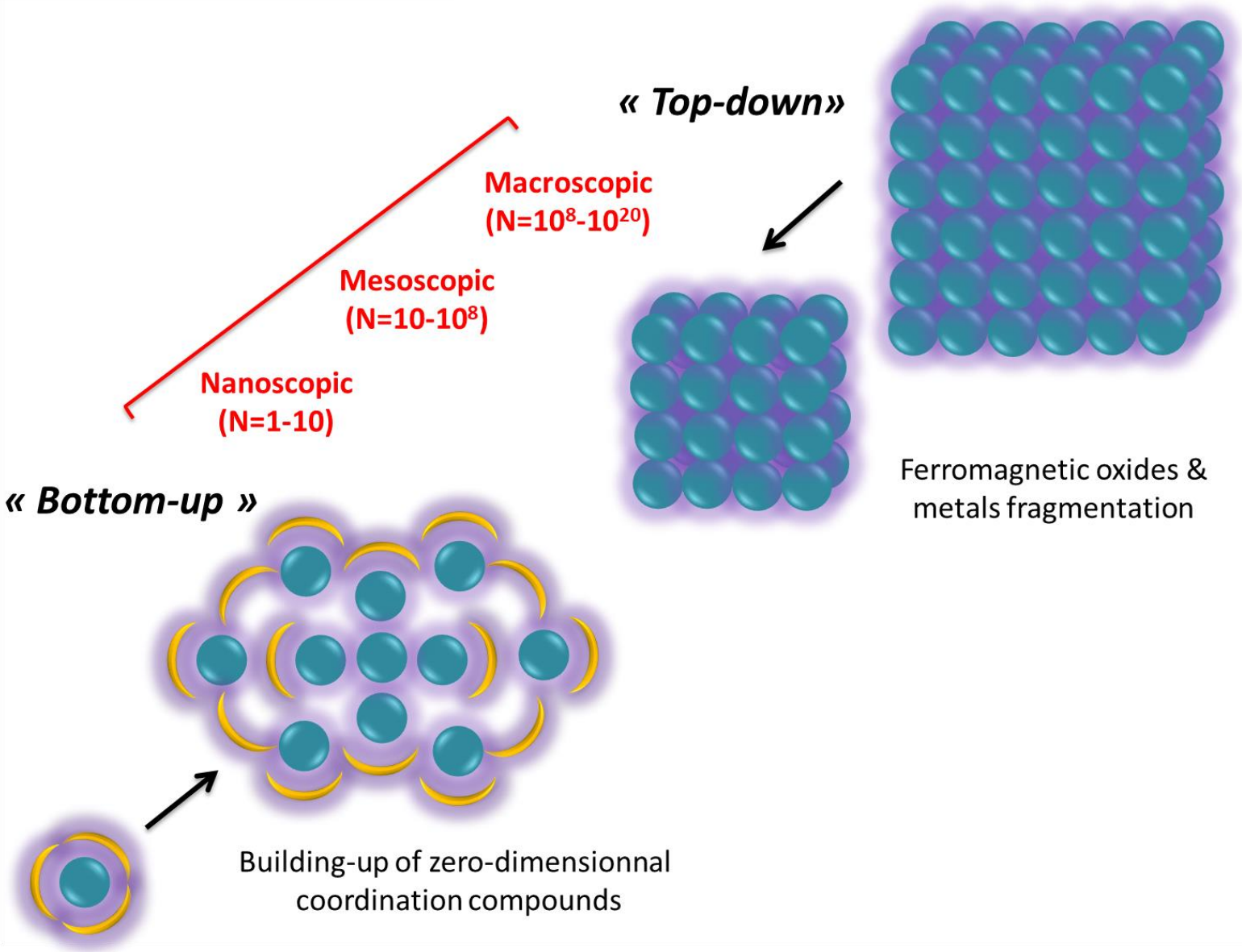
Single-Molecule Magnet



- **Hard (Hc > 5000 Oe) or soft magnet-like hysterese (Hc < 125 Oe)**

- **Hard-magnet-like hysterese with quantum effect (molecular quantum tunneling of the magnetization)**

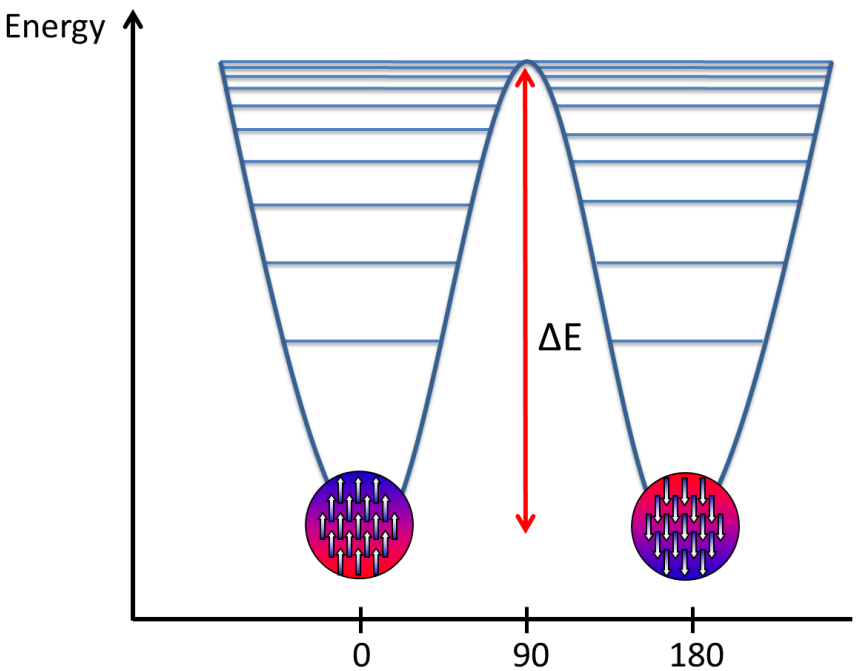
Toward magnetic materials



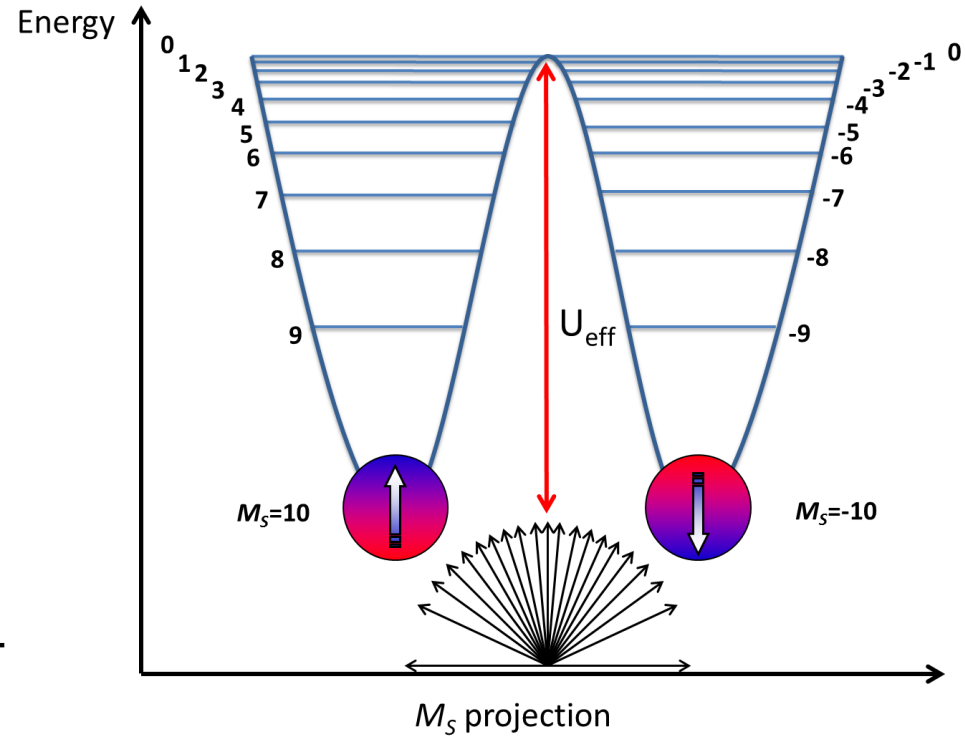
Spin reversal in Superparamagnets

Institut des Sciences Chimiques de Rennes UMR CNRS 6226

Nanoparticle



Single-Molecule Magnet

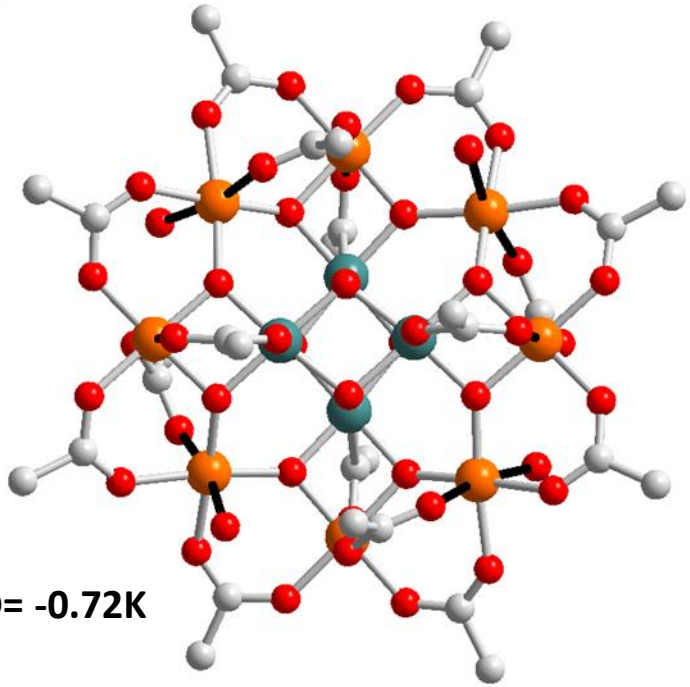


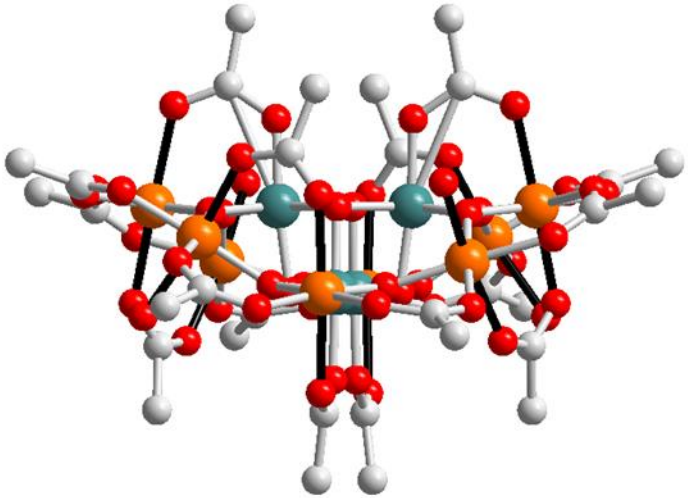
Level's energies: $E = KV\sin^2\phi - \mu_0 MVH\cos(\phi-\theta)$ → **M_S moment projections**

K: anisotropy constant; V: volume; M: magnetization; H: magnetic field
θ: particle magnetization angle; ϕ: magnetic field angle

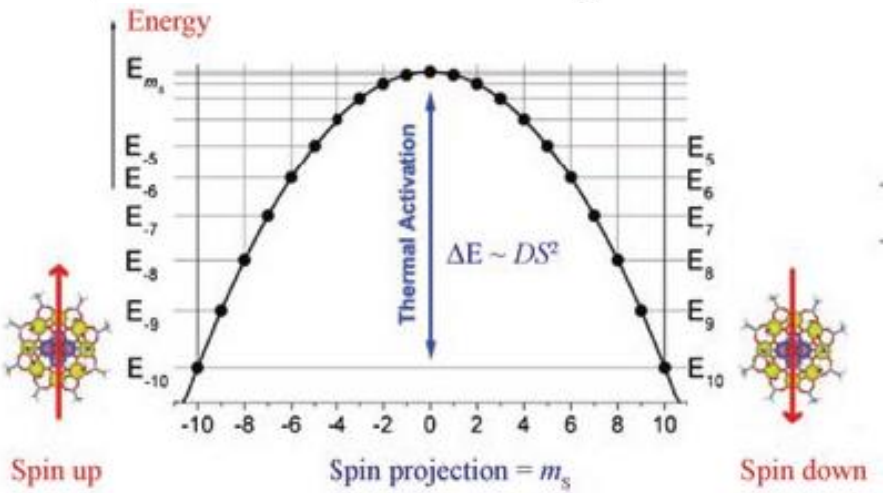
Relaxation above the barrier is $\tau = \tau_0 \exp(KV/k_BT)$ → **$\tau = \tau_0 \exp(U_{eff}/k_BT)$**
→ Stoner-Wohlfarh, Curling, nucléation/propagation/annihilation **→(Orbach)**

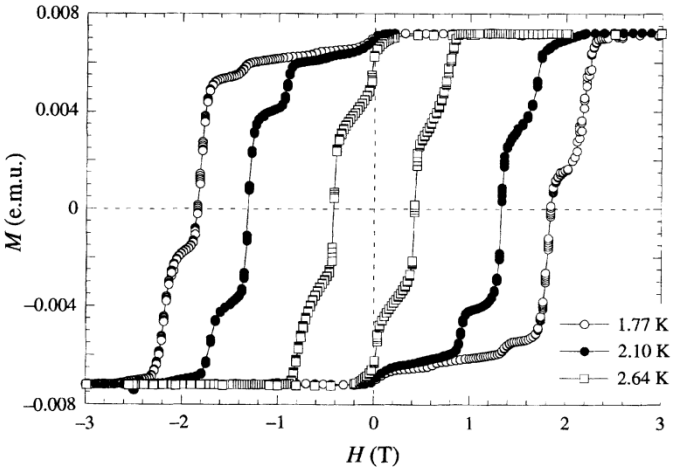
The iconic Mn_{12}





Spin S= 10
Anisotropy D= -0.72K
U_{eff}=72K



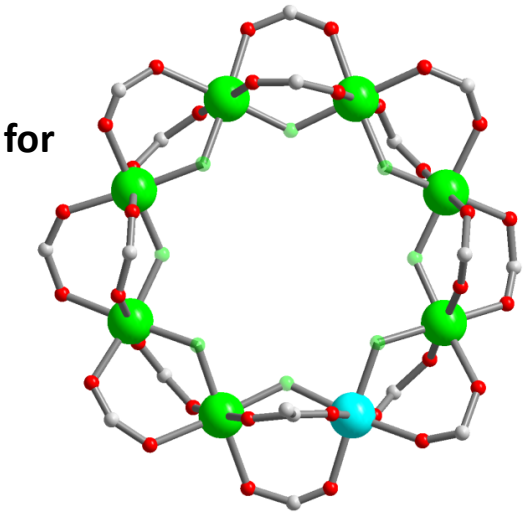


Thomas, L. *et al, . **Nature** 1996*, 383, 145-147.

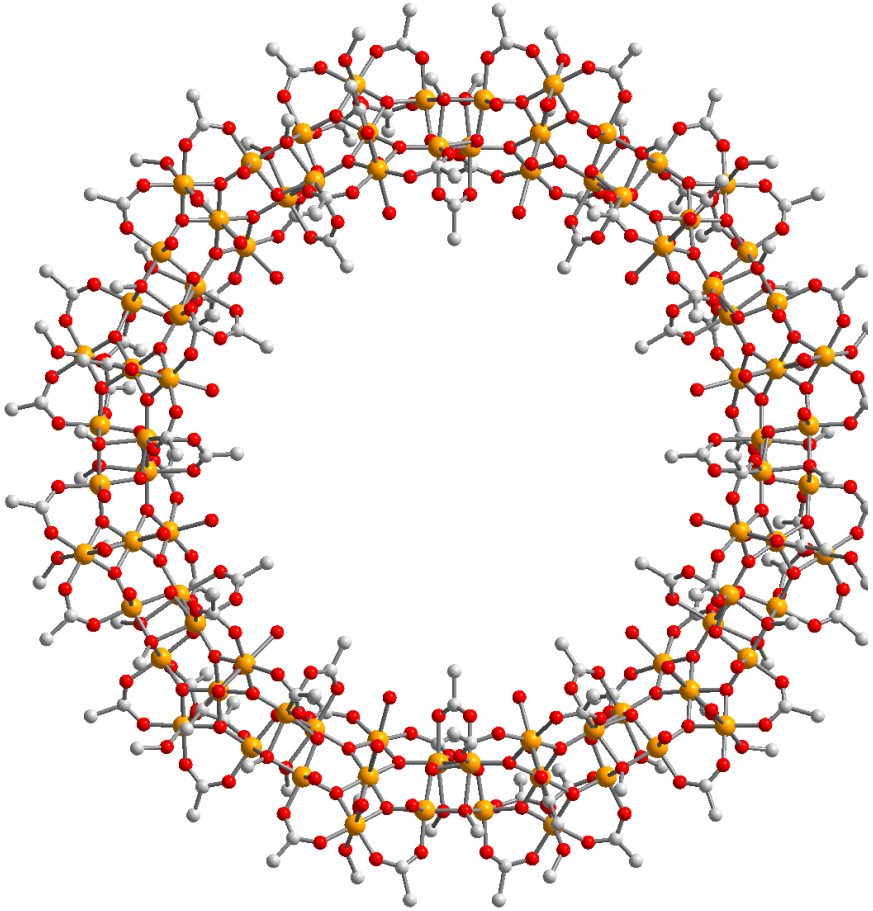
J. Tang, P. Zhang, **Lanthanide Single Molecule Magnets** , Springer, **2015**

Optimizing S…..

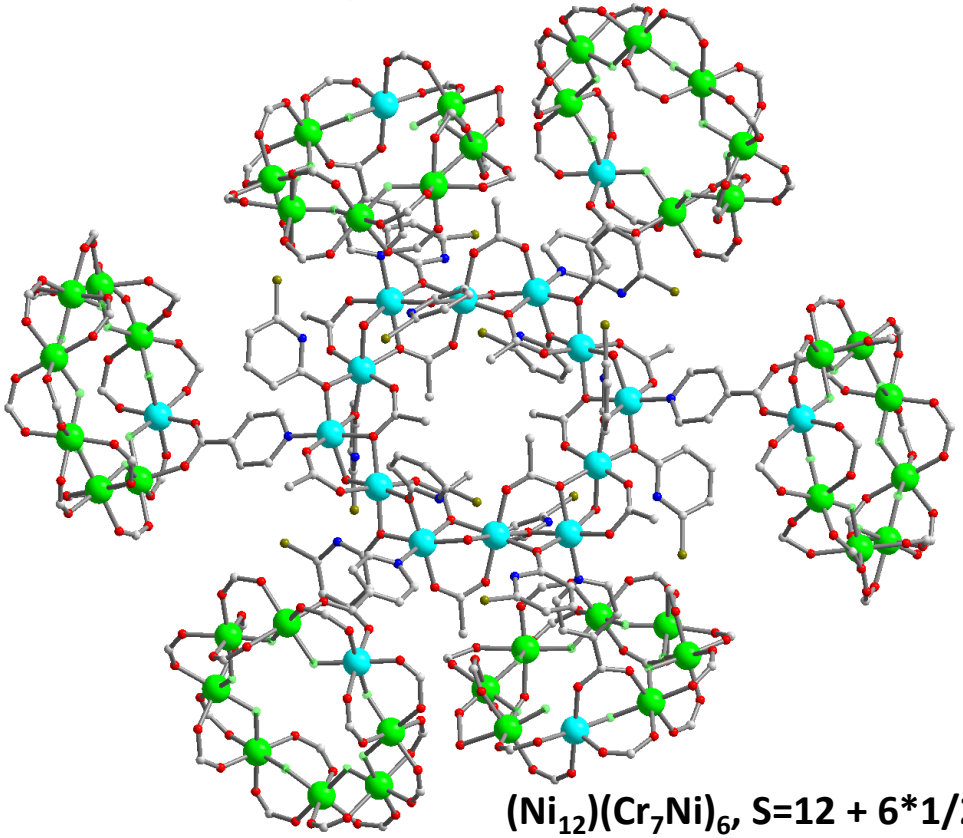
- **Amazingly beautiful molecules but no efficiency for magnetic slow relaxation**



Cr_7Ni, S=1/2



Mn_{84}, S=6, D= -0.21 cm^{-1}

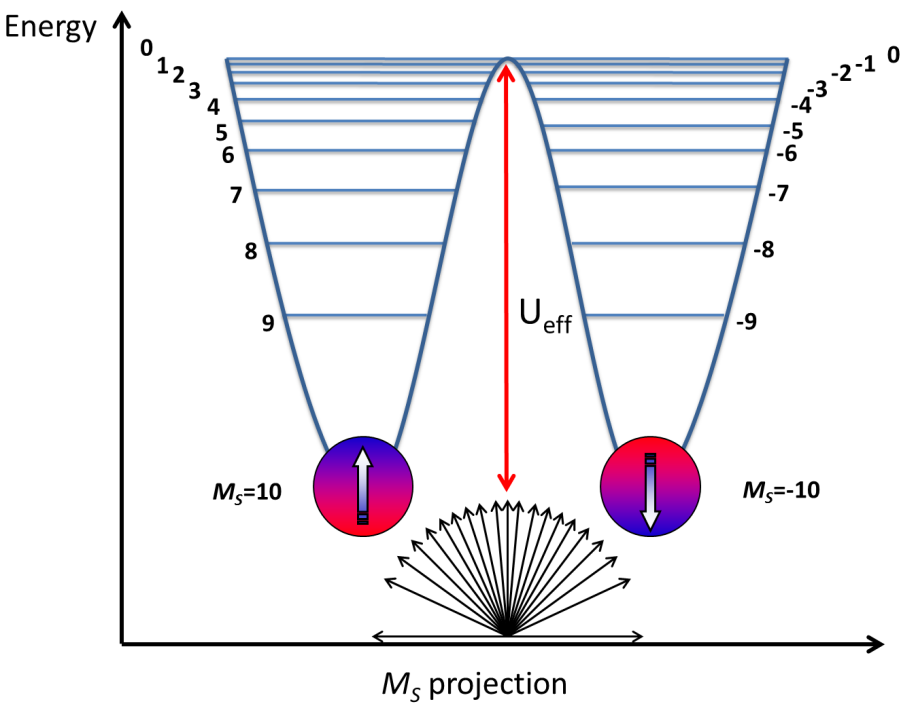


$(Ni_{12})(Cr_7Ni)_6$, S=12 + 6*1/2

Tasiopoulos, A. J. *et al.*, ***Angew. Chem.-Int. Edit***. **2004**, 43, 2117
Timco, G. A.; *et al.*. ***Nat Nano*** **2009**, 4, 173,
Andres, H. *et al.*, ***Chem. Eur. J.*** **2002**, 8, 4867.
Whitehead, G. F. S. *et al.*, ***Angew. Chem.-Int. Ed. 2013***, 52, 9932.

Spin reversal in Superparamagnets

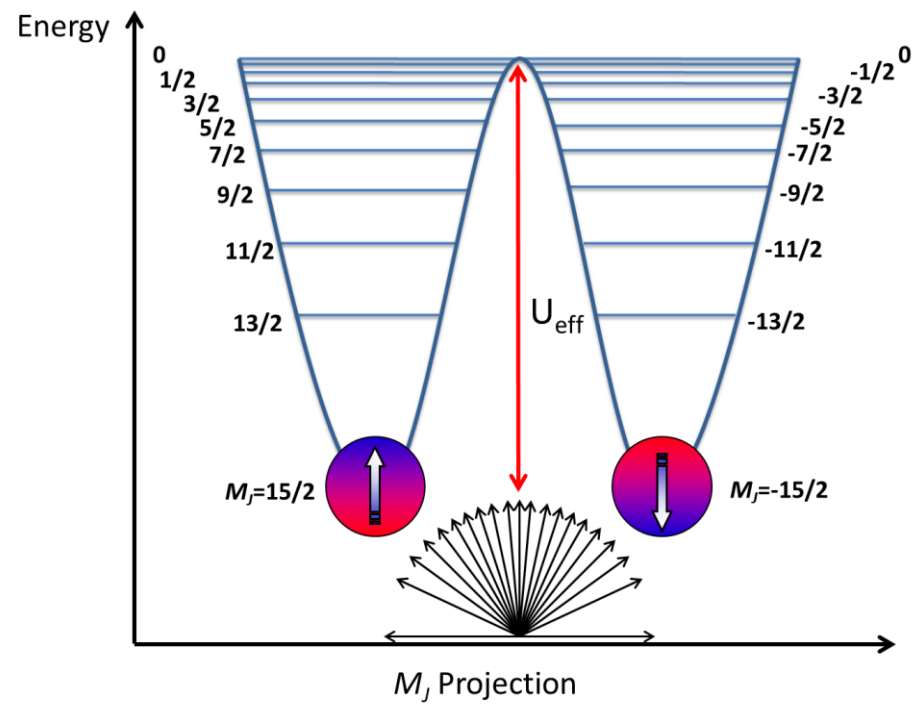
3d-SMM



Mn_{12} S=10

$U_{eff} \rightarrow |D|\ S^2$

4f-SMM



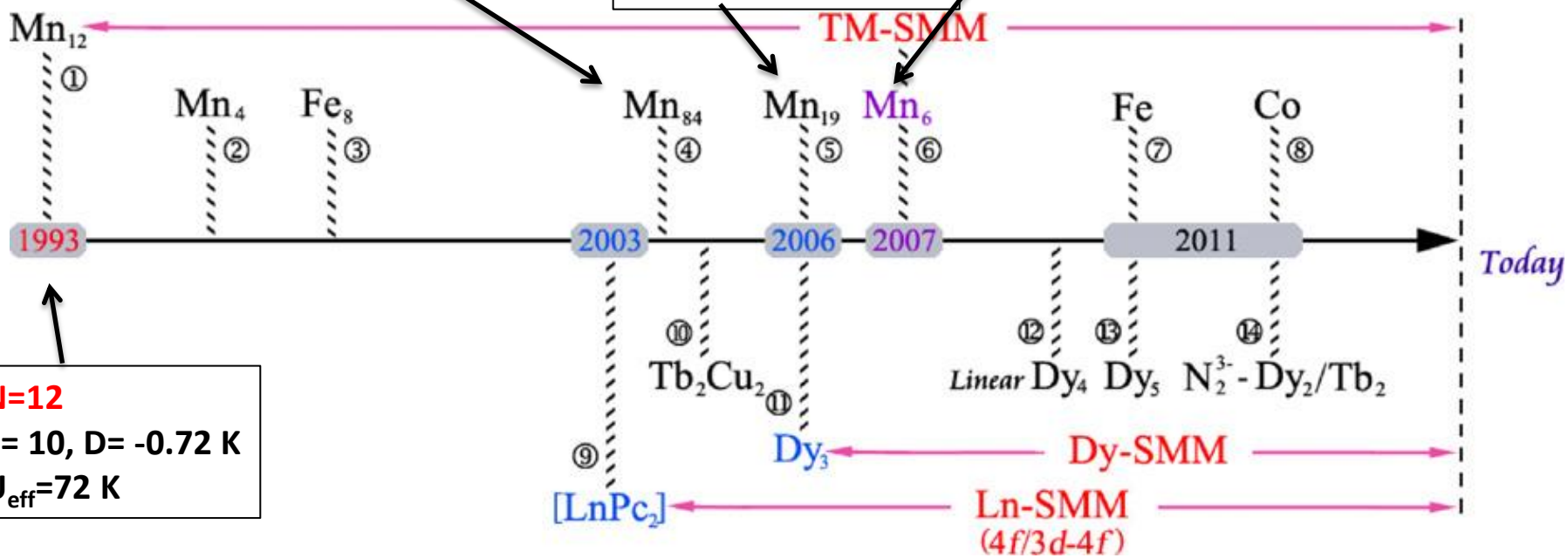
Dy $^6H_{15/2}$

Optimizing magnetic anisotropy

Biggest molecule N=84
S= 6, D=-0.21 cm^{-1}
U_{eff}=18 K

N= 19
Biggest spin S= 83/2
D= -0.004 cm^{-1}
(No SMM)

N= 6
S=12, D= -0.43 cm^{-1}
Biggest U_{eff} = 86.4 K (60 cm^{-1})

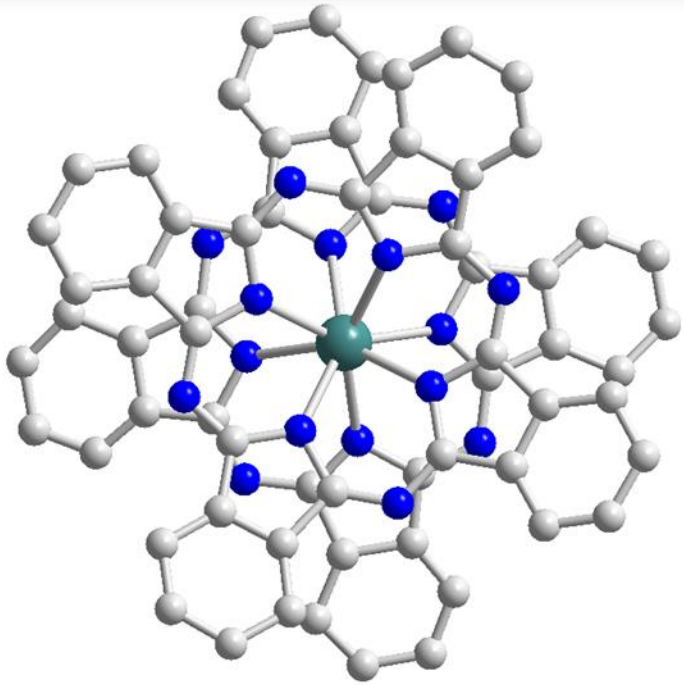


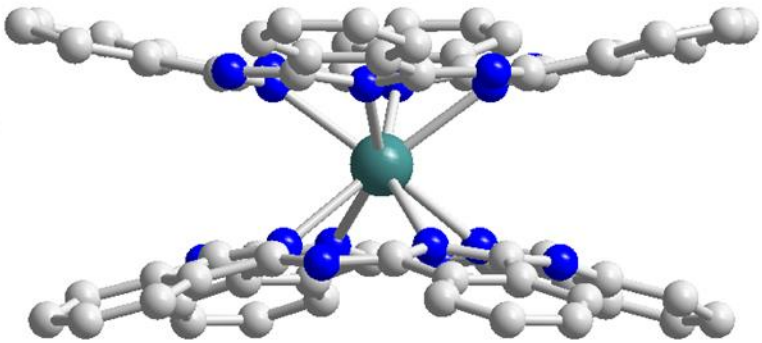
N=12
S= 10, D= -0.72 K
U_{eff}=72 K

Polynuclear SMM:
still a lot to do with 3d ions, but 4f ions are more and more used to design SMM

Mn_6: Milios, C. J.; ***J. Am. Chem. Soc.*** **2007**, *129*, 2754
Mn_{19}: AkoO, A. M.;. ***Angew. Chem.-Int. Ed.*** **2006**, *45*, 4926
Mn_{84}: Tasiopoulos, A. J.; ***Angew. Chem.-Int. Edit.*** **2004**, *43*, 2117
J. Tang, P. Zhang, **Lanthanide Single Molecule Magnets** , Springer, **2015**
Zhang P. et al., **Coord. Chem. Rev., 2013**, 257, 1728

The breaktrough of $TbPc_2$





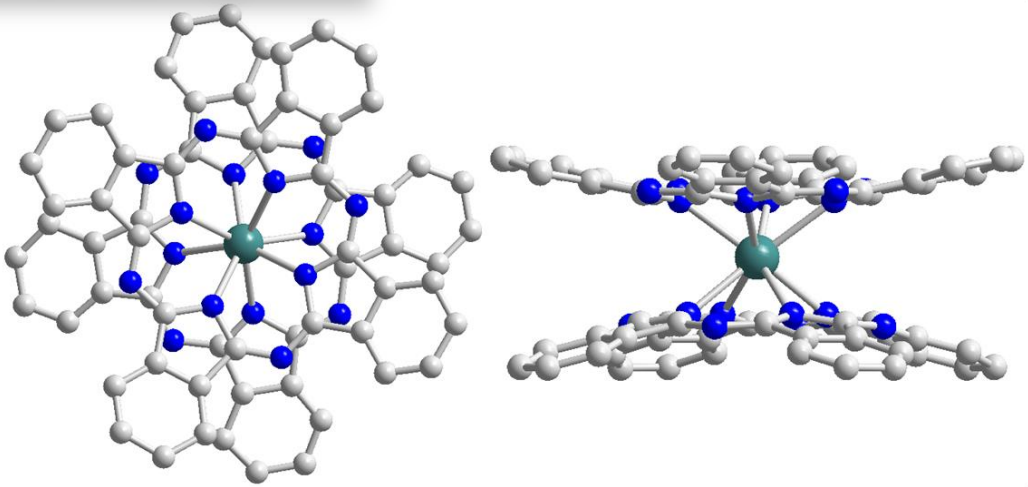
(TbPhtalocyanine$_2$)N(C_4H_9)$_4$ =$TbPc_2$ → U_{eff}= 330 K

In 2003, a revolution in the design of SMM:

- **No need for « giant spins » via polynuclear molecules**
- **Spins of 4f ions are enough and their anisotropy is huge**

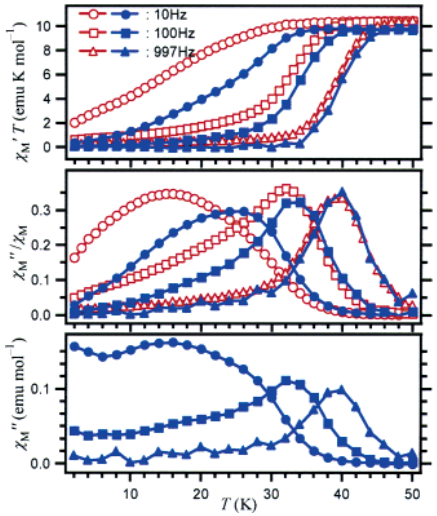
Spin optimization → → → Anisotropy optimization

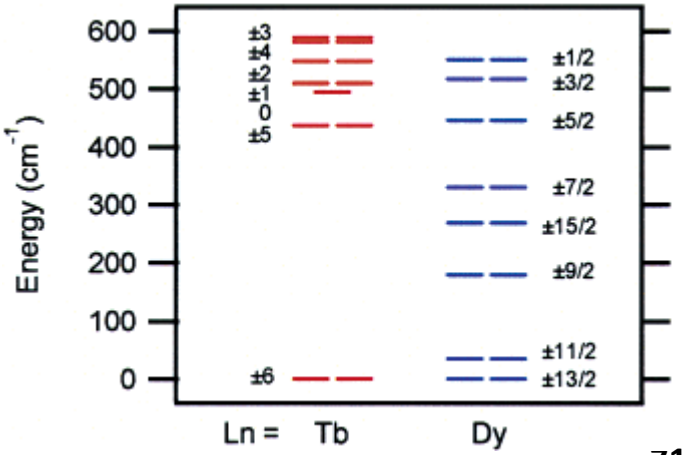
The breaktrough of $TbPc_2$



In 2003, a revolution in the design of SMM:

- **SMM behavior is observable if N=1 provided its anisotropy is huge : Single Ion Magnet**
  → better called « mononuclear SMM »
- **Dilution in isomorphous matrix (Y^{III}) is possible and enhances magnetic relaxation**
- **Sublevels structure (spilling of M_J) can be determined by ^1H NMR**

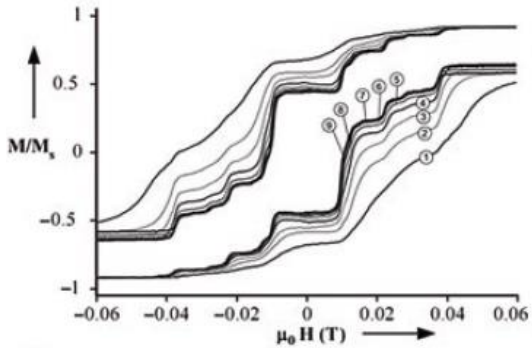




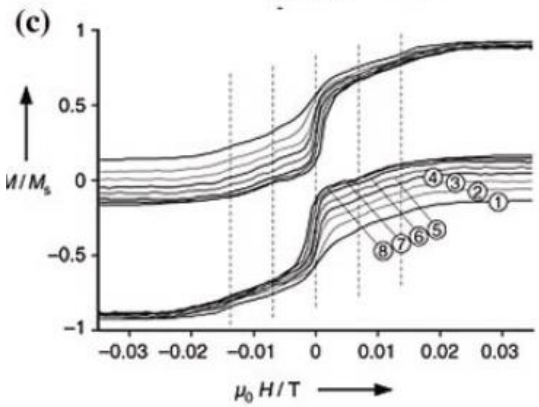
Ishikawa, N.; ***J. Am. Chem. Soc.* 2003**, *125*, 8694

The breaktrough of $TbPc_2$

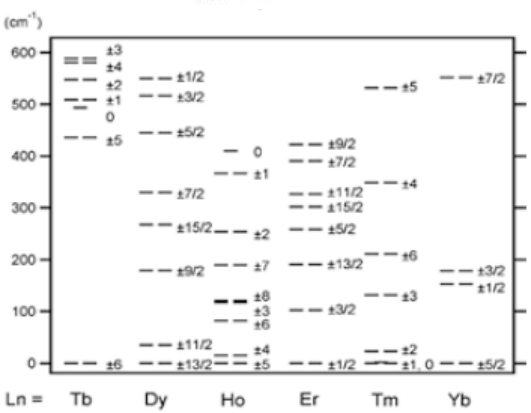
T= 0.04 K



Tb



Dy



Wide possibilities of chemical engineering of $LnPc_2$

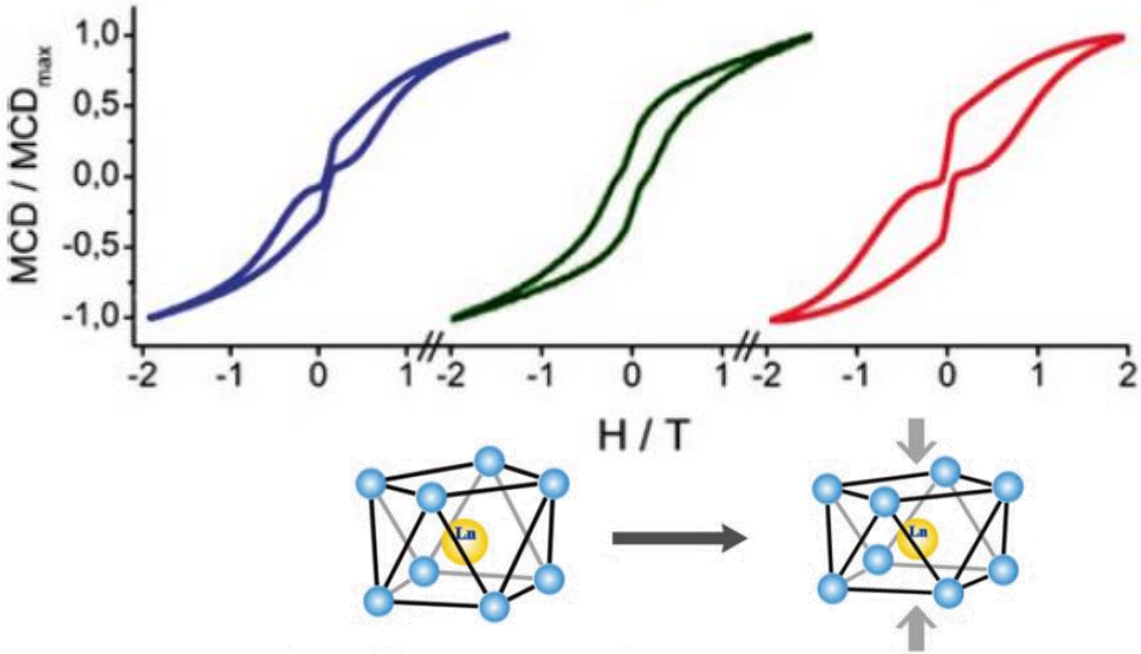
Molecule	U_{eff}/cm^{-1}	τ_0/s
$[Tb(Pc\text{-}OPh)_2]$	504	2.16×10^{-11}
$[Tb(Pc\text{-}Oph)_2]^- N(Me)_4^+$	442	8.2×10^{-11}
$[Tb(Pc\text{-}Oph)_2]^- N(Bu)_4^+$	394	3.45×10^{-10}
$[Tb(Pc)(Pc\text{-}Oph)]$	652	1.1×10^{-11}
$[Tb(Pc)(Pc\text{-}Oph)]^- N(Me)_4^+$	450	3.0×10^{-10}
$[Tb(Pc)(Pc\text{-}Oph)]^- N(Bu)_4^+$	487	7.8×10^{-11}
$[Tb(Pc)(Pc\text{-}Bu)]$	642	2.21×10^{-11}
$[Tb(Pc)(Pc\text{-}Bu)]^- N(Bu)_4^+$	400	4.78×10^{-10}
$[Tb(Pc\text{-}ODOP)_2]$ (order)	480	
$[Tb(Pc\text{-}ODOP)_2]$ (disorder)	422	
$[Tb(Pc\text{-}a)_2]^- N(Bu)_4^+$	445	6.35×10^{-11}
$[Tb(Pc\text{-}b)_2]^- N(Bu)_4^+$	428	1.34×10^{-10}
$[Tb(Pc\text{-}c)_2]^- N(Bu)_4^+$	463	2.22×10^{-11}
$[Tb(Pc\text{-}OBu)_2]_2$	230	1.1×10^{-10}
$[Dy(Pc\text{-}OBu)_2]_2$	44	1.3×10^{-5}
$[Dy(Pc\text{-}CN)_2]$	40	

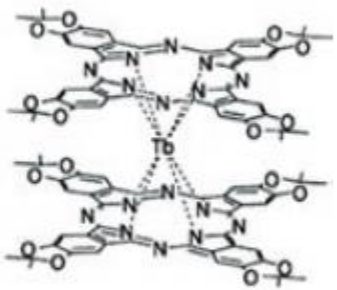
Bagai, R.; Christou, G. , *"The Drosophila of Single-Molecule Magnetism: Mn_{12}.* ***Chem. Soc. Rev. 2009,*** *38, 1011.*

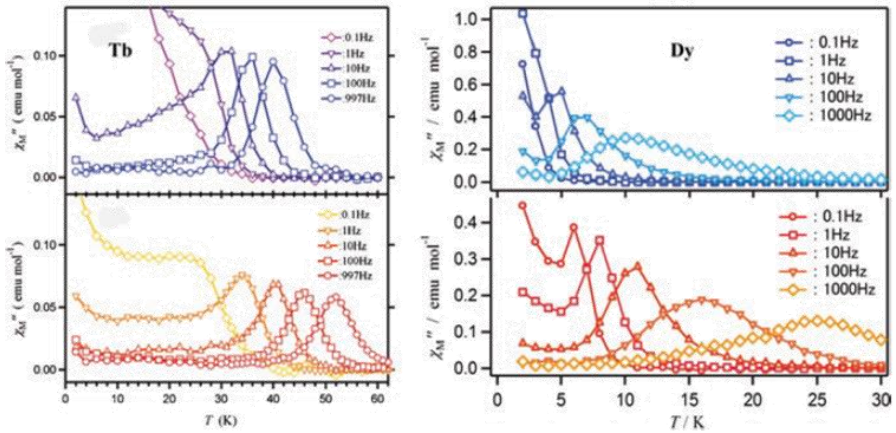
$TbPc_2$ is the 4*f*-SMM drosophila

Playing with $TbPc_2$

$$[Pc_2Tb]^- \xrightleftharpoons{-1e^-} [Pc_2Tb]^0 \xrightleftharpoons{-1e^-} [Pc_2Tb]^+$$





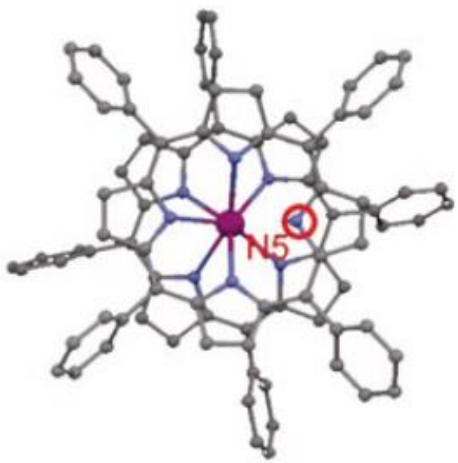


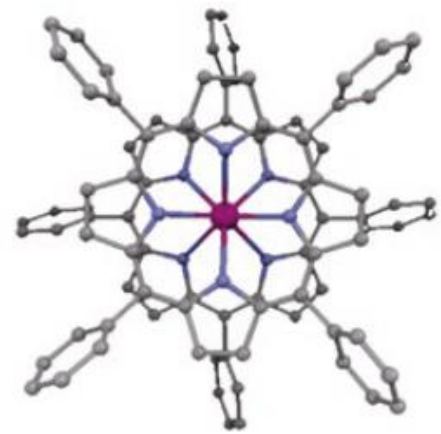
Gonidec M, et al., *J. Am. Chem. Soc.* **2010**, 132(6), 1756

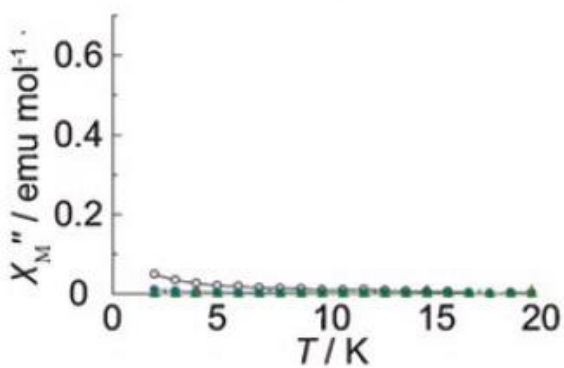
Playing with$TbPc_2$

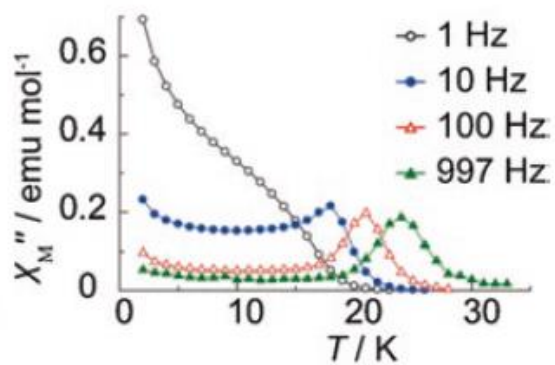
Phtolocyanine analogues (tetraphenylporphyrin) to test the electrostatics around Tb^{III} [TbH$(TPP)_2$]:

Protonated [TbH$(TPP)_2$]: **de-protonated $[Tb(TPP)_2]^-$: U_{eff}= 407 K**



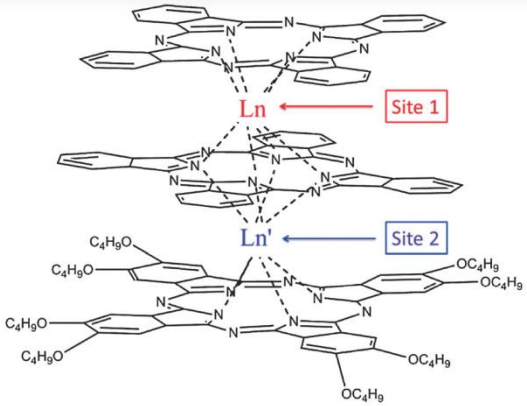


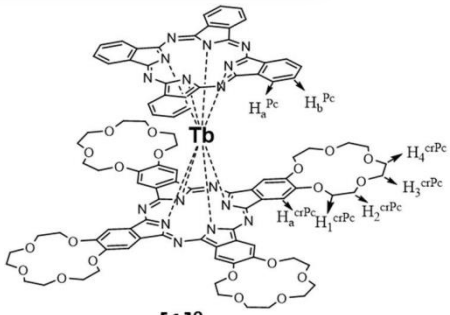




Tanaka D, et al. ***Chem Commun* 2012**, 48(63):7796.

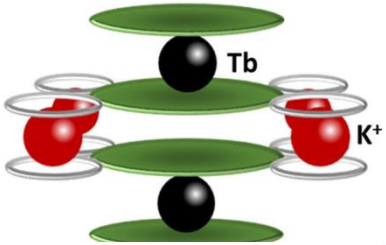
The breaktrough of $TbPc_2$

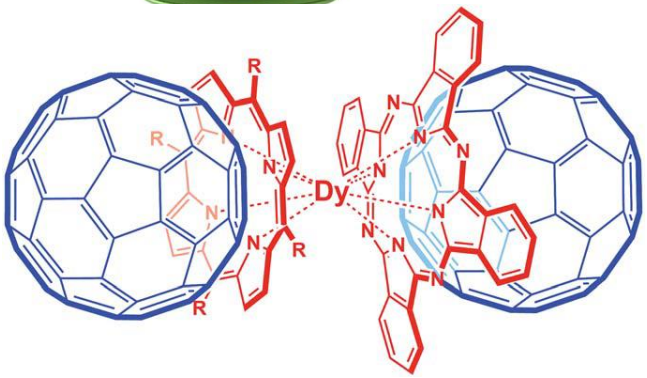


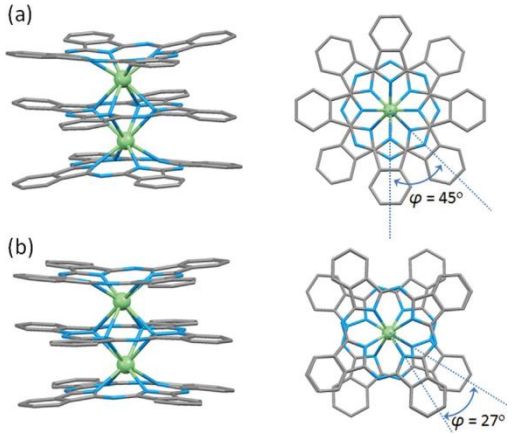


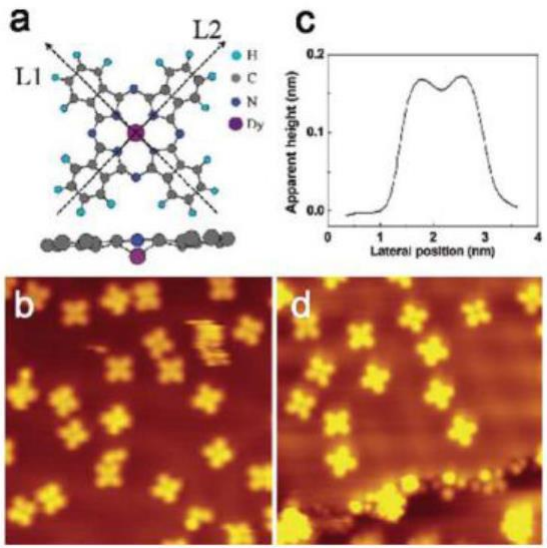
[1]⁰

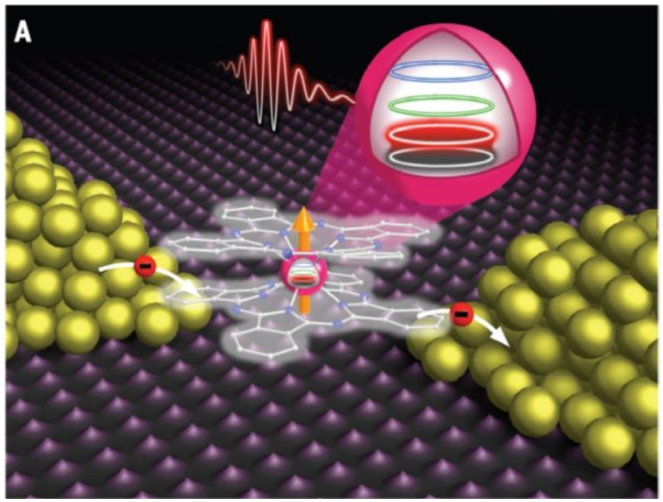
KOAc







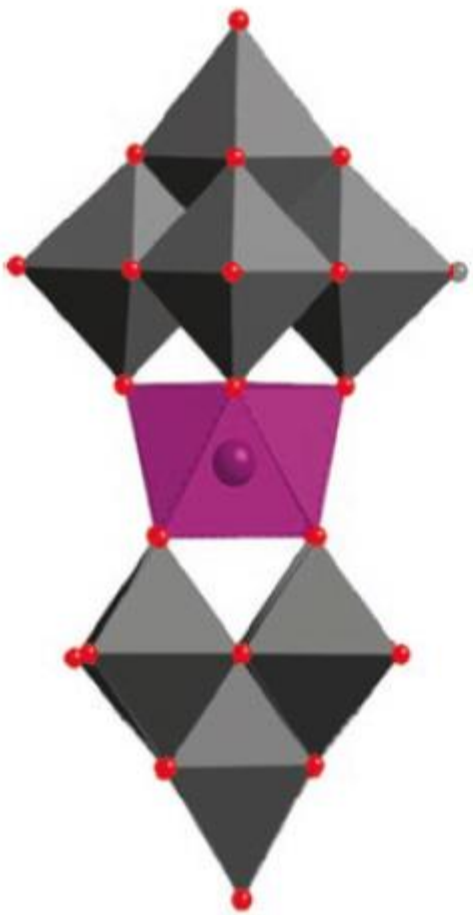


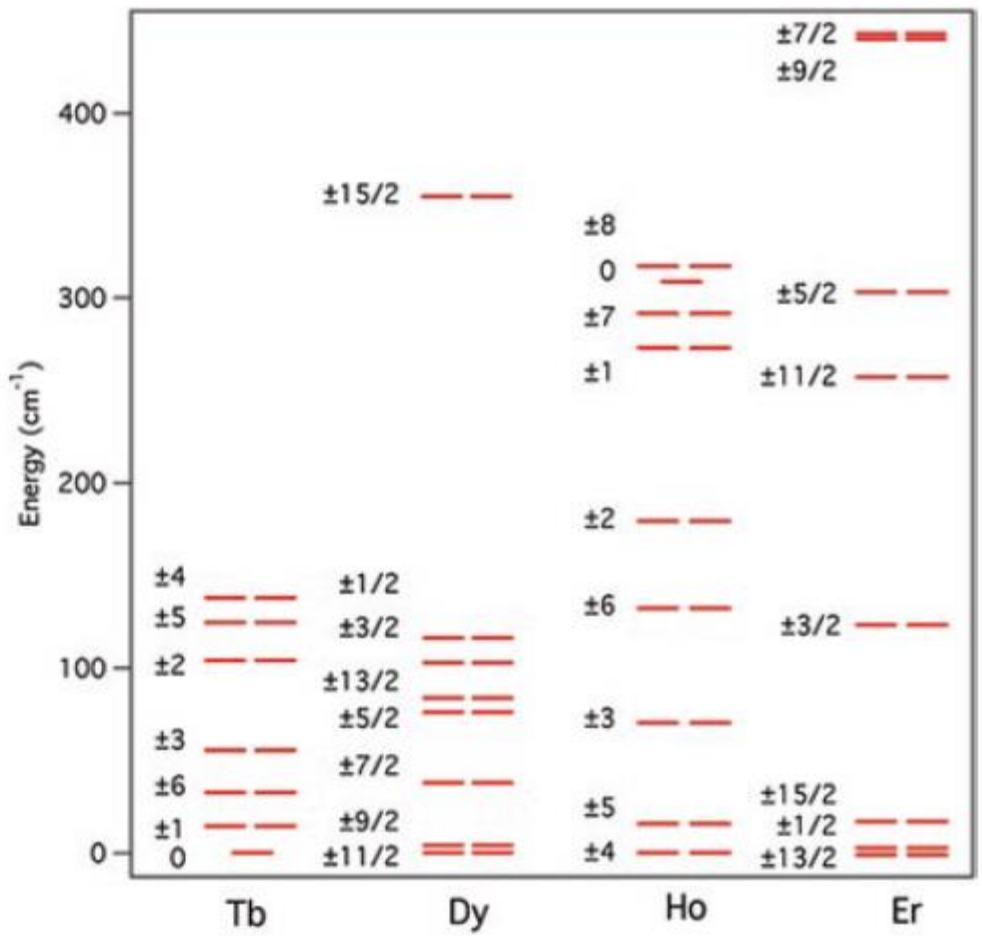


Wang, H. *et al.*, ***Coord. Chem. Rev.*** **2016**, *306*
Wang, H. *et al.* ***Chem. Sci.*** **2014**, *5*, 3214, 195.
Katoh, K. *et al.*, ***Chem. Eur. J.*** **2017**, *23*, 15377
Horii, Y., *et al.* ***Chem. Eur. J.*** **2018**
Thiele , S., *et al.* ***Science*** **2014,** 344, 1135
K. Katoh, et al., ***Dalton Trans.*** **2010**, 39 4708

Ln-POM

- **Ln polyoxometalates → the second 4*f*-SIM family**

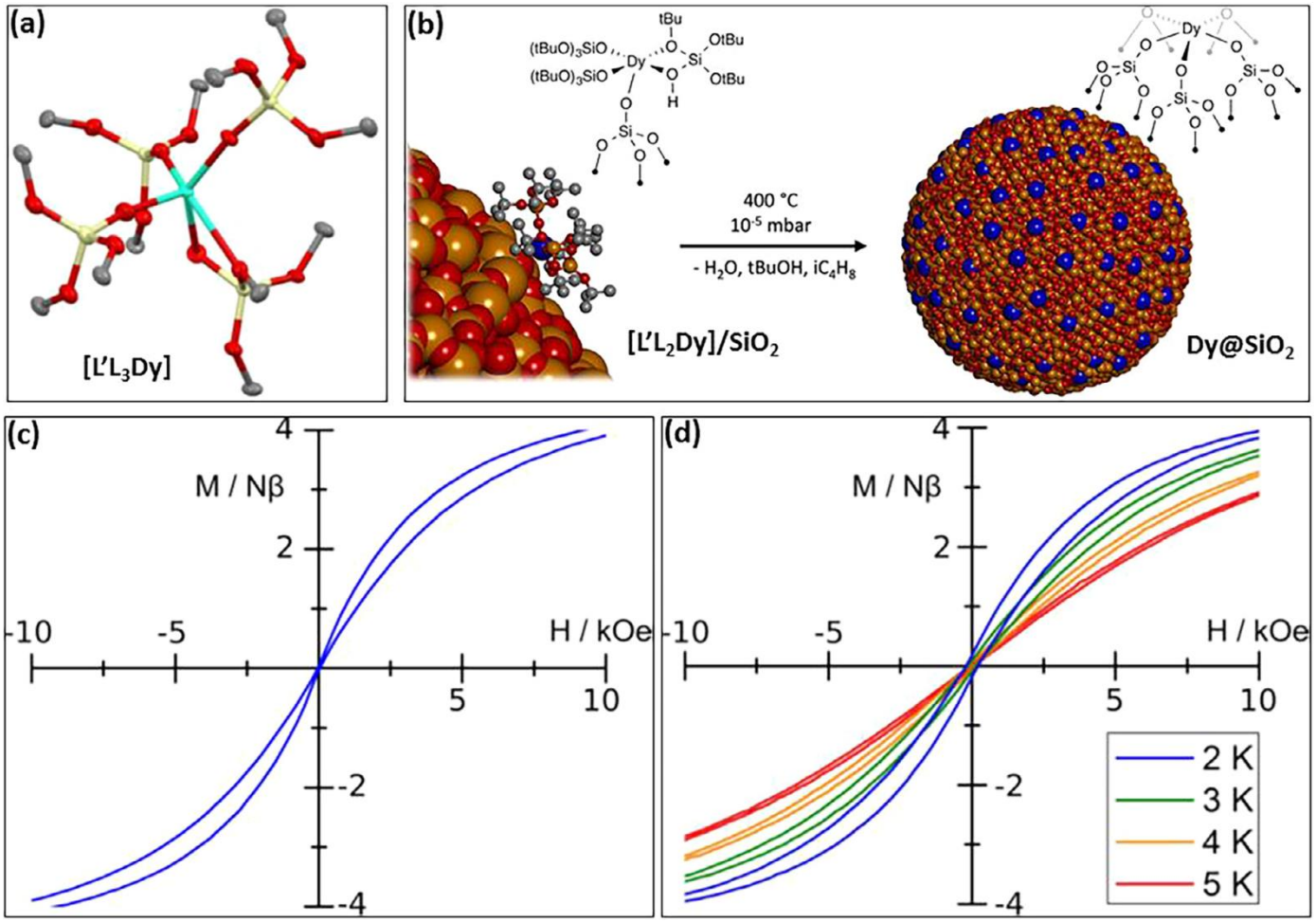




Baldoví, J. J.; et al. , In ***Advances in Inorganic Chemistry***; Academic Press, **2017**; Vol. 69; pp 213-249.

Low coordinate Ln^{III}

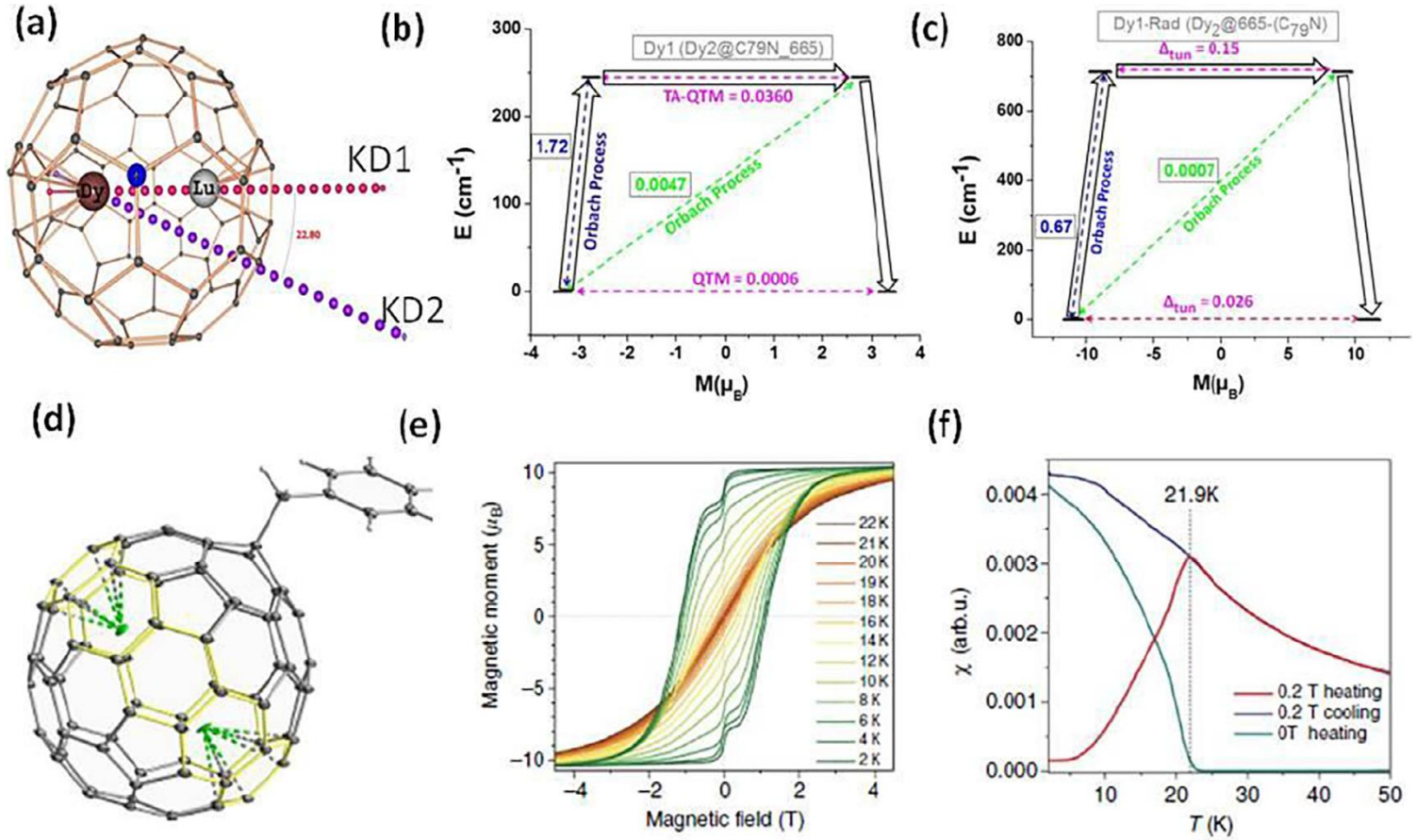
- **via grafting on SIO_2 nanoparticules**



F. Allouche, *et al.*, ***ACS Cent. Sci.* 2017**, 3, 244
Bar A. K. et al., ***Coord. Chem. Rev.* 2018**, 367, 163

Low coordinate Ln^{III}

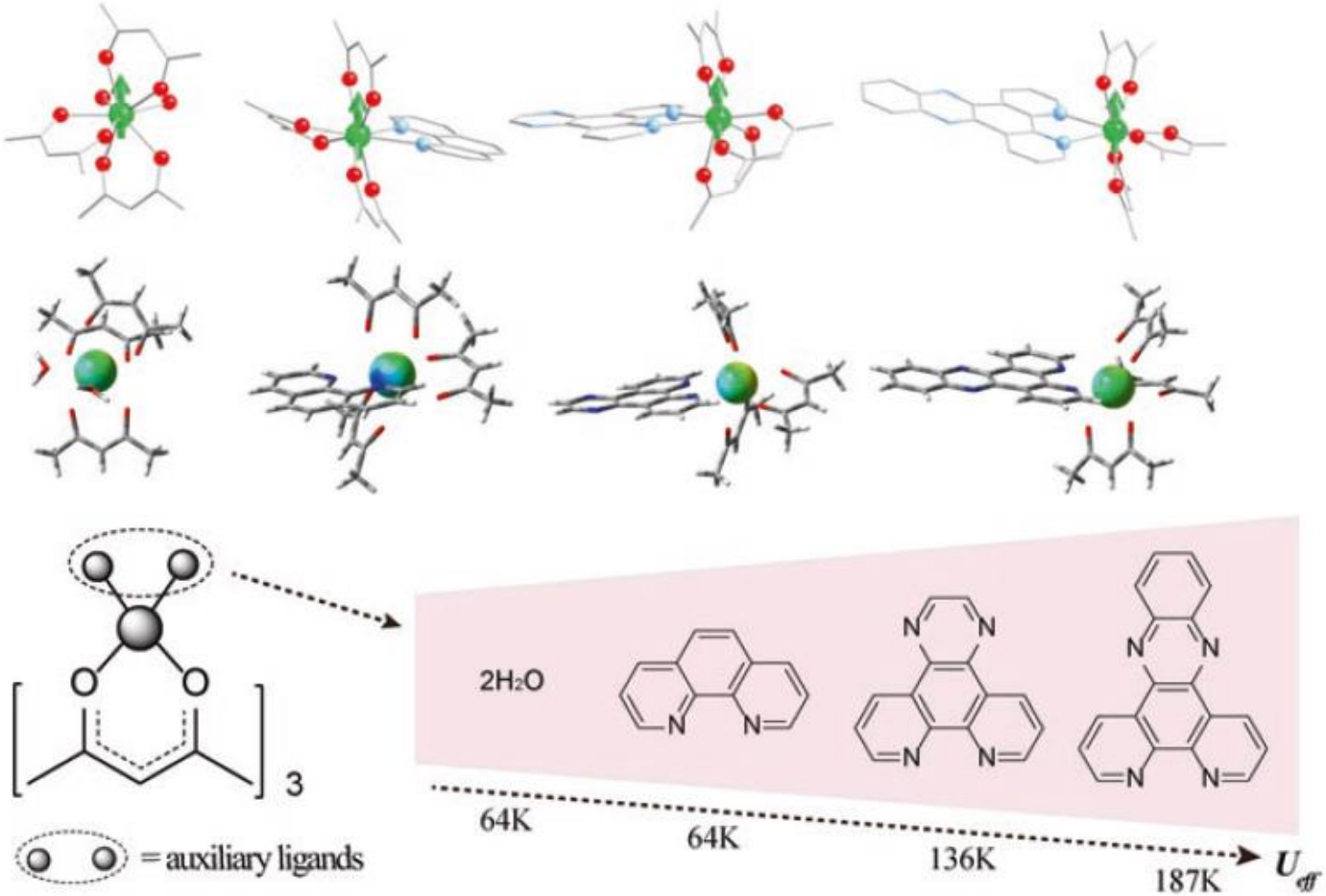
- **via encapsulation in fullerenes derivatives**



F. Liu et al., ***Nat. Commun.* 2017** 8, 16098
Bar A. K. et al., ***Coord. Chem. Rev.* 2018**, 367, 163

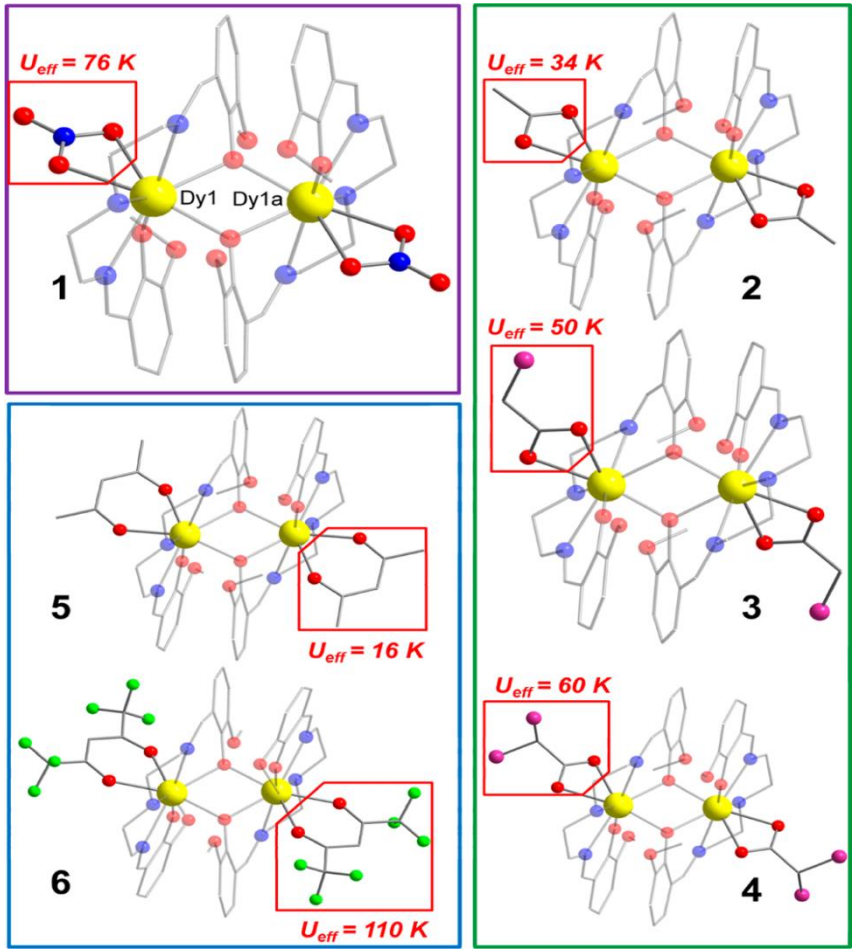
Electrostatics optimization in 4*f*-SMM

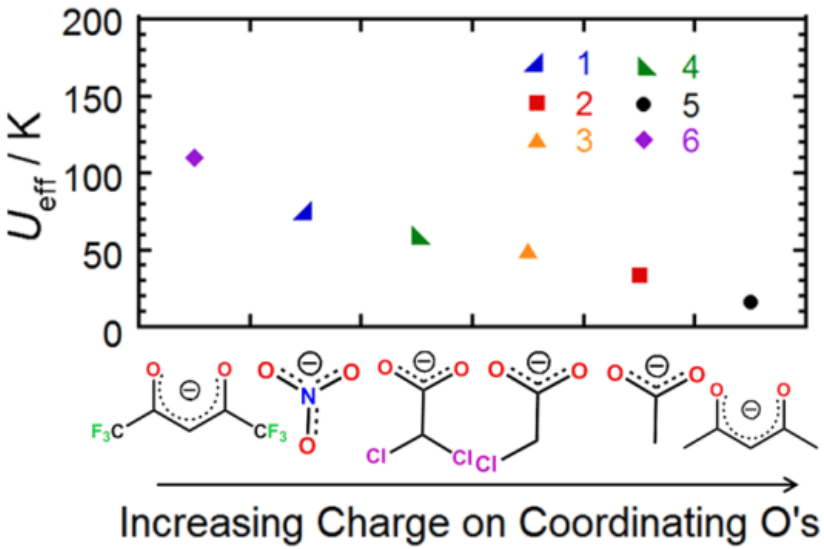
- **Going for polynuclear 4*f*-SMM enhance the possibility of electrostatic modulation of the Ln^{III} surrounding (ancillary or bridging ligand tunning)**



D. Aravena *et al.* ***Inorg Chem* 2013***,* 52(23), 13770

Electrostatics optimization in 4*f*-SMM

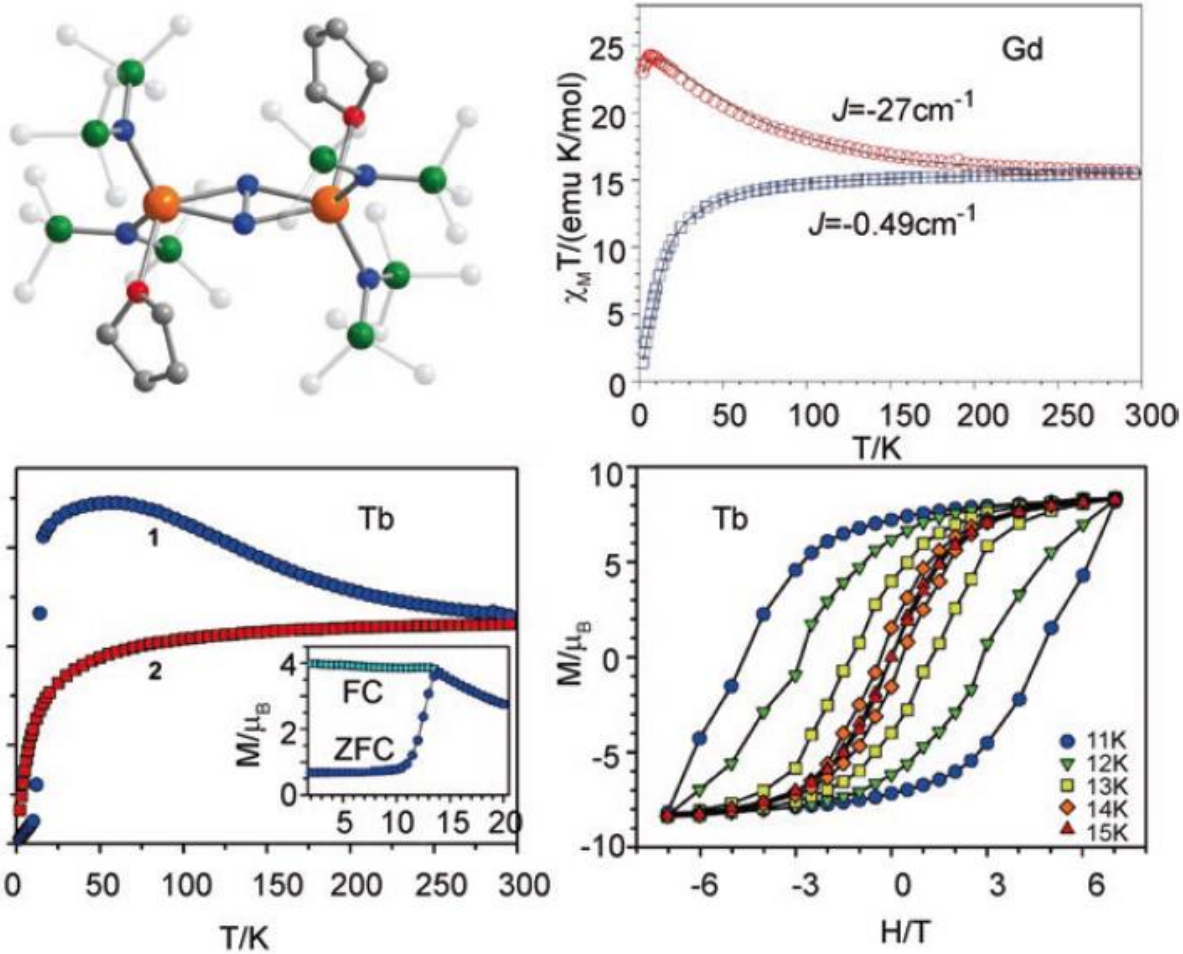




Habib, F.; *et al.* ***J. Am. Chem. Soc.*** **2013**, *135*, 13242

Ln^{III} coupling

$[\{[(Me_3Si)_2N]_2Ln(THF)\}_2(\mu\text{-}\eta^2\text{:}\ \eta^2\text{-}N_2)]_2$



- **Need for radical ligands otherwise 4*f*-4*f* interactions are weak (dipolar + very small exchange)**
- **Need for small ligands → N_2^{3-}**

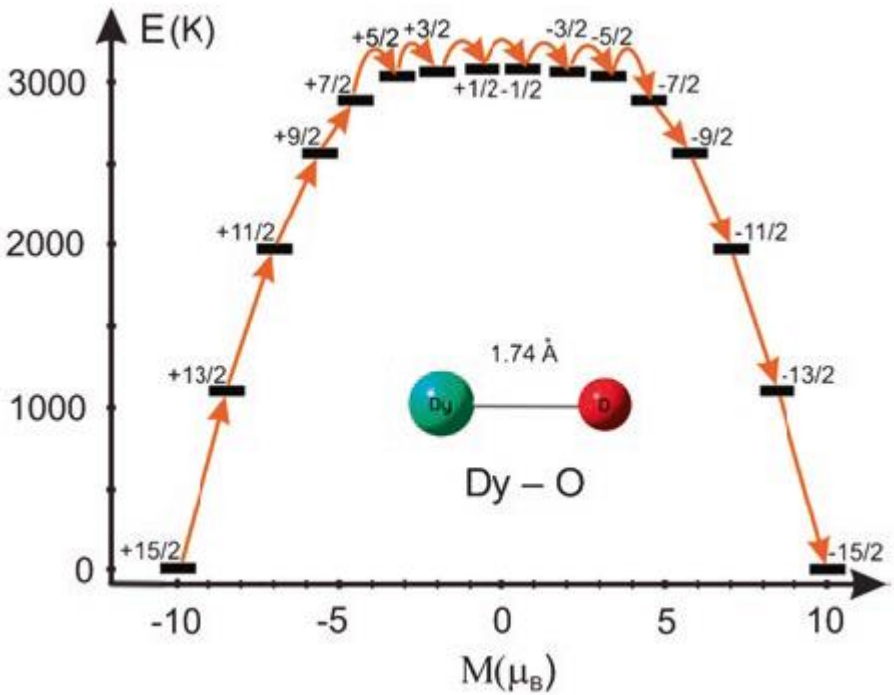
Rinehart, J. D.; *et al.* ***J. Am. Chem. Soc.*** **2011**, *133*, 14236

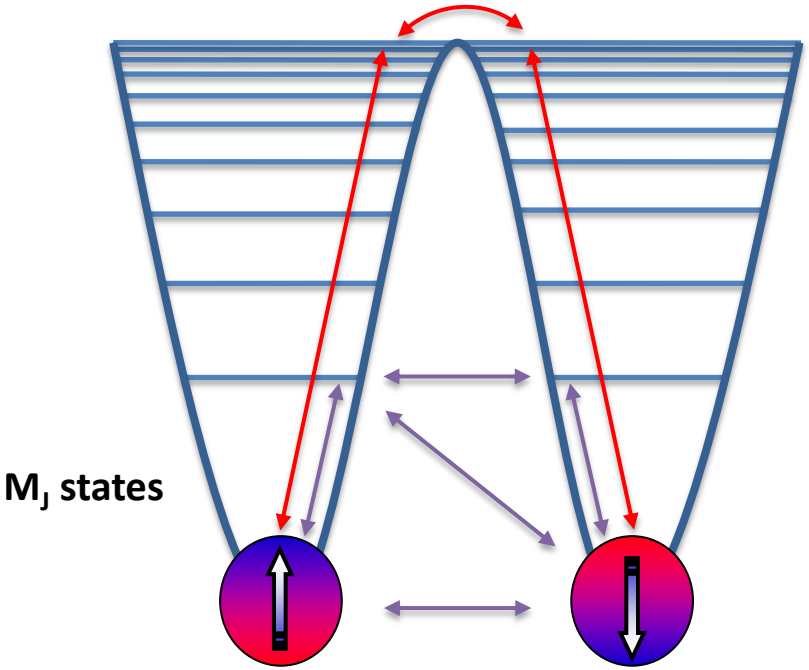
Rinehart, J. D.; *et al.*, ***Nat. Chem.*** **2011**, *3*, 538

Optimizing magnetic anisotropy

Institut des Sciences Chimiques de Rennes UMR CNRS 6226

Theoretical approach of U_{eff}



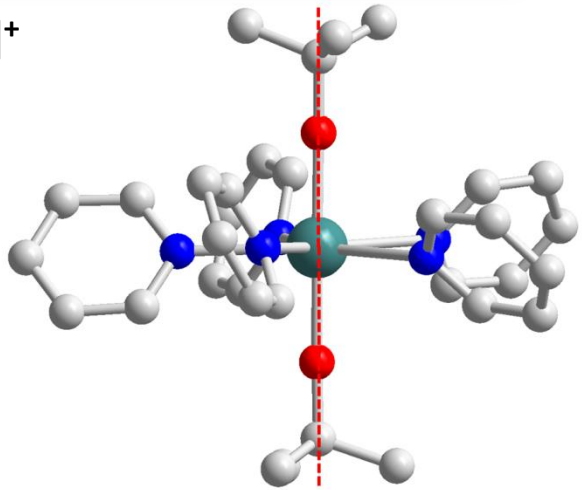


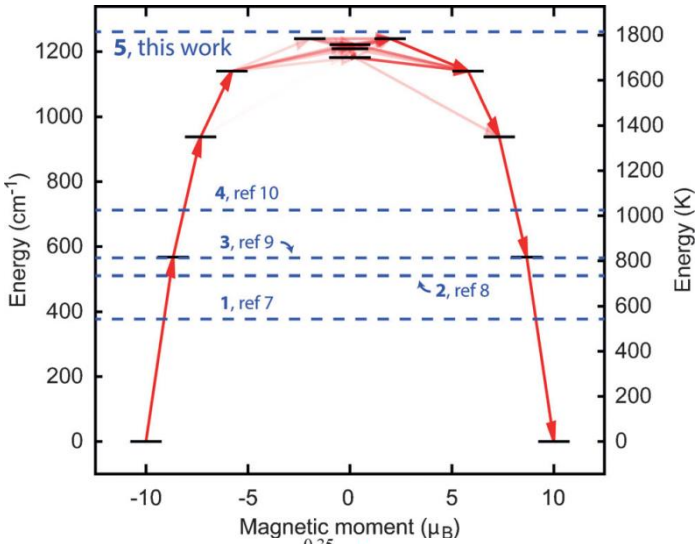
- **For a Dy-O distance of 1.74 Å, theoretical value of U_{eff} can be as high as $U_{eff} \approx 3000$ K**
- **If under-barrier relaxation mechanisms are suppressed, very high T_B can be targeted**

Ungur. L., *et al.* ***Phys. Chem. Chem. Phys.*** **2011**, *13*, 20086

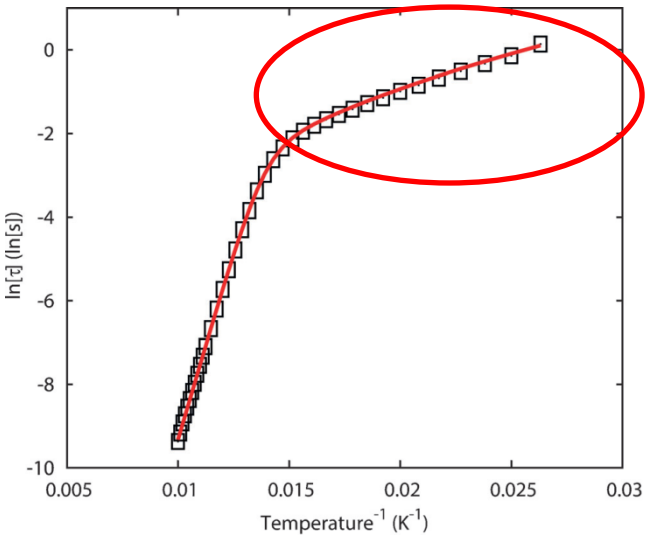
Closer to the perfect Dy symettry

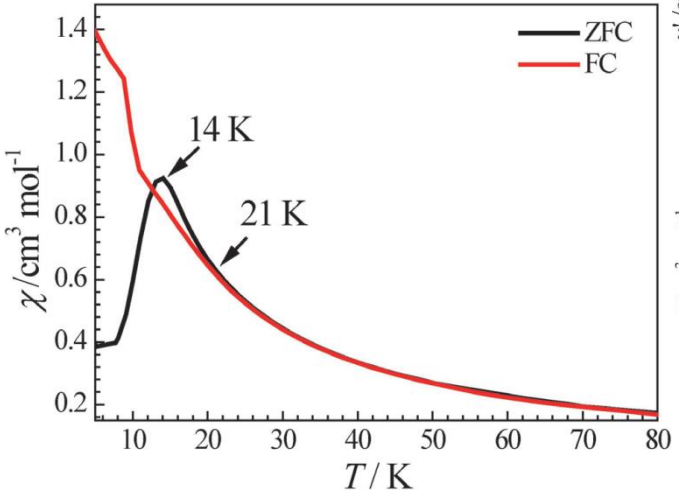
$[Dy(O^tBu)_2(Py)_5]^+$
O-Dy-O= 178.9°
U_{eff}= 1815 K
T_B=14K

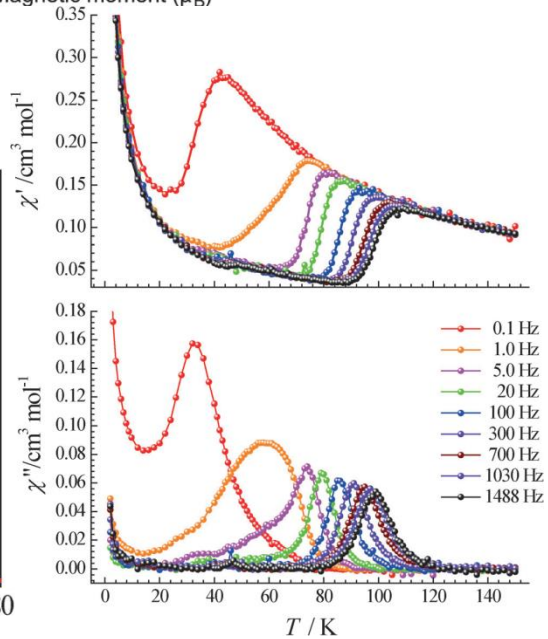




- **Optimization of the M_J= 15/2 stabilization** by increasing the O-Dy-O angle (closer to 180°)
- **Underbarrier relaxation** at low T still possible







Ding, Y.-S. et al., ***Angew. Chem.-Int. Ed.* 2016**, *55*, 16071

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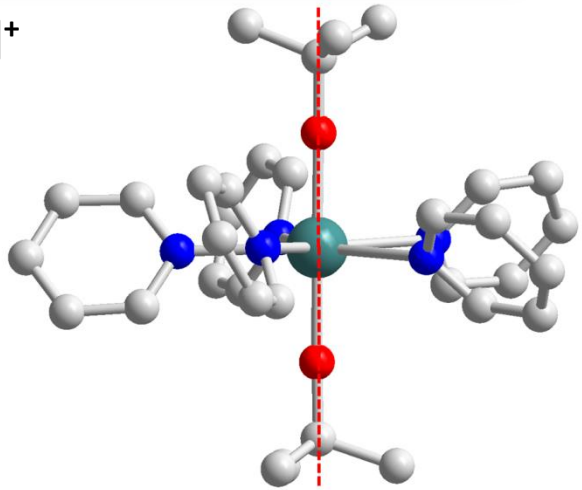

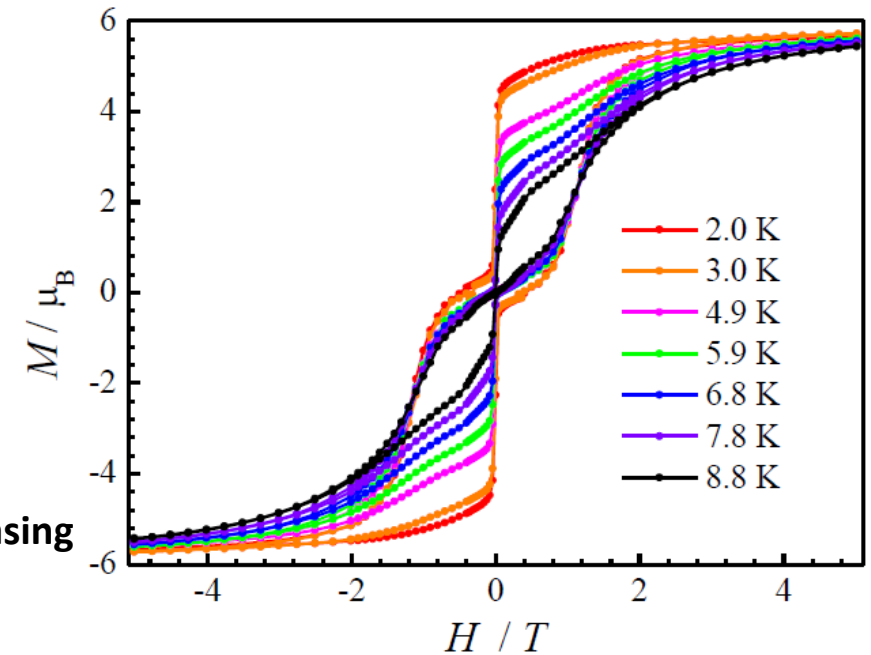

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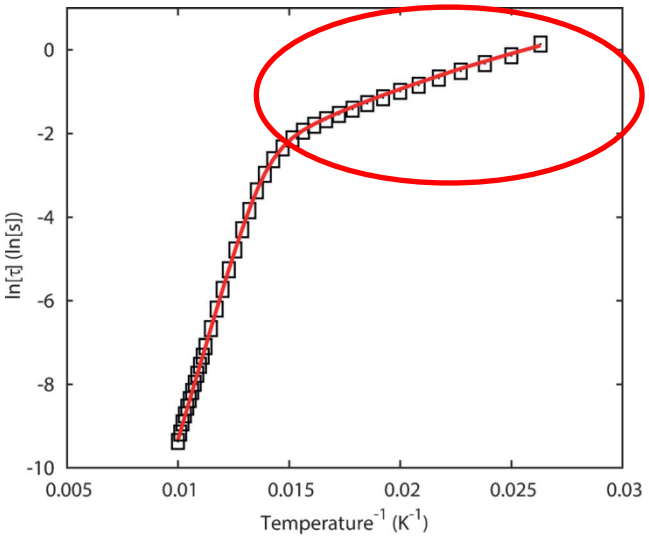
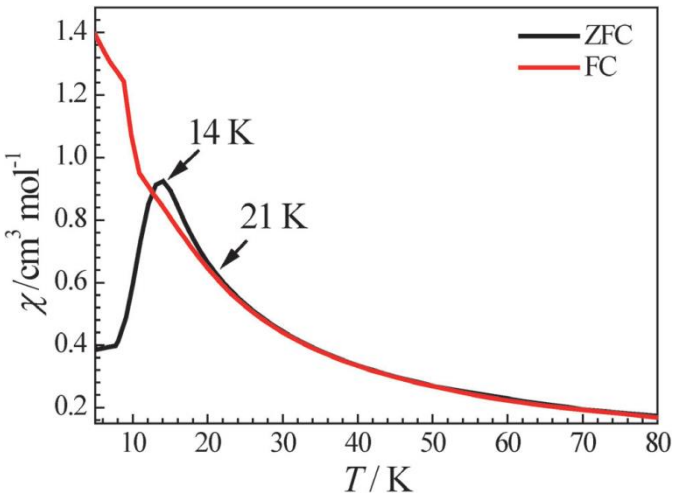
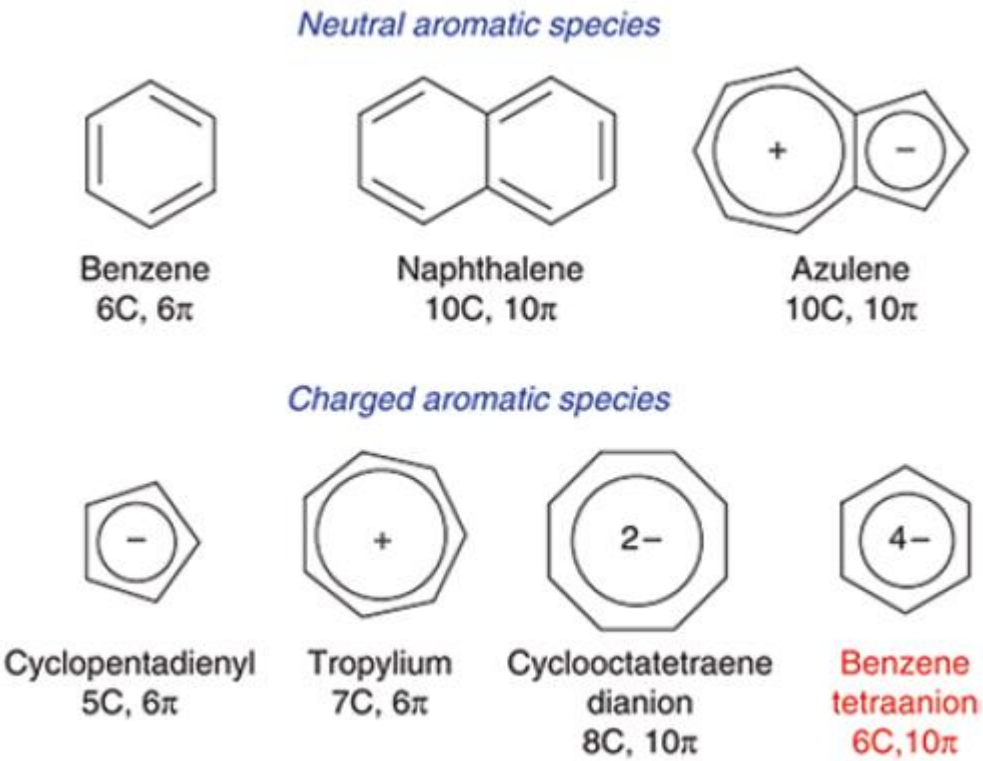
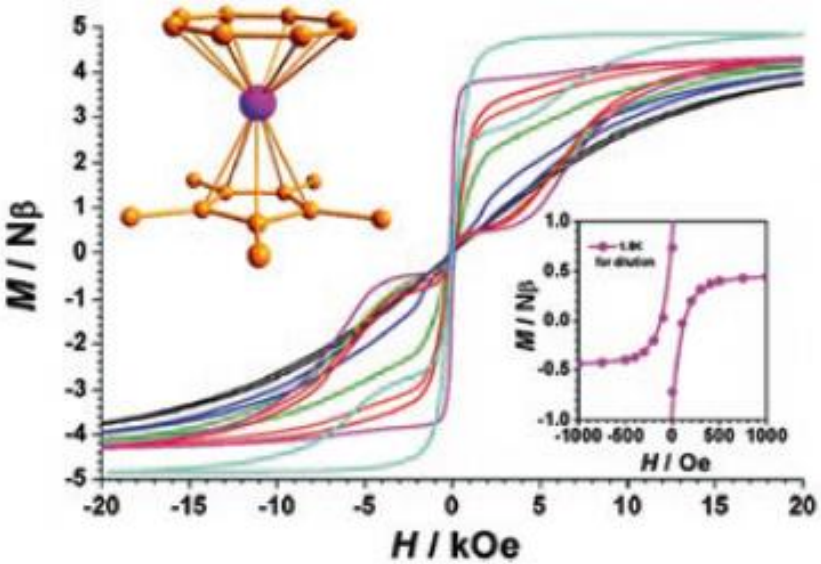




Ding, Y.-S. et al., ***Angew. Chem.-Int. Ed.* 2016**, *55*, 16071

Going above $N_{2\,(l)}$ temperature region





LnCOT family: a curiosity but maybe more…..

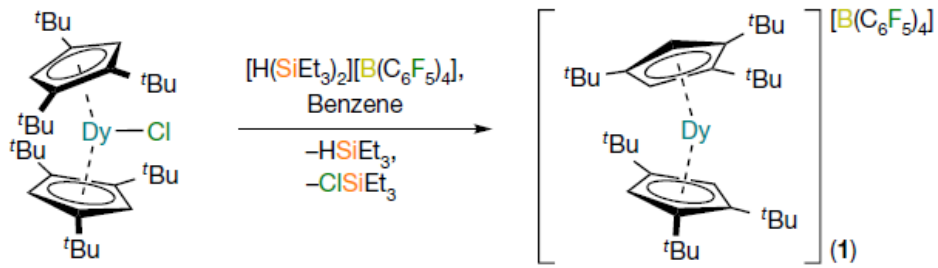
Pentamethylcyclopentadienide (C_5Me_5, Cp*)
Cyclooctatetraenide ($C_8H_8^{2-}$, COT).

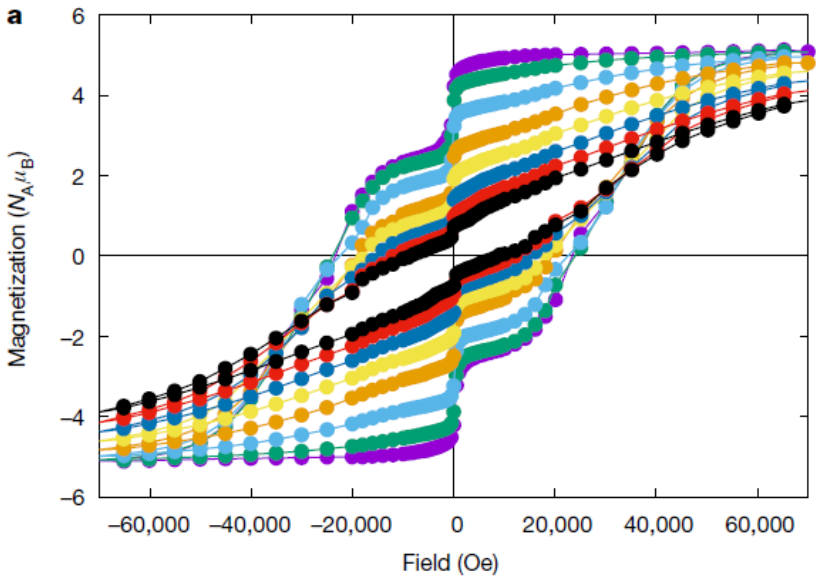
Huang W, *et al.*, ***Nat Commun* 2013**, 4, 1448.
Jiang S-D, *et al.*, ***J. Am. Chem. Soc*. 2011**, 133(13), 4730.

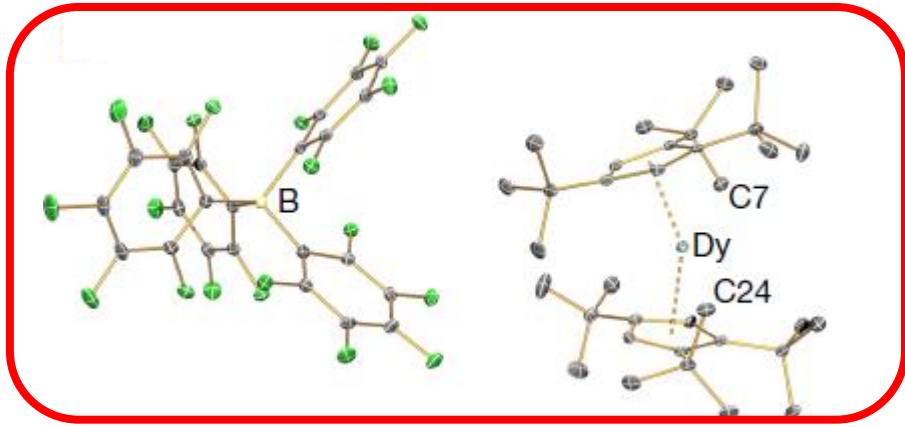
Going above $N_{2\,(l)}$ temperature region

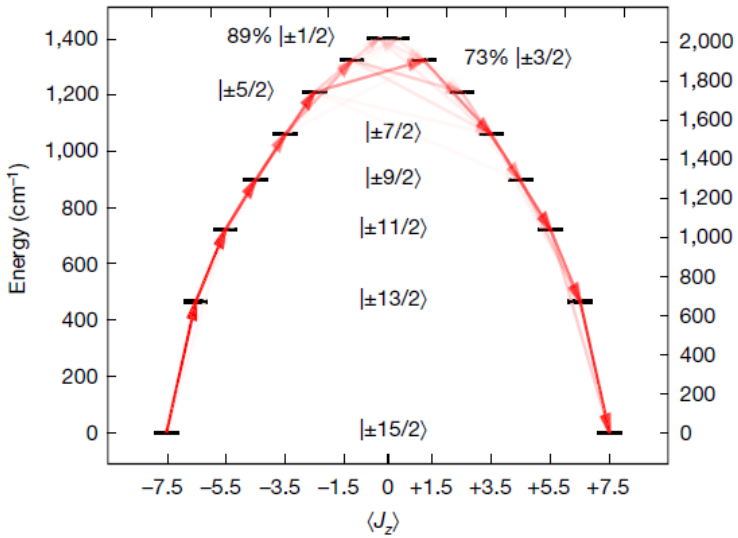
Institut des Sciences Chimiques de Rennes UMR CNRS 6226

$[Dy(Cp^{ttt})_2][B(C_6F_5)_4]$









Blocking temperature as high as T_B=60K

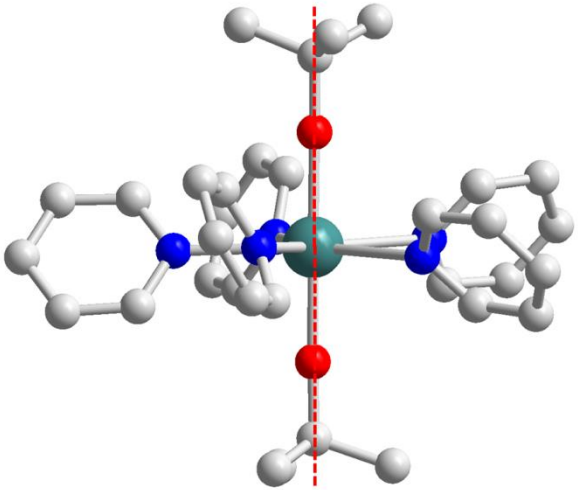
U_{eff}= 1760 K

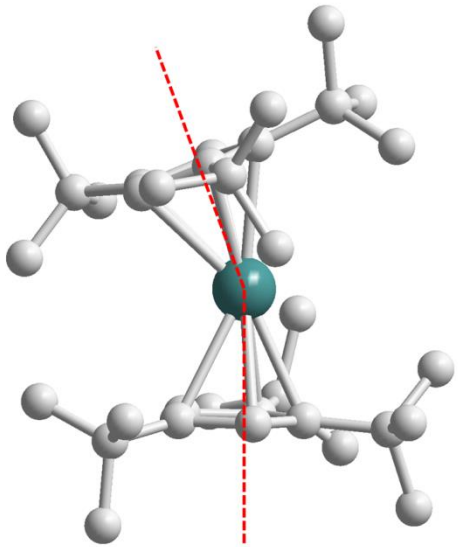
Cp-Dy-Cp= 152.8°

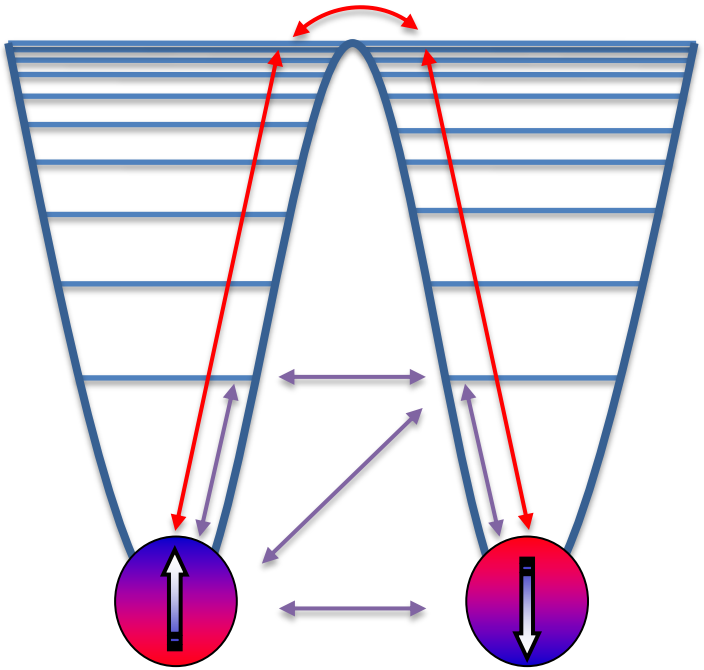
Movie

Goodwin, C. A. P.;. ***Nature* 2017**, *548*, 439

Going above $N_{2\,(l)}$ temperature region







$[Dy(O^tBu)_2(Py)_5]^+$,
angle O-Dy-O= 178.9°,
U_{eff}= 1815 K,
T_B=14K

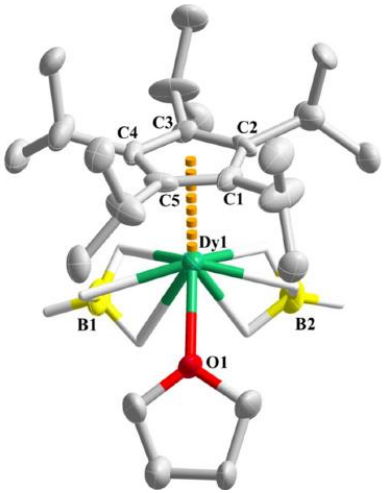
$[Dy(Cp^{ttt})_2]^+$
angle Cp-Dy-Cp= 152.8°,
U_{eff}= 1760 K,
T_B=60K

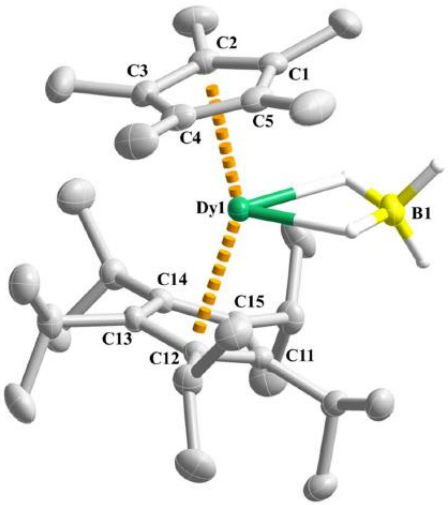
- **Optimization of spin-phonon coupling by increasing the « rigidity » of the molecule skeleton (vibration modes)**

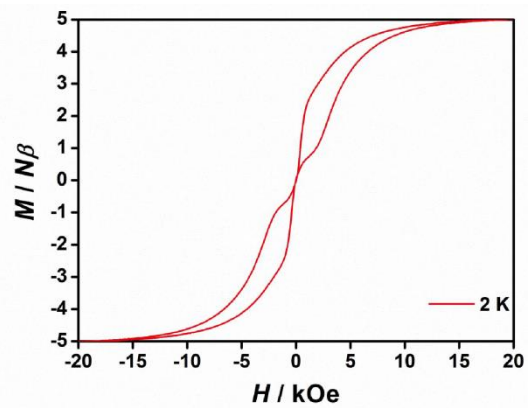
Ding, Y.-S. et al., ***Angew. Chem.-Int. Ed.* 2016**, *55*, 16071
Goodwin, C. A. P.;. ***Nature* 2017**, *548*, 439

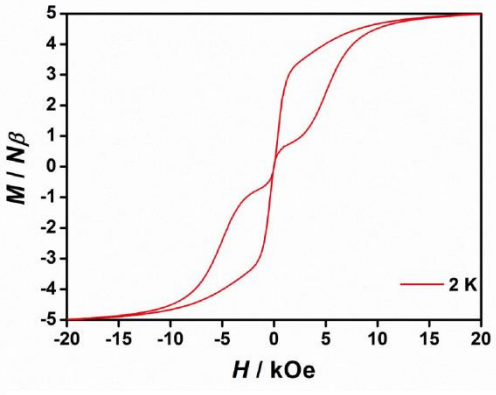
Going above $N_{2\,(l)}$ temperature region

$[(Cp^{iPr5})Dy(Cp^*)]^+$
U_{eff}= 2217K,
T_B=80 K record blocking temperature for a SMM

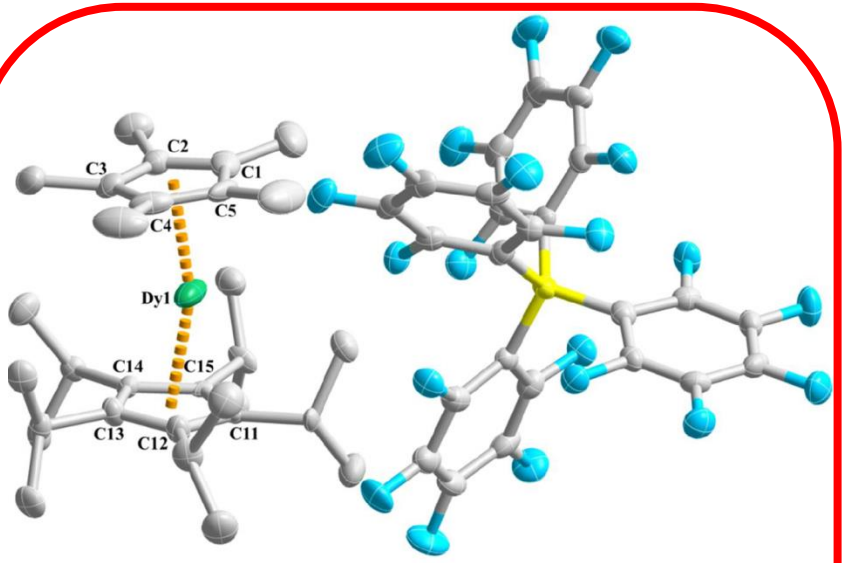


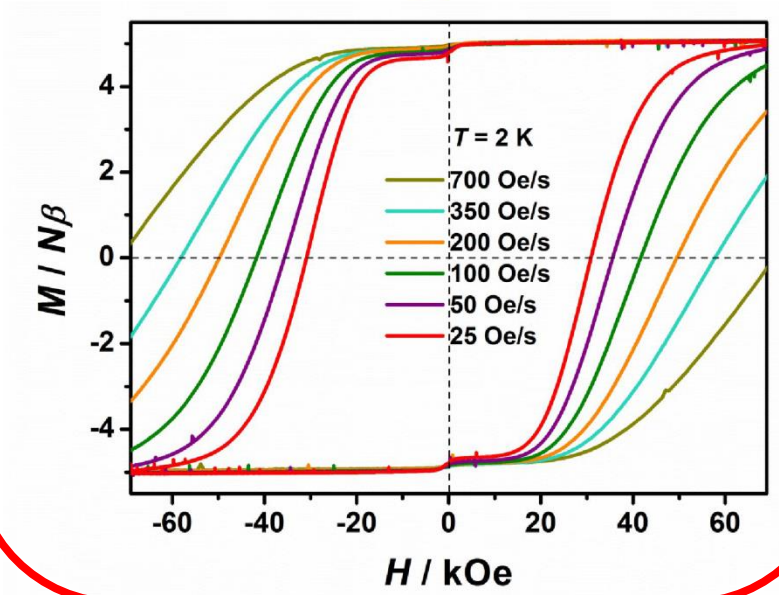






Hard magnet-like behavior

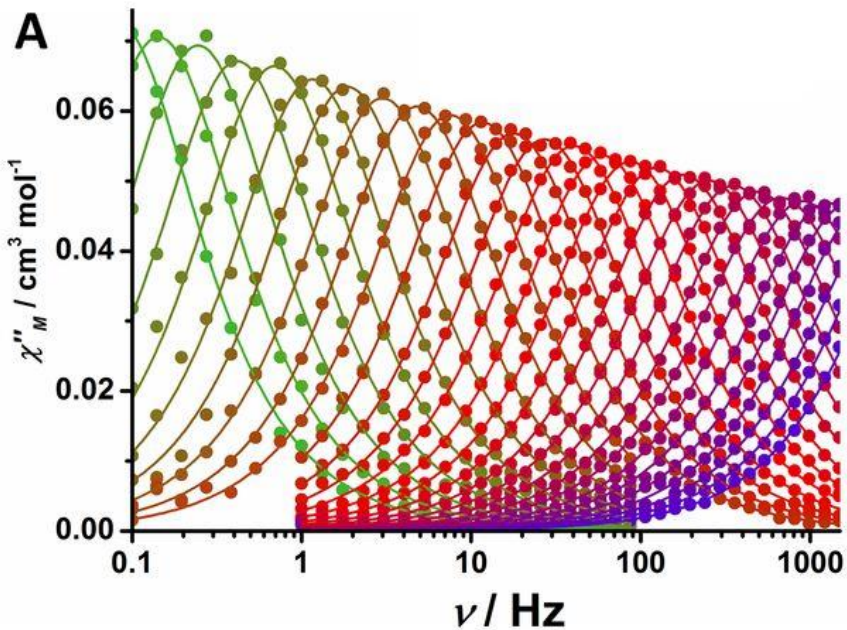


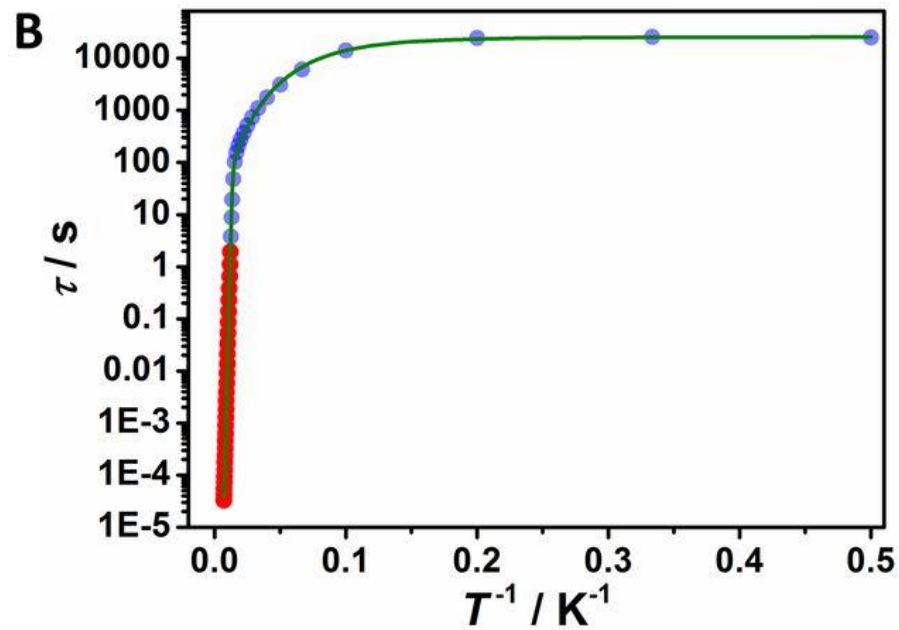


Guo, F.-S, *et al.*, ***Science* 2018**.

Going above $N_{2\,(l)}$ temperature region

Underbarrier relaxation pathways are still present at low T but for relaxation times that are extremely slow





movie

Guo, F.-S, *et al.*, ***Science* 2018**.

Going above $N_{2\,(l)}$ temperature region

$[(Cp^{iPr5})Dy(Cp^*)]^+$
angle Cp-Dy-Cp= 165.5°, U_{eff}= 2217K,
T_B=80 K

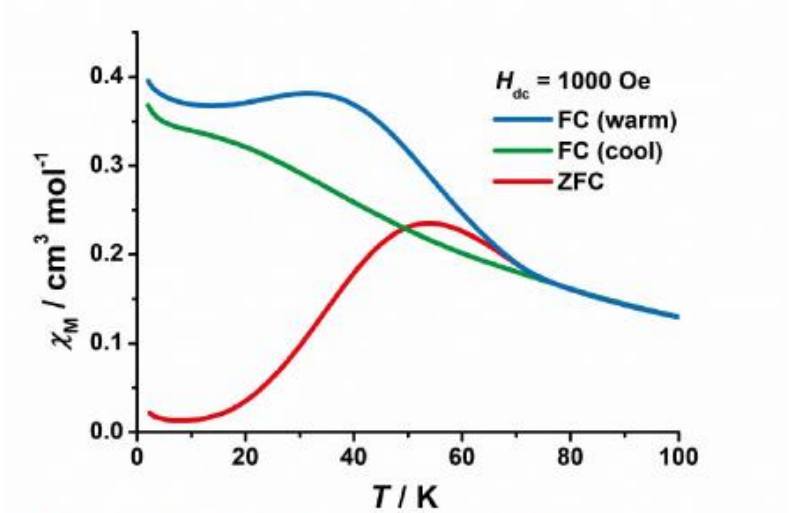
Hard magnet-like behavior

Table S9. Coercive fields for 3 at different sweep rate at 2 K, corresponding to Fig. S49.

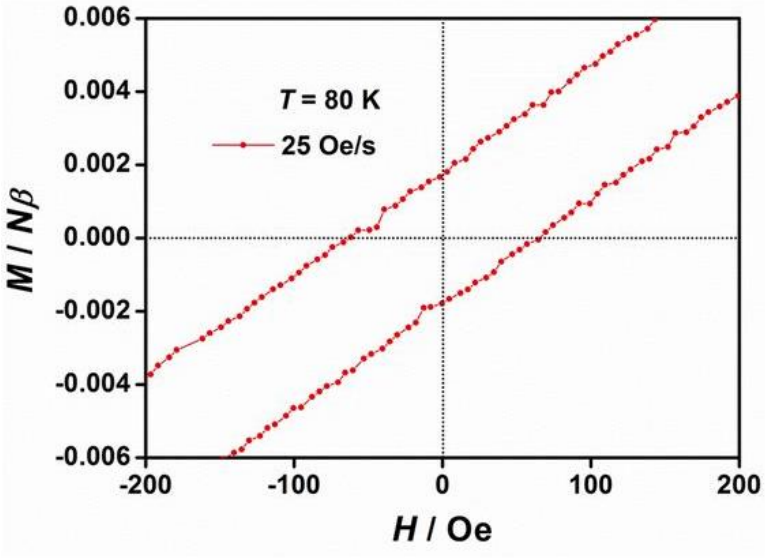
Sweep rate / Oe s^{-1}	Coercive field / Oe
700	> 70000
350	58146
200	49741
100	41722
50	35632
25	30893

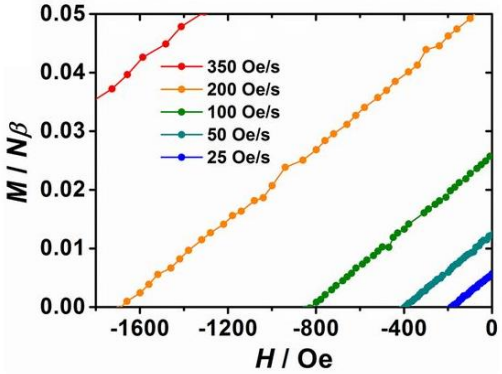
Table S10. Coercive fields at different sweep rate at 77 K, corresponding to Fig. S50.

Sweep rate / Oe s^{-1}	Coercive field / Oe
700	5802
350	2946
200	1688
100	825
50	398
25	191



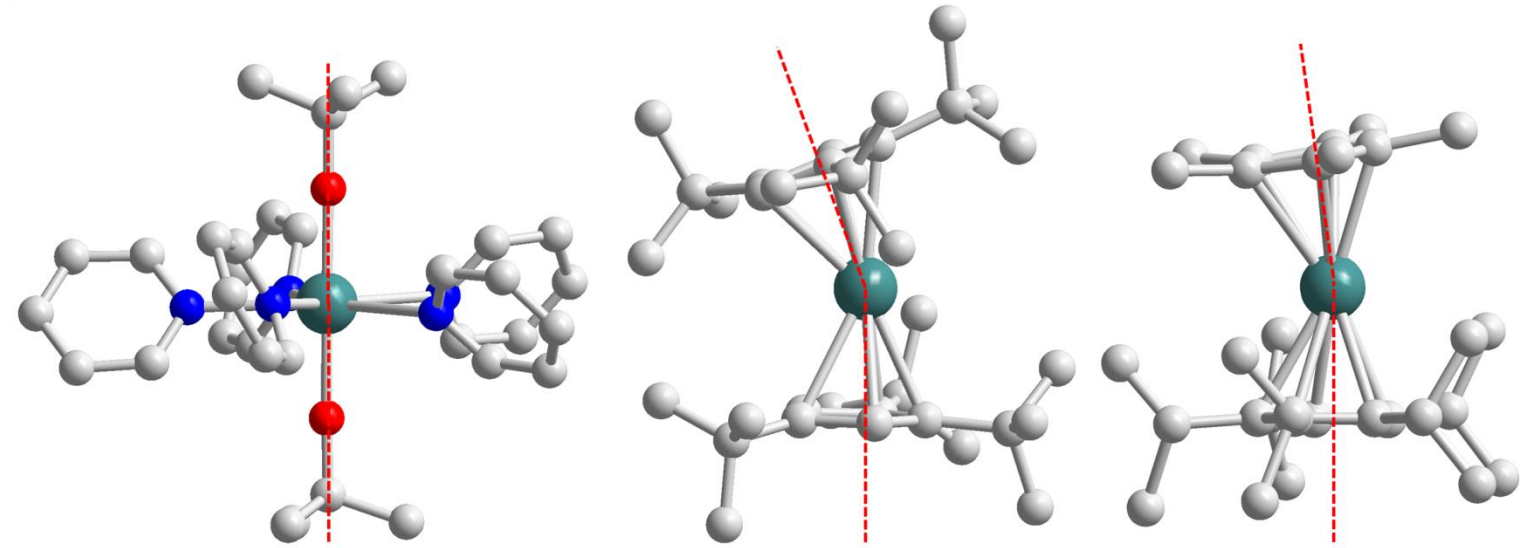
1. Field-cooled (FC, blue line) and zero-field-cooled (ZFC, red line) variable-temperature ic susceptibility for 3Dy under 1000 Oe DC filed in warm mode (2 K/min) from 2 to 100





Guo, F.-S, *et al.*, ***Science* 2018**.

Going above N_2 temperature region



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$[(Cp^{iPr5})Dy(Cp^*)]^+$
angle Cp-Dy-Cp= 165.5°,
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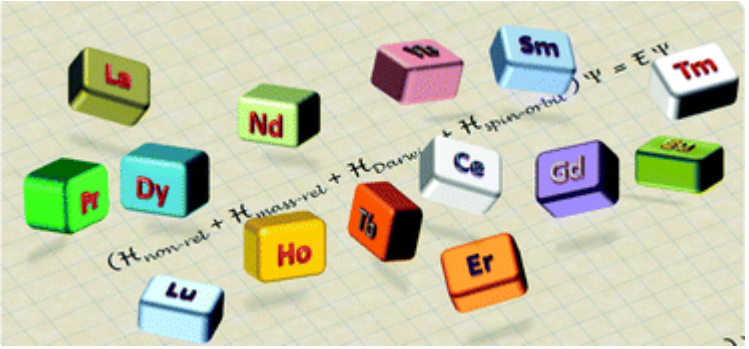
T_B=80 K

- **Optimization of spin-phonon coupling** by increasing the **« rigidity »** of the molecule skeleton (vibration modes)
- **Optimization of the M_J= 15/2 stabilization (electrostatics around Dy^{III})** by increasing the **X-Dy-X angle** (closer to 180°)

Key Points



- Rare-Earth (RE) elements are not rare
- RE have similar chemical properties
- Their high cost is due to the separation cost of indiv. RE oxide and to the high demand

- LS (spin-orbit)> CF (crystal field) , J is a good quantum number
- M_S states on 3d, M_J states on 4*f*, (energy barrier is DS^2 and U_{eff} resp.)
- M_J states can be investigated by luminescence spectroscopy
- Magnetic anisotropy can be investigated by angular-resolved magnetometry

- Spin and magnetic anistropy are the two ingredients for SMM behavior
- Giant spins (polynuclear molecules) do not always provide SMM behavior
- Strong anisotropy of single–ion can be enough to provide SMM behavior

- $TbPc_2$ was the first familly of 4*f*-SMM
- Strong axiality of the electrostatics around Dy^{III} is needed
- Vibration modes (molecule rigidity) could be responsible for under-barrier relaxation
- Organometallic 4*f* molecules verify these last two requisites and affords high-performance 4*f*-SMM
- The quest for stable (air, moisture,…), depositable (surfaces) and adressable SMMs continues…

Somes references on 4*f*-SMM

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