ELECTRONIC SUPPORTING INFORMATION

A Carbon-Rich Ruthenium Decorated Dysprosium Single Molecule Magnet.

Lucie Norel,[a] Kevin Bernot,[b] Min Feng,[a] Thierry Roisnel,[a] Andrea Caneschi,[c] Roberta Sessoli[c] and Stéphane Rigaut[a]

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1. Synthetic procedures

General comments: The reactions were carried out under an inert atmosphere using Schlenk techniques. Solvents were dried and distilled under argon using standard procedures. High resolution mass spectra (HRMS) were recorded in Rennes at the CRMPO (Centre Régional de Mesures Physiques de l'Ouest) on Bruker MicrO-Tof-Q II spectrometer. The complexes *trans*-[Ru(dppe)$_2$(-C≡C-Ph)(-C≡C-bpy)][1] and Dy(hfac)$_3$.2H$_2$O[2] have been obtained as previously reported.

***trans*-[Ph-C≡C-(dppe)$_2$Ru-C≡C-bipy-κ^2-N,N'-Dy(hfac)$_3$)] (2):**

In a Schlenk tube, Dy(hfac)$_3$.2H$_2$O (30 mg, 0.037 mmol) and *trans*-[Ru(dppe)$_2$(-C≡C-Ph)(-C≡C-bpy)] **(1)** (43 mg, 0.037 mmol) were dried under vacuum for one hour and then dissolved with CH$_2$Cl$_2$ (2 mL). The obtained red solution was stirred at ambient temperature for 16 hours. The mixture was taken to dryness under vacuum. The residue was washed with pentane to yield a red powder (53 mg, 73%). The sample used for SQUID measurement was further precipitated from ether and pentane and dried under vacuum. Alternatively, crystals suitable for single crystal XRD study can be grown by slow diffusion of pentane directly into the dichloromethane reaction mixture solution at 5°C.

^{1}H-NMR (500 MHz, CD$_2$Cl$_2$, ppm), δ (integration, line width, attribution) : 109.5 (3H , 400 Hz, hfac), 4.95 (4H, 44 Hz, H$_7$), 4.50 (1H, 20 Hz, H$_1$), 4.17 (2H, H$_2$ or H$_3$), 3.78 (4H, 21 Hz, H$_4$), 2.74 (8H, 22 Hz, H$_5$), 2.10 (2H, H$_2$ or H$_3$), -0.44 (8H, 22 Hz, H$_6$), -5.81 (8H, 90 Hz, H$_8$), -9.78 (4H, 36 Hz, H$_{11}$), -10.55 (1H, 78 Hz, H$_{bpy}$), -14.94 (9H, 57 Hz, H$_9$ + H$_{bpy}$), -17.40 (4H, 58 Hz, H$_{10}$), -24.8 (1H, 165 Hz, H$_{bpy}$), -25.9 (1H, 87 Hz, H$_{bpy}$), -44.7 (1H, 164 Hz, H$_{bpy}$). Two signals for the ortho-bpy protons are not observed, probably because of a very important paramagnetic shift and line broadening.[3] ^{31}P-NMR (400 MHz, CD$_2$Cl$_2$, ppm): 35.6. UV-vis: λmax = 290 nm (ε = 40 600 L mol^{-1} cm^{-1}) and 480 nm (ε = 22 000 L mol^{-1} cm^{-1}). IR (KBr, cm^{-1}): 2038 ($\upsilon_{C\equiv C}$) (s), 1667 (m) and 1651 (s) ($\upsilon_{C=O}$), 1259, 1208, 1148 ($\upsilon_{C\text{-}F}$) (s). ESI (+) HRMS (*m/z*) [M]$^+$ = 1963.1692 (calcd 1963. 1679). Elemental Analysis: C 51.77, H 3.05, N 1.44 (Calcd for [C$_{87}$H$_{63}$N$_2$O$_6$F$_{18}$P$_4$RuDy].CH$_2$Cl$_2$: C 51.64, H 3.20, N 1.37).

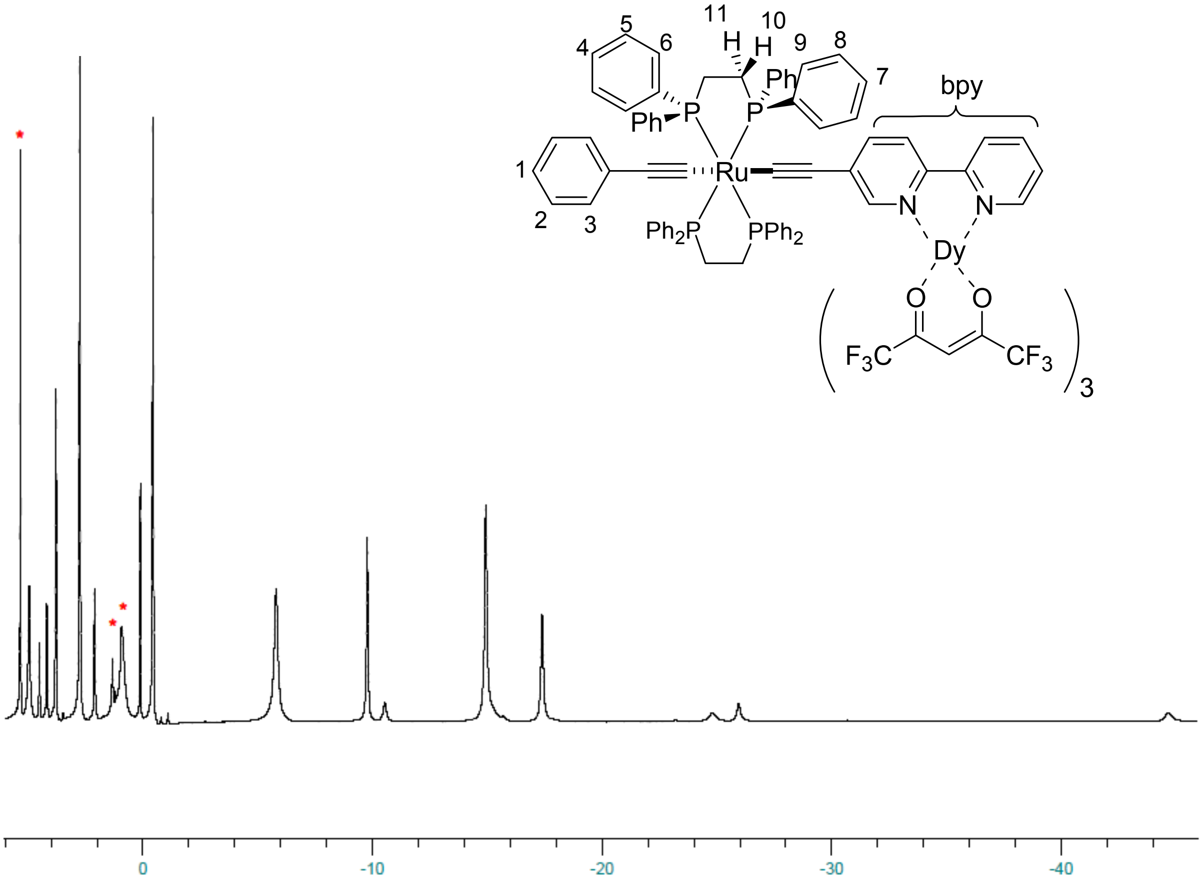

Figure S1: ^{1}H NMR spectrum of (**2**) in CD_2Cl_2 between 6 and -46 ppm. Peaks from residual dichloromethane and pentane traces are marked with an asterisk.

2. XRD Structure

Crystal data and structure refinement details are given in the table below. It led to a crystallographic cell containing both complex **2** and solvent molecules. Identification of the solvent was made difficult given the large cell volume (about 18 000 Å^3) and the disordered character of this solvent. The SQUEEZE procedure was then used to refine the structure, leading to satisfactory results.

Table S1: Crystal data and structure refinement for **2**.

	2
Empirical formula	$C_{87}H_{63}O_6F_{18}N_2P_4RuDy$
Formula weight	1961.84
Crystal size [mm^3]	0.3 x 0.25 x 0.04
Color, Habit	red plates
Crystal system	tetragonal
space group	P4/n
a = b [Å]	27.0767(10)
c [Å]	24.9978(10)
$\alpha = \beta = \gamma$ [°]	90
Volume [Å^3]	18327.1(10)
Z	8
T (K)	150 K
Θ range[°]	2.97 to 27.48
h, k, l range	-28/22, -16/35, -32/19
Reflections collected /independant	75357 / 20858
Reflections [$I > 2\sigma(I)$]	11498
Number of parameters	1009
R_1 ($I > 2\sigma(I)$)	0.0591
R_1 (all)	0.1161
ωR_2 ($I > 2\sigma(I)$)	0.1527
ωR_2 (all)	0.1714
Largest diff. peak & hole [e/Å^3]	2.824 / -1.139

Table S2: Selected bond distances (Å) of the ruthenium acetylide moiety and dysprosium coordination sphere in **2**. The numbering refers to Fig. 1.

Ruthenium-acetylide		Ruthenium coordination sphere		Dysprosium coordination sphere	
C_{Ph}-C1	1.526(11)	**Ru-C3**	2.049(6)	**Dy -O1**	2.359(4)
C1-C2	1.118(9)	**Ru-C2**	2.105(7)	**Dy-O2**	2.360(4)
C4-C_{Py}	1.423(8)	**Ru-P1**	2.3364(15)	**Dy-O3**	2.348(4)
C3-C4	1.210(7)	**Ru-P2**	2.3481(15)	**Dy-O4**	2.346(4)
C1-C2-Ru	173.4(5)	**Ru-P3**	2.3505(14)	**Dy-O5**	2.333(4)
C2-Ru-C3	175.1(2)	**Ru-P4**	2.3648(15)	**Dy-O6**	2.341(4)
Ru-C3-C4	179.2(5)			**Dy-N2**	2.496(4)
				Dy-N1	2.515(4)

Table S3: Dihedral angles in the square antiprism dysprosium coordination polyhedron.

Plane 1	Plane 2	Angle (°)
N2-N1-O6	**O6-N2-O5**	41.53(16)
O6-N2-O5	**N2-O5-O2**	56.52(16)
N2-O5-O2	**O5-O2-O4**	45.10(11)
O5-O2-O4	**O2-O4-O1**	59.15(17)
O2-O4-O1	**O4-O1-O3**	42.14(17)
O4-O1-O3	**O1-O3-N1**	58.96(16)
O1-O3-N1	**O3-N1-O6**	46.82(12)
O3-N1-O6	**N1-O6-N2**	59.33(17)
O2-O1-N2	**N2-N1-O1**	5.78(23)
O3-O5-O4	**O3-O5-O6**	1.00(30)

3. Magnetic measurement

The powder was embedded in grease to avoid in field orientation of the crystallites.

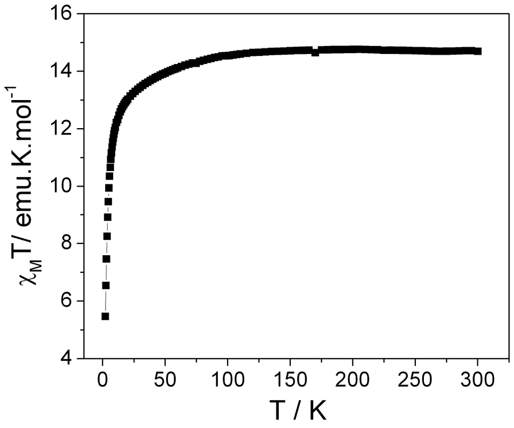

Figure S2: Temperature dependence of $\chi_M T$.

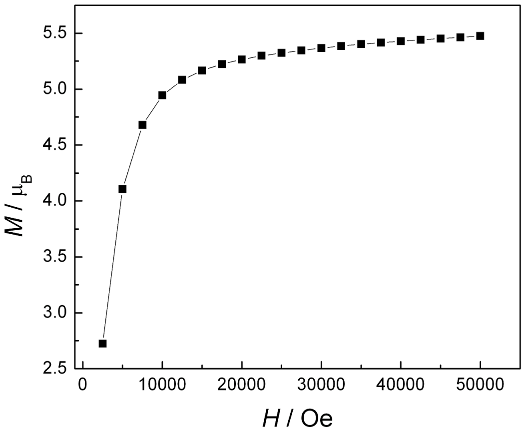

Figure S3: Field dependence of the magnetization at 1.8 K.

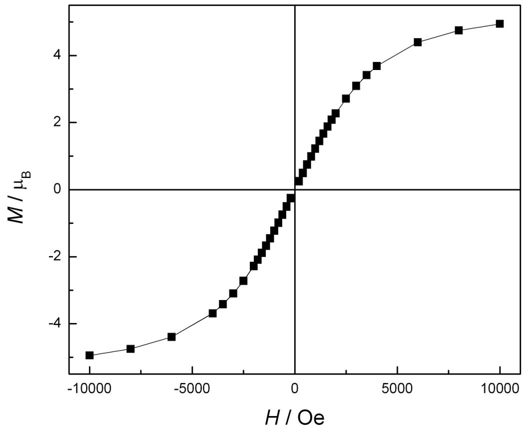

Figure S4: Magnetization loop recorded at 1.8 K.

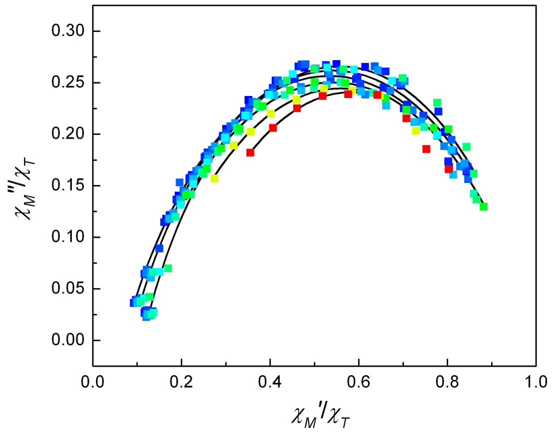

Figure S5: Normalized Cole-Cole diagrams for a 0 Oe dc field with some of the best fits (alpha between 0.33 and 0.36). Color mapping for temperatures ranging from 1.8 K (blue) to 5 K (red) with a 0.1 K step.

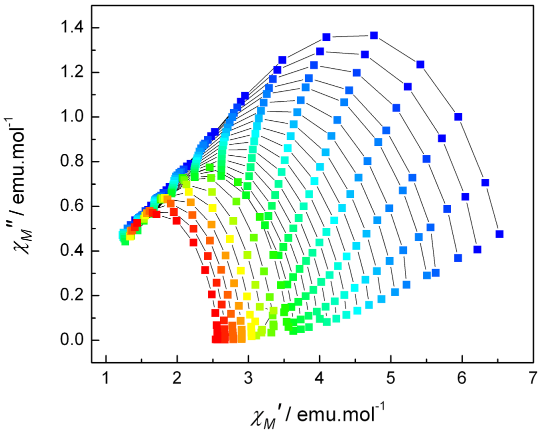

Figure S6: Cole-Cole diagrams for a 480 Oe dc field. Color mapping for temperatures ranging from 1.8 K (blue) to 5 K (red) with a 0.1 K step.

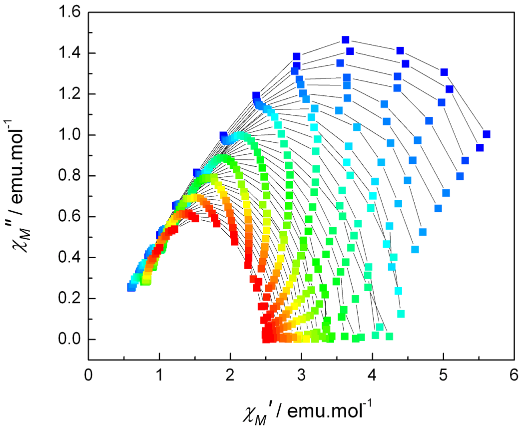

Figure S7: Cole-Cole diagrams for a 1000 Oe dc field. Color mapping for temperatures ranging from 1.8 K (blue) to 5 K (red).

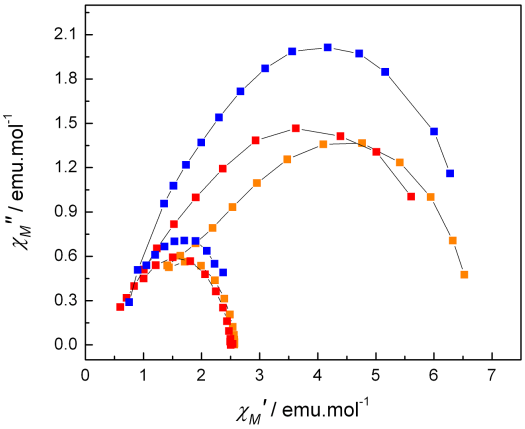

Figure S8: Cole-Cole diagrams for 0 (blue), 480 (orange) and 1000 Oe (red) dc field. Biggest circles corresponds to T = 1.8 K, Smallest to T = 5 K.

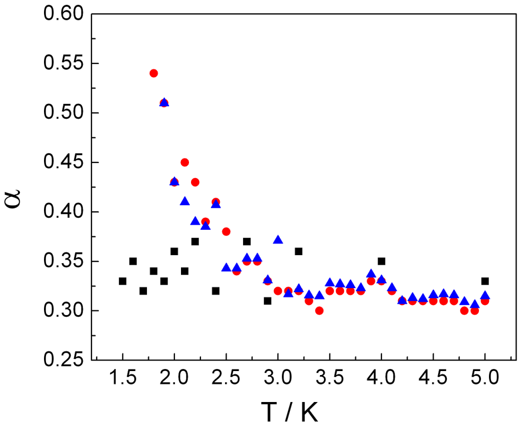

Figure S9: Temperature dependence of the alpha value as extracted from the fit of the χ_M'' *vs frequency* curves for zero (squares), 480 (circles) and 1000 Oe (triangles) external field.

1 E. Di Piazza, L. Norel, K. Costuas, A. Bourdolle, O. Maury and S. Rigaut, *J. Am. Chem. Soc.*, 2011, **133**, 6174-6176.

2 K. Bernot, L. Bogani, A. Caneschi, D. Gatteschi and R. Sessoli, *J. Am. Chem. Soc.*, 2006, **128**, 7947-7956.

3 a) Z. Ahmed and K. Iftikhar, *Inorg. Chim. Acta*, 2010, **363**, 2606-2615; b) U. Casellato, S. Tamburini, P. Tomasin, P. A. Vigato, S. Aime and M. Botta, *Inorg. Chem.*, 1999, **38**, 2906-2916.