Electronic Supplementary Information

Self-assembly of lanthanide-based Single-Ion Magnets (SIMs) into 1D networks via Re(IV)-based metalloligands

Carolina Ferrari-Argachá,[a] Santiago Valiero,[a] Carlos Rojas-Dotti,[a] Aparicio Loaces,[a] Raúl Chiozzone,[a] Nicolás Moliner,[b] Leopoldo Suescun,[c] Joan Cano,[b] Francesc Lloret,[b] José Martínez-Lillo,[b*] Ricardo González[a*]

[a] Área Química Inorgánica, Departamento Estrella Campos, Facultad de Química, Universidad de la República, General Flores 2124, Montevideo, Uruguay

[b] Departament de Química Inorgánica/Instituto de Ciencia Molecular (ICMol), University of Valencia, c/ Catedrático José Beltrán 2, Paterna, Valencia 46980, Spain

[c] Cryssmat-Lab/DETEMA, Facultad de Química, Universidad de la República, General Flores 2124, Montevideo, Uruguay

Table of contents

Additional comments on the synthesis and crystal structure elucidation.

Crystals obtained from slow solvent evaporation were separated from the mother solution and instantly covered with Paratone oil to protect them, and immediately the X-ray diffraction data collection was performed. The bulk of the synthetized compounds, used for the rest of the measurements, were stored under aerobic conditions with no temperature control. For **2** a **3**, after several days, samples loose solvent and the formula that fits systematically the elemental analysis is the one reported in the main text. The samples stored under these conditions were subsequently used to measure the magnetic properties of the compounds.

Disordered molecules of solvent were treated with the SQUEEZE tool in the refinement procedures of **2** and **3**. By assuming ethanol was the main solvent present, a total of 23 molecules of solvent were masked in both structures and a volume of 80 Å per molecule was considered. Although the resolution of the structure of **2** is relatively low, the total amount of crystallization solvent can be reasonably assumed since compounds **2** and **3** are isostructural compounds. The structure of the chain was not affected by this change and, therefore, the consequent crystal structure description of the main motif of the compounds was not affected by the omission of the disordered solvent.

Table S1: Summary of Crystal Data and Structure Refinement Parameters of **1**-**6**.

Compound	**1**	**2·nEtOH**	**3·nEtOH**	**4**	**5**	**6**
Formula	$H_{119}C_{62}N_5O_9Br_{10}Re_2$	$H_{131.5}C_{72.5}N_6O_{16.75}Br_{10}Re_2Dy$	$H_{131.5}C_{72.5}N_6O_{16.75}Br_{10}Re_2Tb$	$C_{20}H_{35}N_5O_9Br_5ReDy$	$C_{20}H_{35}N_5O_9Br_5ReTb$	$C_{20}H_{35}N_5O_9Br_5ReGd$
M_r/gmol^{-1}	2250.1	2504.4	2499.3	1237.8	1234.2	1232.53
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic	Triclinic	Triclinic
Space group	*P2$_1$/c*	*P2$_1$/c*	*P2$_1$/c*	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a /Å	27.5898(10)	18.4013(8)	18.4143(7)	8.2710(4)	8.2660(8)	8.2309(4)
b /Å	18.1029(7)	35.5993(10)	35.6069(10)	14.8570(8)	14.8230(14)	14.7812(7)
c /Å	17.3668(6)	15.7948(10)	15.8737(8)	15.907(11)	15.8730(16)	15.6635(8)
α /º	90	90	90	111.97(2)	111.92(3)	111.653(2)
β /º	107.9450(10)	113.833 (6)	113.926 (5)	95.81(2)	95.89(4)	95.272(2)
γ /º	90	90	90	104.97(2)	104.94(3)	105.196(2)
V /Å^3	8252.0(5)	9464.5(8)	9513.7(7)	1708.02(17)	1700.0(3)	1671.04(15)
Z	4	4	4	2	2	2
D_c/gcm^{-3}	1.811	1.753	1.737	2.410	2.411	2.450
μ (Mo-K$_\alpha$)mm^{-1}	7.82	7.61	7.53	11.609	40.633	11.615
F(000)	813	1021	986	434	373	414
Goof	1.069	1.071	1.086	1.022	1.023	1.034
R_1 [I>2σ(I)]	0.037	0.070	0.066	0.026	0.026	0.025
wR_2 [I>2σ(I)]	0.071	0.124	0.113	0.050	0.047	0.057
CCDC Number	2407414	2407412	2407411	2407413	2407409	2407410

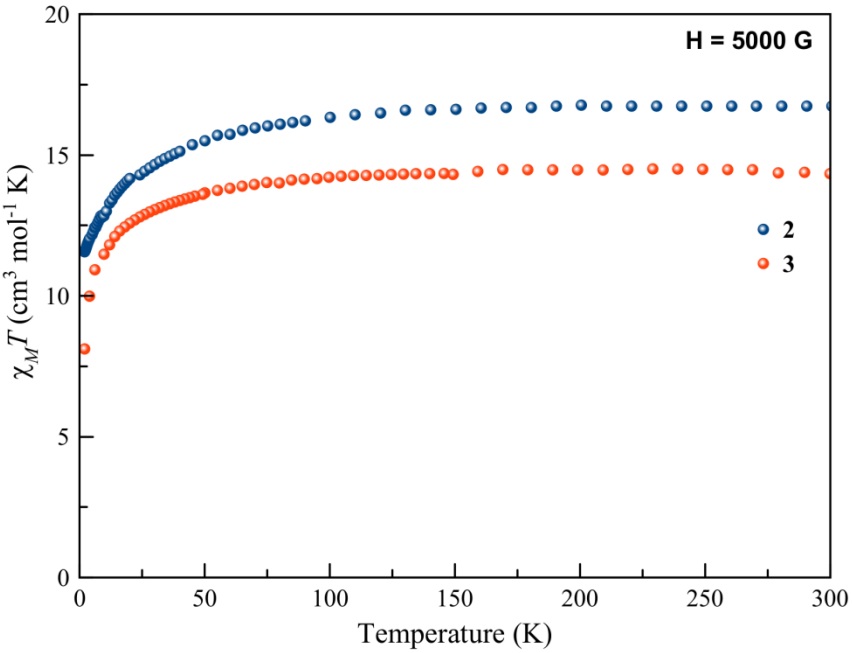

Figure S1: Thermal variation of $\chi_M T$ for **2** and **3**.

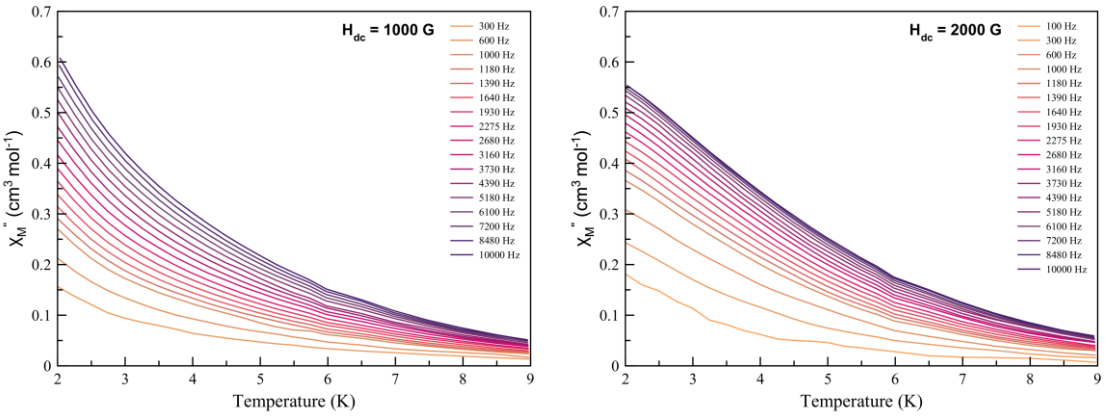

Figure S2: Thermal variation of the χ_M'' for **2** under 1000 (left) and 2000 G (right) external dc magnetic fields.

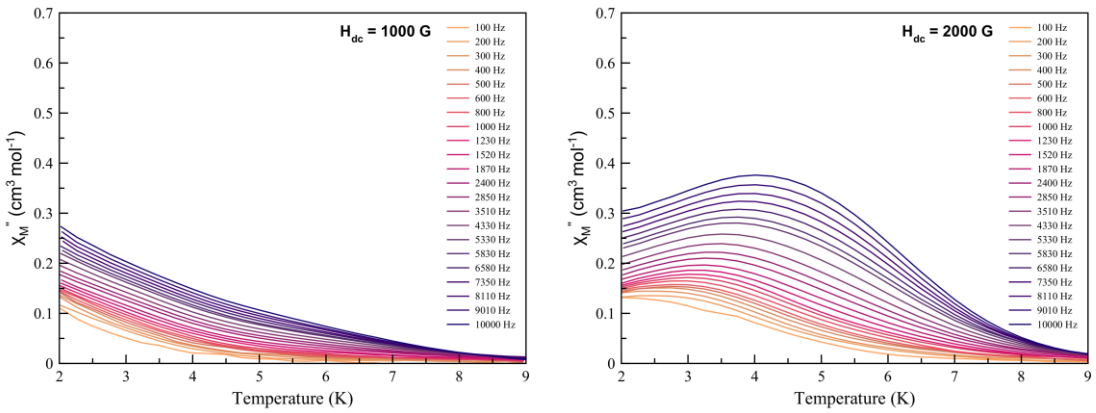

Figure S3: Thermal variation of the χ_M'' for **4** under 1000 (left) and 2000 G (right) external dc magnetic fields.

On the cropped models for theoretical calculations

In order to calculate magnetic parameters such as the magnetic exchange (*J*), Landé *g* factors and Zero-Field Splitting (ZFS) terms, three cropped model (CM) structures were prepared based on the crystalline structure of compound **6**.

For CM1, coordinating metalloligand groups that bridged Gd^{III} ions and formed the chain were cut at the carboxylate level in order to maintain the local electronic configuration while simultaneously simplifying the system, that is, changing the metalloligand by an acetate molecule. In the necessary cases, H atoms were manually added to satisfy sp^3 carbon's bonding requirements. All hydrogens were optimized at the DFT level using PBE and the def2-svp basis set. The evaluation of coulomb and exchange two-electron integrals were accelerated by using the resolution of identity (RI) and the chains of spheres (COSX) approximations with an automatically generated auxiliary basis set. All other atoms were constrained to their crystallographic positions.

For CM2 and CM3, the metalloligands were cut from the crystalline structure, mantaining their positions. In these cases, no geometry optimizations were necessary.

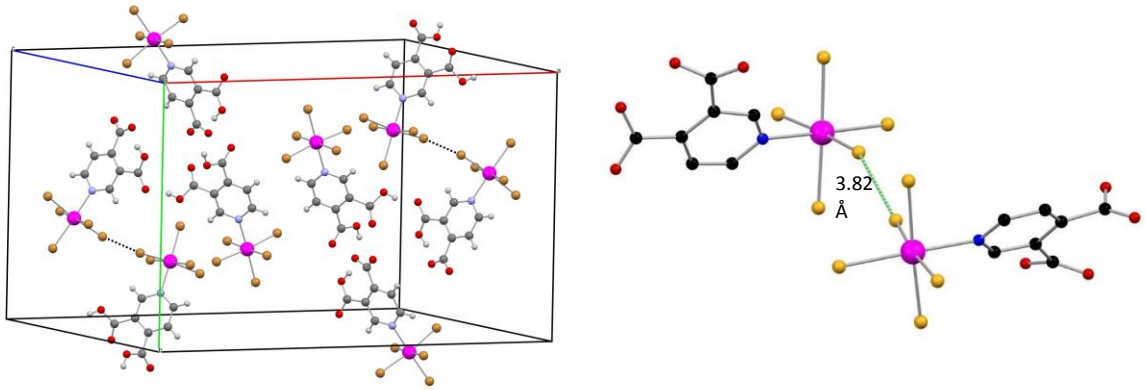

Figure S4: Shortest Br···Br contact in **1**. Cropped model (CM) used in the theoretical calculations.

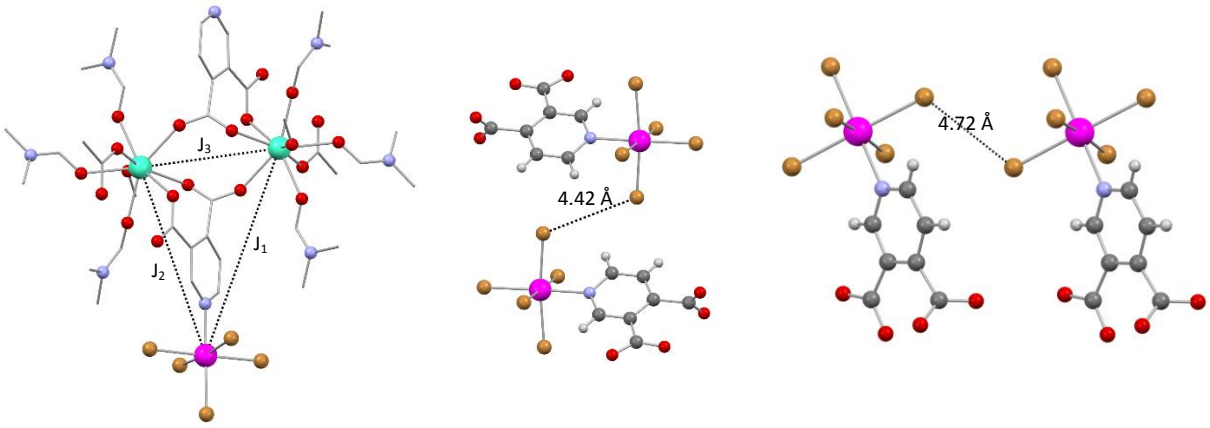

Figure S5: Cropped models (CM), CM1 (left), CM2 (center) and CM3 (right), used in the theoretical calculations.