Supporting Information

Luminescence Thermometry and Field Induced Slow Magnetic Relaxation based on a Near Infrared Emissive Heterometallic Complex.

Karachousos-Spiliotakopoulos, Konstantinos,[a] Vassilis Tangoulis,[a*] Nicos Panagiotou,[b] Anastasios Tasiopoulos,[b] Eufemio Moreno-Pineda,[c] Wolfgang Wernsdorfer,[d,e*] Michael Schulze,[e] Alexandre M. P. Botas,[f] Luis D. Carlos,[f*]

a. *Department of Chemistry, Laboratory of Inorganic Chemistry, University of Patras, 26504, Patras, Greece.*
b. *Department of Chemistry, University of Cyprus, Nicosia 1678, Cyprus*
c. *Depto. de Química-Física, Escuela de Química, Facultad de Ciencias Naturales, Exactas y Tecnología, Universidad de Panamá, Panamá, Panamá.*
d. *Institute for Quantum Materials and Technology (IQMT), Karlsruhe Institute of Technology (KIT), Hermann-von-Helmholtz-Platz 1, D-76344 Eggenstein-Leopoldshafen, Germany.*
e. *Physikalisches Institut, Karlsruhe Institute of Technology, D-76131 Karlsruhe, Germany.*
f. *Phantom-g, CICECO – Aveiro Institute of Materials, Department of Physics, University of Aveiro, 3810-193 – Aveiro, Portugal*

FT-IR

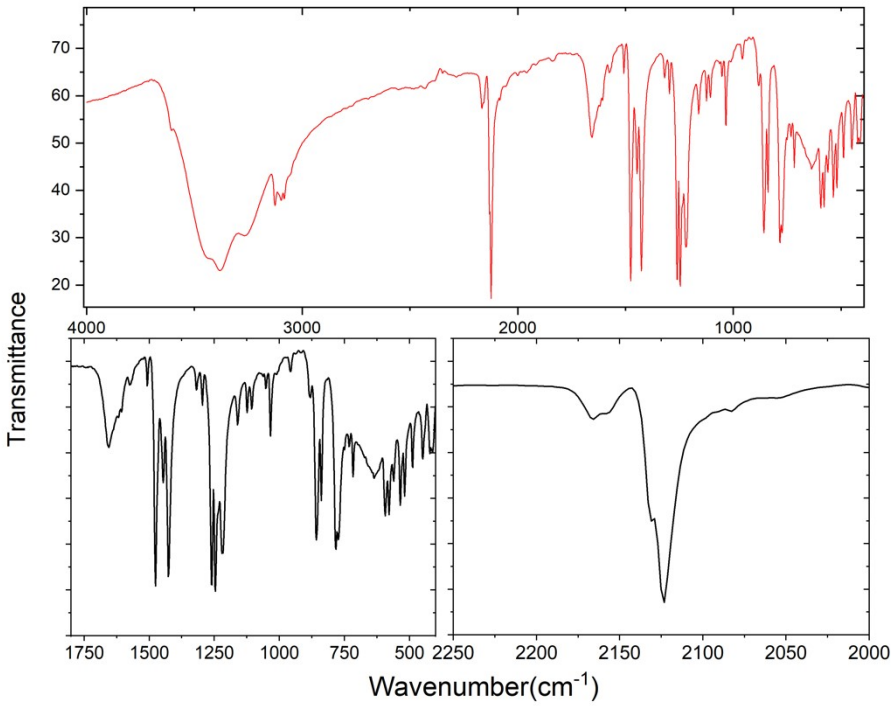

Figure S1. IR spectra of **1**·4H_2O in the range 4000-400 cm^{-1}. Enlarged regions (1600- 400) cm^{-1} and (2200-2080) cm^{-1} are also presented. The bands in the 1560-1420 cm^{-1} region (highlighted region on the left) are assigned to the stretching vibrations of the heterocyclic rings of coordinated bpyO2.

Crystal Packing

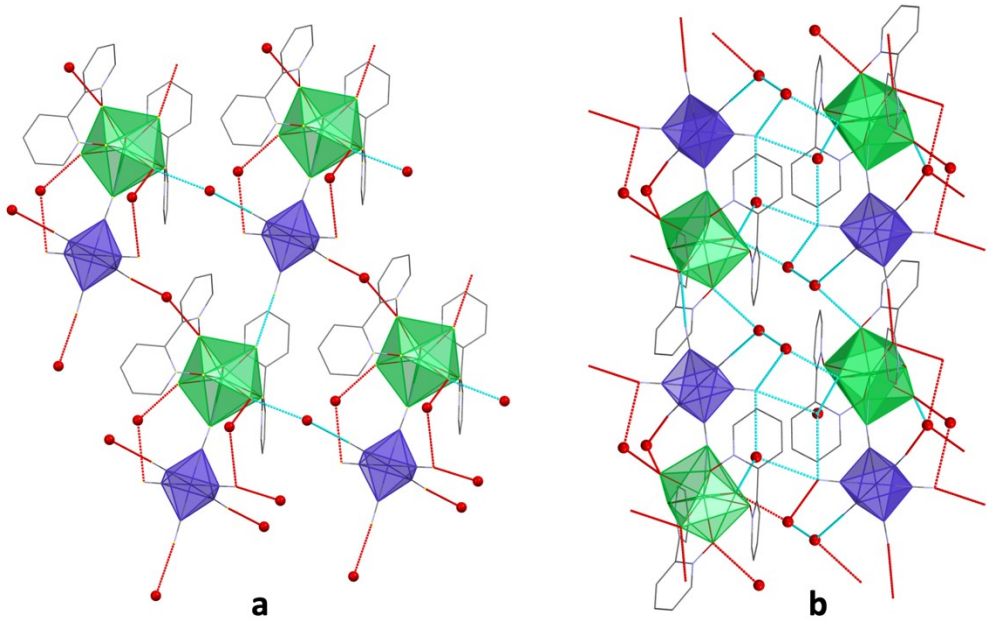

Figure **S2**. **a**) A layer of the 3D architecture of compound **1** parallel to the *ab* plane. The O-H···O/N intermolecular H bonds connecting the molecules in the layer are shown in blue and red dotted lines; hanging contacts to atoms on adjacent layers are drawn with red dotted lines. **c)** interconnected layers through the lattice solvent H_2O molecules (oxygens are denoted as red solid spheres). The hydrogens of the solvent molecules have not been located.

Magnetic measurements

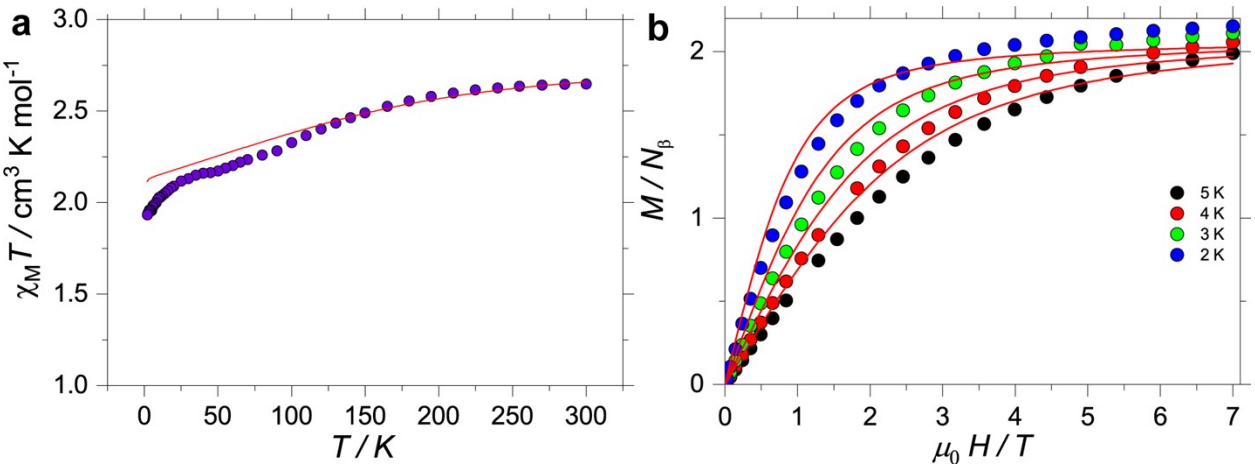

Figure S3. (a) $\chi_M T$ profile for 1 collected with H_{DC} = 1 kOe and (b) $M(H)$ at different temperatures. Solid lines are simulation obtained employing CASSCF results (see text for details).

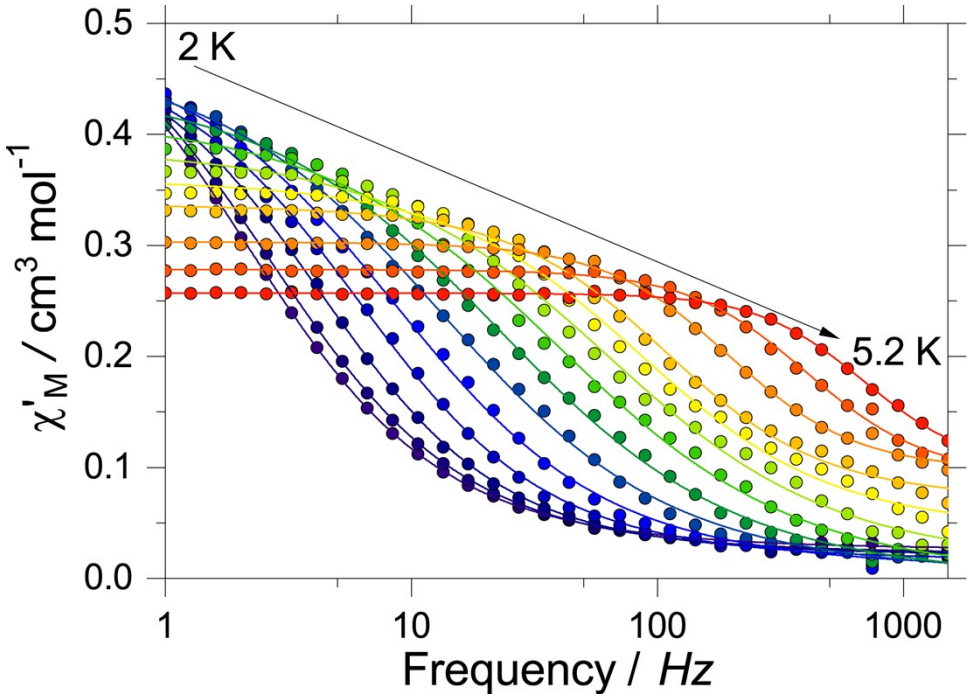

Figure S4. In-phase frequency dependent ($\chi'(\nu)$) magnetic susceptibility for **1** obtained with an oscillating field of 3.5 Oe and H_{DC} = 1.25 kOe in the temperature range of 2 to 5.2 K and employing frequencies between 1 to1.512 Hz.

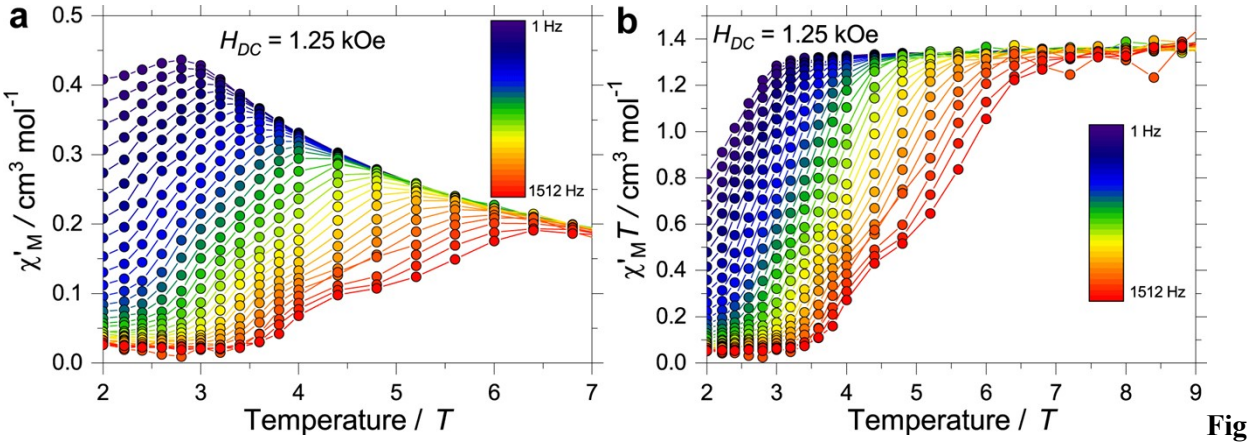

Figure S5. (a) In-phase temperature dependent ($\chi'(T)$) magnetic susceptibility and (b) ($\chi'T(T)$) for **1** obtained employing an oscillating field of 3.5 Oe and H_{DC} = 1.25 kOe.

Luminescence Thermometry

The relative thermal sensibility (S_r) and the temperature uncertainty (δT) are defined as:[1]

$$S_r = \frac{1}{\Delta}\left|\frac{\partial \Delta}{\partial T}\right| \quad and \quad \delta T = \frac{1}{S_r}\left|\frac{\delta \Delta}{\Delta}\right| \qquad (S1)$$

where $\frac{\delta \Delta}{\Delta}$ is the relative uncertainty in Δ. The temperature uncertainty was obtained considering the experimental uncertainty associated with the thermometric parameter as:

$$(\delta \Delta)^2 = \left(\frac{\partial \Delta}{\partial I_1}\delta I_1\right)^2 + \left(\frac{\partial \Delta}{\partial I_2}\delta I_2\right)^2 = \Delta^2\left[\left(\frac{\delta I_1}{I_1}\right)^2 + \left(\frac{\delta I_2}{I_2}\right)^2\right] \qquad (S3)$$

where δI_1 and δI_2 are the uncertainties in I_1 and I_2, respectively, determined considering the standard error ($SE = 1 \times 10^5$) of the mean value of the noise signal of the spectrum (measured at 16 K in the 5882-8000 cm^{-1} range), taken $SE = \frac{\sigma}{\sqrt{N}}$, where σ is the standard derivation and $N = 577$ is the number of points.

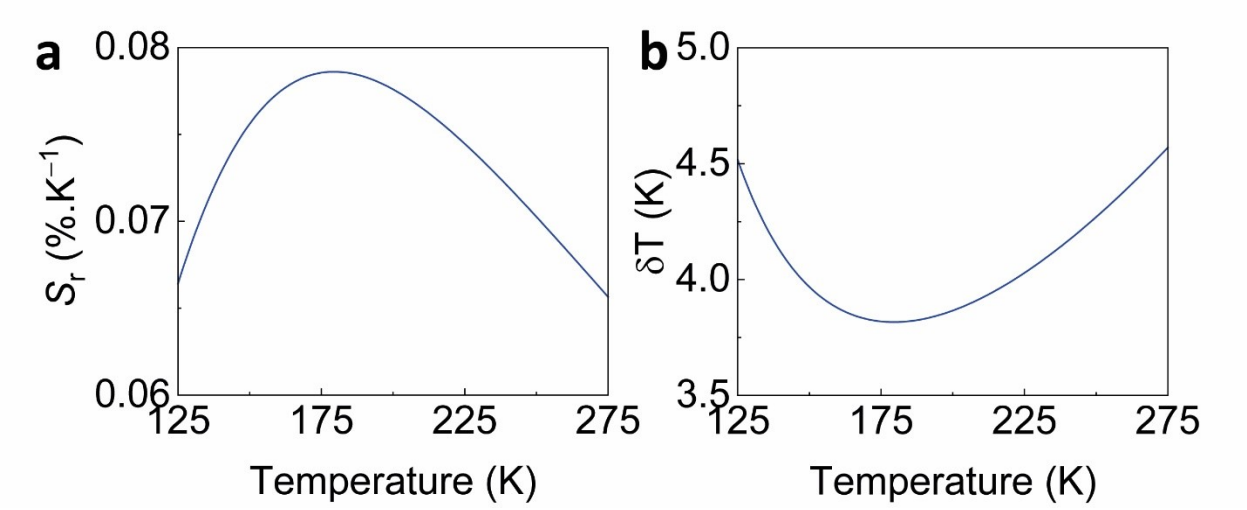

Figure S6. Temperature dependence of (a) S_r and (b) δT.

1. C. D. S. Brites, A. Millán, L. D. Carlos, Lanthanides in Luminescent Thermometry. In Handbook on the Physics and Chemistry of Rare Earths, Gshneidner, K. A.; Bünzli, J.-C.; Pecharsky, V., Eds. Elsevier: 2016; Vol. 48, pp 339-427.

Crystallographic Data

Table S1. Crystallographic Data for Complex **1**·$4H_2O$,

Empirical formula	$C_{26}H_{16}CoN_{10}O_{11}Yb$
Formula weight	876.46
Temperature [K]	100(2)
Wavelength [Å]	0.71073
Crystal system	Triclinic
Space group	P -1
a [Å]	10.1974(4)
b [Å]	12.2711(5)
c [Å]	13.8414(5)
a [°]	85.275(3)
b [°]	87.856(3)
c [°]	70.730(4)
Volume [$Å^3$]	1629.33(12)
Z	2
Density (calculated)[g/cm^3]	1.786
Absorption coefficient [mm^{-1}]	3.434
F(000)	854
Crystal size [mm^3]	0.120 x 0.075 x 0.055
Theta range for data collection [deg]	3.326 to 27.498
Reflections collected	23274
Independent reflections	7335 [R(int) = 0.0669]
Completeness to theta = 25.242°	99.8 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7335 / 0 / 442
Goodness-of-fit on F^2	1.055
Final R indices [I>2sigma(I)]	$R_{obs}{}^a$ = 0.0388, $wR_{obs}{}^b$ = 0.0797
R indices (all data)	R_{all} = 0.0480, wR_{all} = 0.0847
Deposition Number	**2159777**

[a]$R = \Sigma||F_o|-|F_c|| / \Sigma|F_o|$, $wR = \{\Sigma[w(|F_o|^2 - |F_c|^2)^2] / \Sigma[w(|F_o|^4)]\}^{1/2}$ and [b]$w=1/[\sigma^2(F_o^2)+(mP)^2+nP]$ where $P=(Fo^2+2Fc^2)/3$ and m and n are constants

Table S2. Selected Interatomic Distances (Å) and Angles (deg) for **1**·$4H_2O$,

Distance	
Yb···Co1	5.425(1)
O(1)-Yb(1)	2.346(3)
O(2)-Yb(1)	2.288(3)
O(3)-Yb(1)	2.361(3)
O(4)-Yb(1)	2.246(3)
O(5)-Yb(1)	2.325(3)
O(6)-Yb(1)	2.323(3)
O(7)-Yb(1)	2.323(3)
N(5)-Yb(1)	2.424(4)
Co1−C21	1.889(5)
Co1−C22	1.907(5)
Co1−C23	1.907(5)
Co1−C24	1.881(5)
Co1−C25	1.906(5)
Co1−C26	1.905(5)
Angle	
O1−Yb−O2	71.61(11)
O3−Yb−O4	74.27(11)
O5−Yb−O6	72.14(10)
O6−Yb−O7	144.45(11)
O2−Yb−N5	103.76(12)
O4−Yb−N5	88.92(13)
Yb−N5−C21	165.9(4)
C21−Co1−C26	177.80(19)
C22−Co1−C24	179.0(2)
C23−Co1−C25	178.3(2)
Co1−C21−N5	177.0(4)
Co1−C26−N10	178.6(4)

Table S3. Continuous Shape Measures (CShM) values for the potential coordination polyhedra of the Ln^{III} ion in the structure of complex **1**·$4H_2O$

CShM value [a]	Symmetry	Polyhedron
1		
32.231	D_{8h}	Octagon
23.167	C_{7v}	Heptagonal pyramid
15.012	D_{6h}	Hexagonal bipyramid
11.809	O_h	Cube
2.350	D_{4d}	Square antiprism
0.929	$\boldsymbol{D_{2d}}$	**Triangular dodecahedron**
12.316	D_{2d}	Johnson gyrobifastigium J26
28.752	D_{3h}	Johnson elongated triangular bipyramid J14
2.084	C_{2v}	Biaugmented trigonal prism J50
1.429	C_{2v}	Biaugmented trigonal prism
2.941	D_{2d}	Snub diphenoid J84
12.622	T_d	Triakis tetrahedron
25.220	D_{3h}	Elongated trigonal bipyramid

[a] The polyhedron with the smallest CShM value (in bold) is the real coordination polyhedron of the Ln^{III} center in the complex.