Electronic Supplementary Material (ESI) for Dalton Transactions
This journal is © The Royal Society of Chemistry 2012

Supplementary Information

Ytterbium Can Relax Slowly Too : Field induced Yb_2 Single-Molecule Magnet.

Po-Heng Lin,[a] Wen-Bin Sun,[b]* Yong-Mei Tian,[b] Peng-Fei Yan,[b]* Liviu Ungur,[c] Liviu. F. Chibotaru[c]* and Muralee Murugesu[a]*

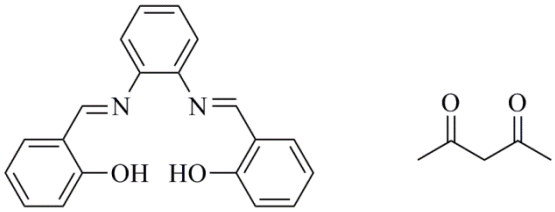
University of Ottawa, Department of Chemistry, 10 Marie Curie, Ottawa, ON, K1N6N5, Canada.

Key Laboratory of Functional Inorganic Material Chemistry, Ministry of Education, No. 74, Xuefu Road, Nangang District, Harbin 150080, PR China.

Division of Quantum and Physical Chemistry and INPAC—Institute for Nanoscale Physics and Chemistry, Katholieke Universiteit Leuven, Celestijnenlaan, 200F, 3001, Belgium.

Preparation of N,N-bis(salicylidene)-*o*-phenylenediamine:

The salen-type ligand, N,N′-bis(salicylidene)-*o*-phenylenediamine (H_2L), was obtained by using previously reported synthetic methods.[i]



H_2L acac

Scheme S1. Representation of the salen-type (H_2L) and acac ligands

This journal is © The Royal Society of Chemistry 2012

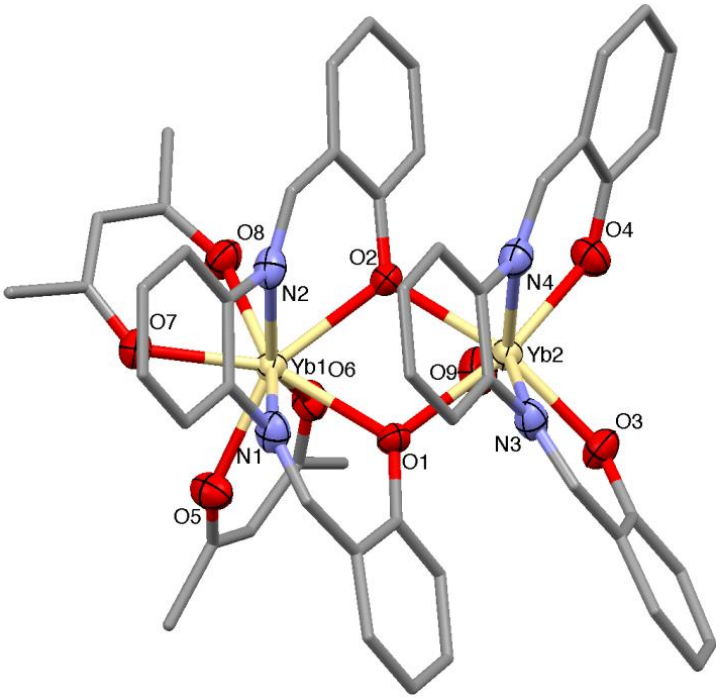


Figure S1. Partially labelled molecular structure of $[Yb_2L_2(acac)_2(H_2O)]$, **1**. Yb1 is in a distorted square antiprism environment, Yb2 is in a distorted capped trigonal prism environment. Colour code: Yb (yellow), O (red), N (blue) C (grey). H atoms were omitted for clarity.

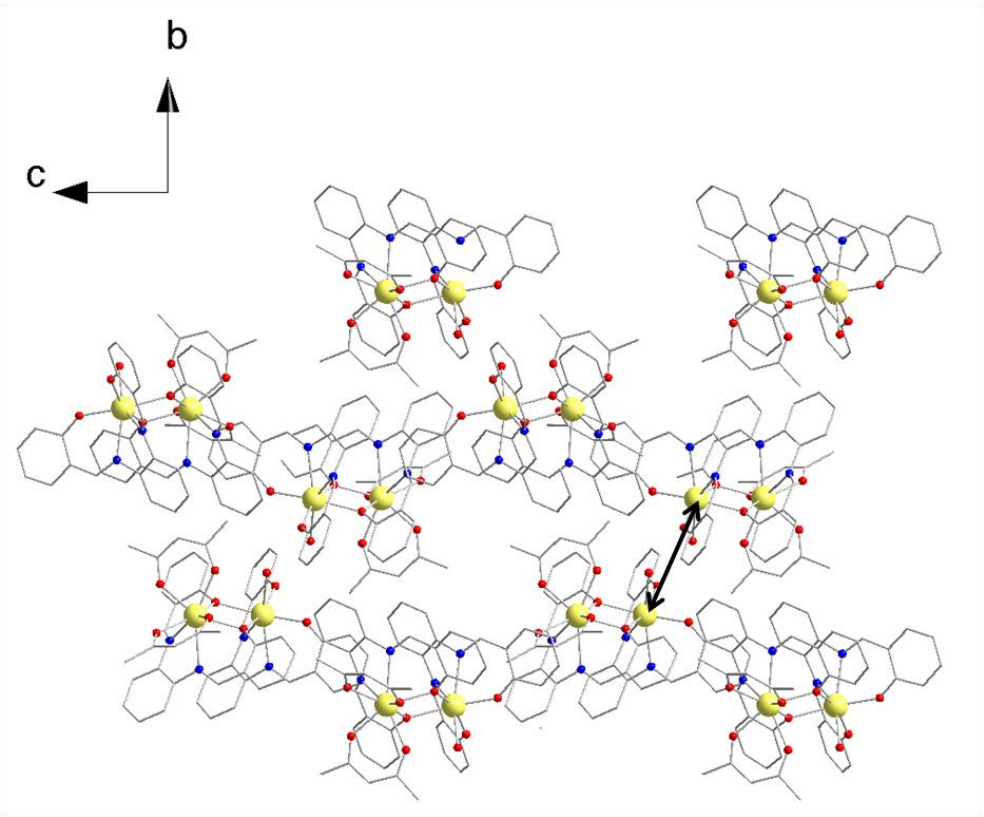


Figure S2. Crystal packing diagram of complex **1** along the crystallographic *a* axis. The arrow shows the closest intramolecular contact between Yb2···Yb2a (5.94 Å). Colour code: Yb (yellow), O (red), N (blue) C (grey). H atoms were omitted for clarity.

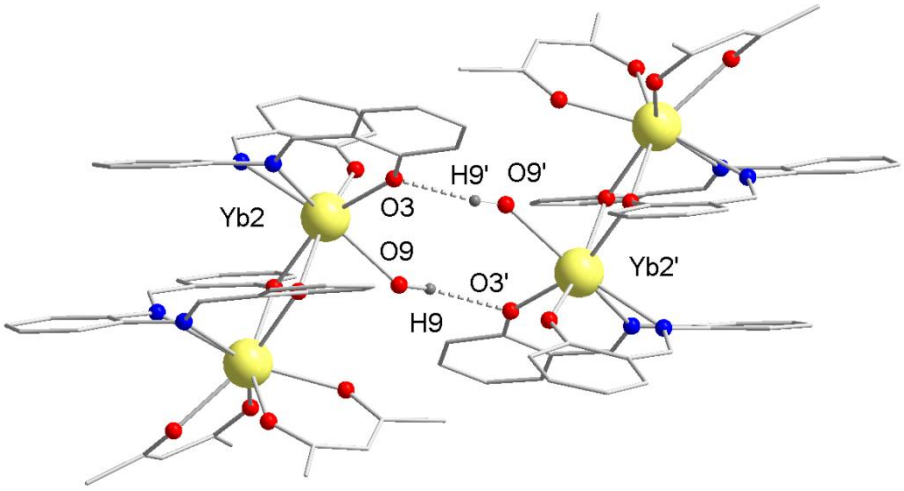


Figure S3. The two hydrogens bonds between two neighboring molecules. Colour code: The two hydrogens bonds between two neighboring molecules. Colour code: Yb (Yellow), O (red), N (blue) C (grey) and Black (H).

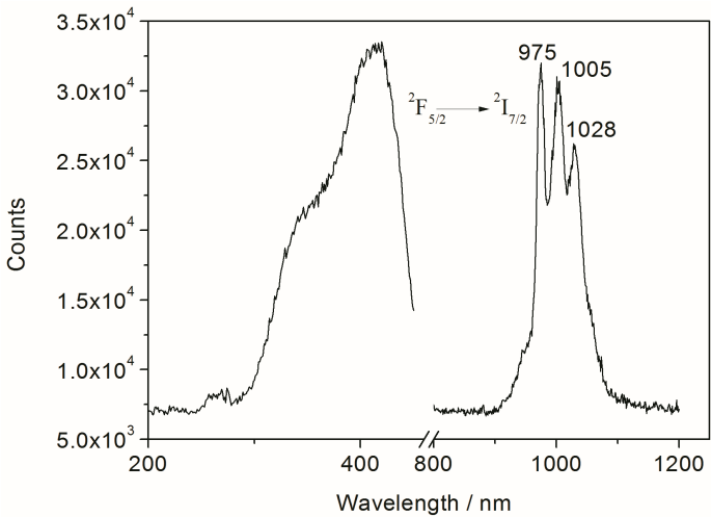


Figure S4. The NIR fluorescence of **1** in CH_2Cl_2 (1.0×10^{-5} M).

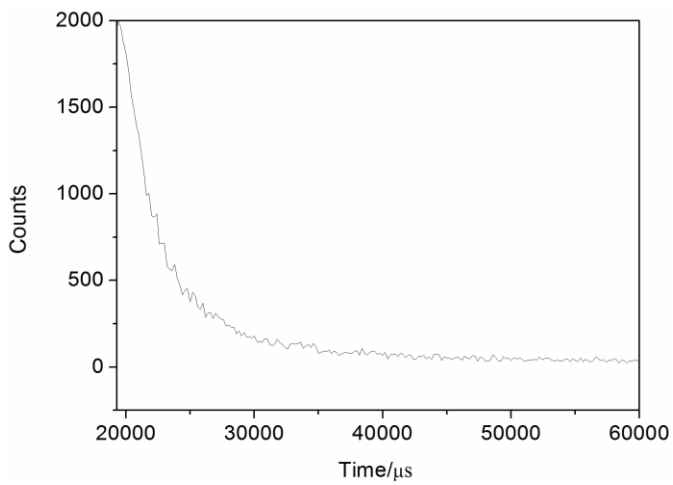


Figure S5. The decay curve of excited states for lifetime value of **1** in CH_2Cl_2 at room temperature.

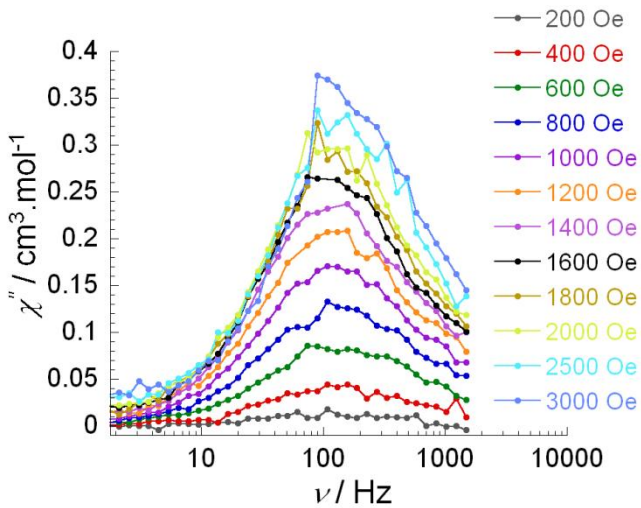


Figure S6. Out-of-phase susceptibility χ'' *vs*. frequency υ in the field range 0 - 3000 Oe for complex **1**.

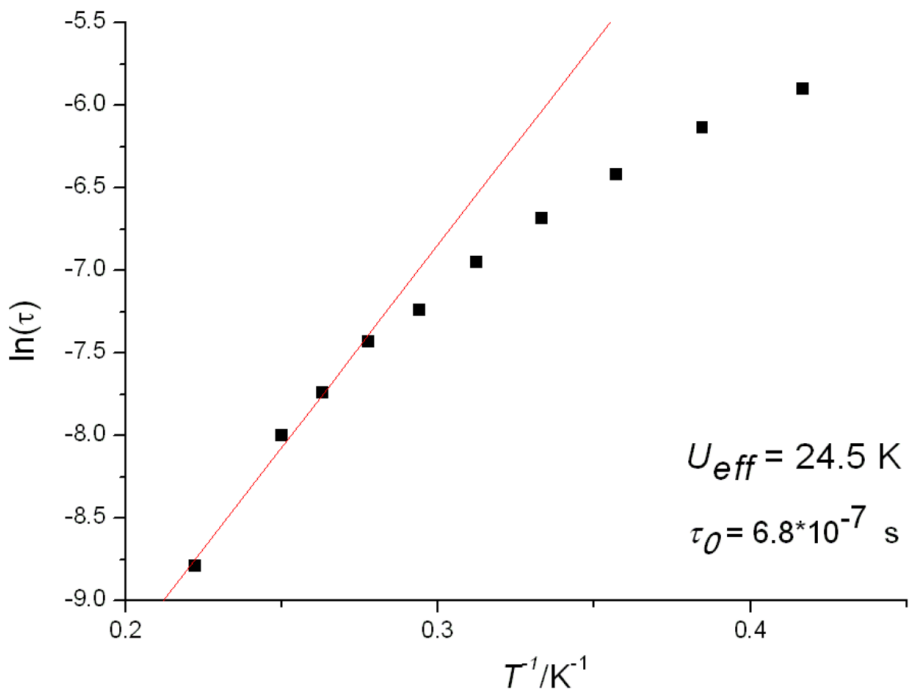


Figure S7. Ln(τ) *vs*. T^{-1} plot at H_{dc} 1600 Oe representing thermally activated relaxation regime. The solid lines represent an Arrhenius fit of the data.

Computational details

All calculations were done with MOLCAS 7.6 and are of CASSCF/RASSI/SINGLE_ANISO type.

Computational models:

We have employed 2 structural approximations for each fragment Yb1 and Yb2: (**A** – a reduced fragment of the molecule and **B** – the entire molecule) and 2 basis set approximations (**1** –small and **2**-large), resulting in 4 computational approximations for molecule Yb_2 (**A1**, **A2**, **B1**, **B2**).

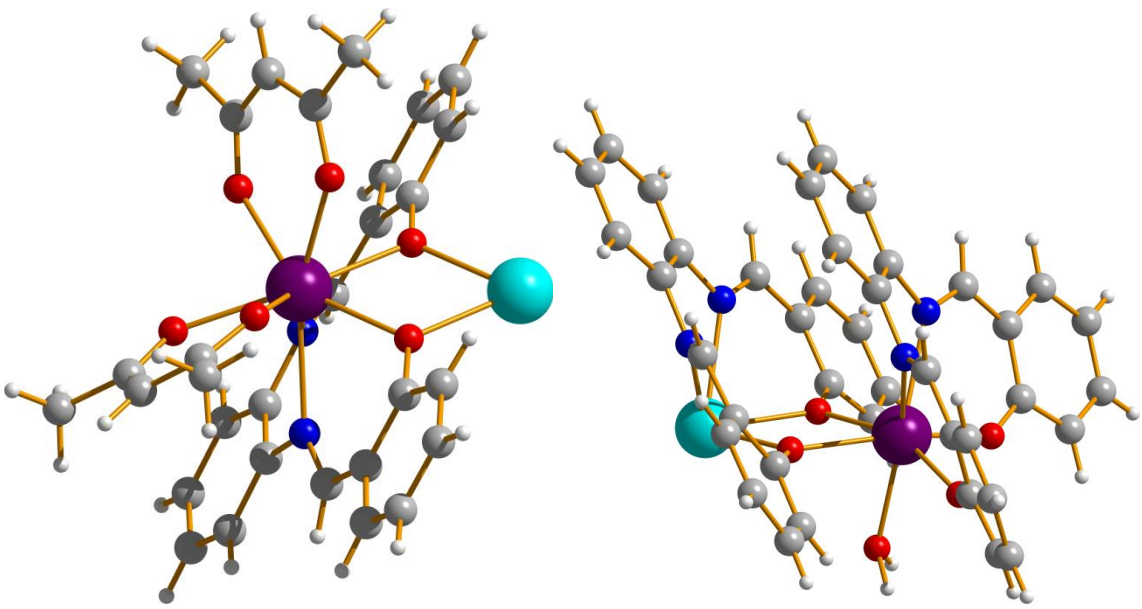


Figure S8. Structure of the fragments **A** (right - Yb1, left - Yb2) of the complex Yb_2. Color scheme: Yb - violet, La – light turquase, N – blue, O – red, C – grey, H – white.

Table S1. Contractions of the employed basis sets in computational approximations **1** and **2**.

Basis 1	Basis 2
Yb.ANO-RCC...7s6p4d3f1g.	Yb.ANO-RCC...8s7p5d4f2g1h.
La.ECP.deGraaf.0s.0s.0e-La(LaMnO3).	La.ECP.deGraaf.0s.0s.0e-La(LaMnO3).
Lu.ANO-RCC...7s6p4d3f1g.	Lu.ANO-RCC...7s6p4d3f1g.
O.ANO-RCC...3s2p1d. (close)	O.ANO-RCC...4s3p2d. (close)
O.ANO-DK3.Tsuchiya.12s8p.2s1p. (distant)	O. ANO-RCC...3s2p. (distant)
N.ANO-RCC...3s2p1d. (close)	N.ANO-RCC...4s3p2d. (close)
N.ANO-DK3.Tsuchiya.12s8p.2s1p. (distant)	N.ANO-RCC...3s2p. (distant)
C.ANO-DK3.Tsuchiya.12s8p.2s1p.	C.ANO-RCC...3s2p.
H. ANO-DK3.Tsuchiya.6s.1s.	H.ANO-RCC...2s.

Active space of the CASSCF method included 13 electrons in 7 orbitals (4*f* orbitals of Yb^{3+} ion).
We have mixed 7 (all) doublet states by spin-orbit coupling.

On the basis of the resulting spin-orbital multiplets SINGLE_ANISO program computed local magnetic properties (g-tensors, magnetic axes, local magnetic susceptibility, etc.) The program POLY_ANISO computed the exchange spectrum and the magnetic properties of the dimer.

Table S2. Energies (cm^{-1}) and *g* tensors of the lowest Kramers doublets (KD).

Center Yb1:

KD		A1		A2		B1		B2	
		E	*g*	E	*g*	E	*g*	E	*g*
1	g_X		0.7535		0.7981		0.9589		0.9928
	g_Y	0.000	1.8032	0.000	1.7566	0.000	1.8002	0.000	1.8549
	g_Z		5.5557		5.5748		6.1164		5.9508
2	g_X		0.4490		1.3024		1.3521		1.6832
	g_Y	167.350	1.4623	176.508	2.5822	190.491	2.3911	189.051	2.0574
	g_Z		5.4069		4.1061		3.8016		4.0340
3	g_X		0.4103		0.5872		0.3459		0.0547
	g_Y	193.747	1.1712	210.833	1.4094	281.227	0.7774	287.500	0.8393
	g_Z		5.3322		6.4771		5.9109		6.4418
4	g_X		0.1508		0.1088		0.3383		0.2371
	g_Y	353.267	0.3557	368.142	0.2797	366.083	0.5861	368.463	0.5015
	g_Z		7.5950		7.6600		7.0809		7.2326

Center Yb2:

KD		A1		A2		B1		B2	
		E	*g*	E	*g*	E	*g*	E	*g*
1	g_X		0.1586		0.2079		0.3516		0.3852
	g_Y	0.000	1.2241	0.000	0.9301	0.000	1.0588	0.000	0.9707
	g_Z		6.7491		7.1406		7.0683		7.1998
2	g_X		3.7271		4.0783		4.6849		4.4380
	g_Y	239.769	3.2701	310.566	2.9533	292.947	3.2959	336.958	3.3772
	g_Z		0.1948		0.2906		1.0972		1.3410
3	g_X		0.4871		0.9129		0.0897		0.2195
	g_Y	353.371	1.7251	430.746	1.9830	485.888	1.0006	539.921	1.2105
	g_Z		5.1016		5.9542		6.0237		6.1096
4	g_X		0.0646		0.0277		0.4713		0.4504
	g_Y	595.182	0.1815	664.731	0.0988	591.200	0.9833	645.598	1.1120
	g_Z		7.7980		7.8212		7.2086		7.1132

Table S3. Angles between the g_Z axes of the lowest Kramers doublets (KD) in all computational models (degrees).

center	model	center Yb1				center Yb2			
		A1	A2	B1	B2	A1	A2	B1	B2
Yb1	A1	0.000	0.391	28.040	25.887	135.675	136.763	135.003	135.678
	A2	0.391	0.000	28.379	26.228	135.325	136.418	134.651	135.328
	B1	28.040	28.379	0.000	2.167	163.602	164.773	162.862	163.590
	B2	25.887	26.228	2.167	0.000	161.497	162.638	160.775	161.489
Yb2	A1	135.675	135.325	163.602	161.497	0.000	1.584	0.948	0.150
	A2	136.763	136.418	164.773	162.638	1.584	0.000	2.531	1.693
	B1	135.003	134.651	162.862	160.775	0.948	2.531	0.000	0.851
	B2	135.678	135.328	163.590	161.489	0.150	1.693	0.851	0.000

Table S4. Energies and the corresponding tunneling gaps of the lowest 4 exchange doublet states of the complex Yb_2.

A1		A2		B1		B2	
energy	Δ_t	energy	Δ_t	energy	Δ_t	energy	Δ_t
0.00000000 0.01485504	1.4855E-02	0.00000000 0.01159313	1.1593E-02	0.00000000 0.01282147	1.2821E-02	0.00000000 0.01189421	1.1894E-02
0.12655795 0.14729532	2.0737E-02	0.13602336 0.15357224	1.7549E-02	0.15408078 0.17536270	2.1282E-02	0.15445619 0.17542771	2.0972E-02
167.34771880 167.37159324	2.3874E-02	176.52952647 176.57500080	4.5474E-02	190.52159106 190.56716357	4.5573E-02	189.08635133 189.13064831	4.4297E-02
167.47314081 167.49850140	2.5361E-02	176.58982768 176.64039430	5.0567E-02	190.58279051 190.63472791	5.1937E-02	189.13857178 189.19102023	5.2448E-02

i (a) C. Subrahmanyam, M. Seshasayee and G. Aravamudan, G. *Cryst. Struct. Commun.* 1982, **11**, 1719. (b) K. Ambroziak, Z. Rozwadowski, T. Dziembowska, and B. J. Bieg, *Mol. Struct.* 2002, **615**, 109.