Electronic Supplementary Material (ESI) for Dalton Transactions.

Electronic Supplementary Information

Half-sandwich lanthanide crown ether complexes with the slow relaxation of magnetization and photoluminescent behaviors

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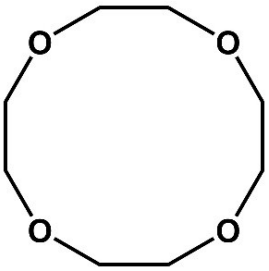

Scheme S1 Structure of 1,4,7,10-tetraoxacyclododecane (12-crown-4 ether).

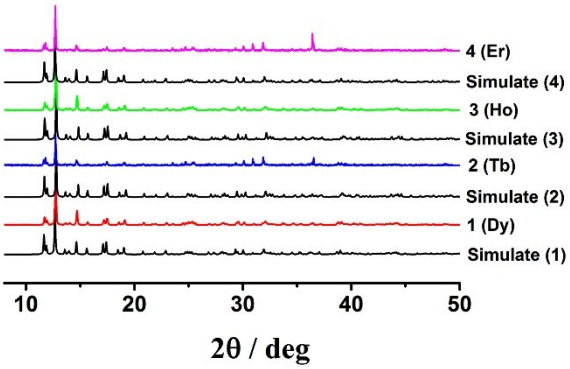

Fig. S1 Experimental and simulated powder XRD patterns of all the complexes.

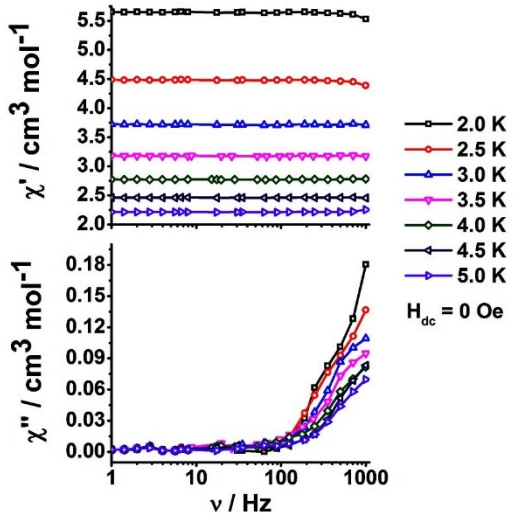

Fig. S2 Frequency-dependent in-phase (χ') and out-of-phase (χ'') ac susceptibilities from 2.0 to 5.0 K for **1** under H_{dc} = 0 Oe.

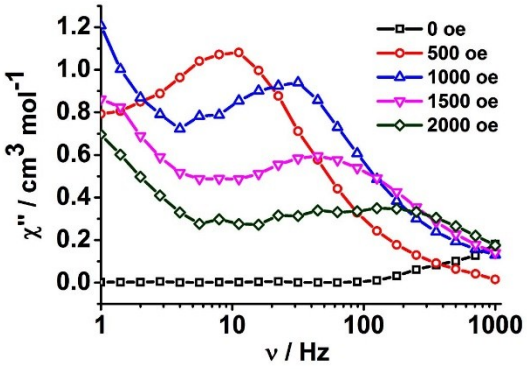

Fig. S3 Frequency-dependent out-of-phase (χ'') ac susceptibilities for **1** at 2.0 K under different external fields.

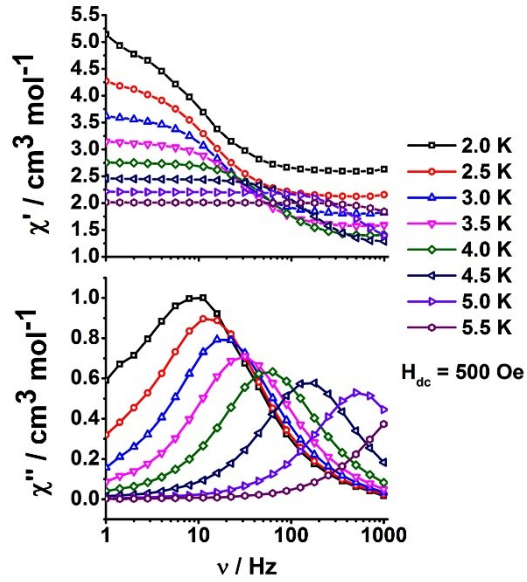

Fig. S4 Frequency-dependent in-phase (χ') and out-of-phase (χ'') ac susceptibilities from 2.0 to 5.5 K for **1** under H_{dc} = 500 Oe.

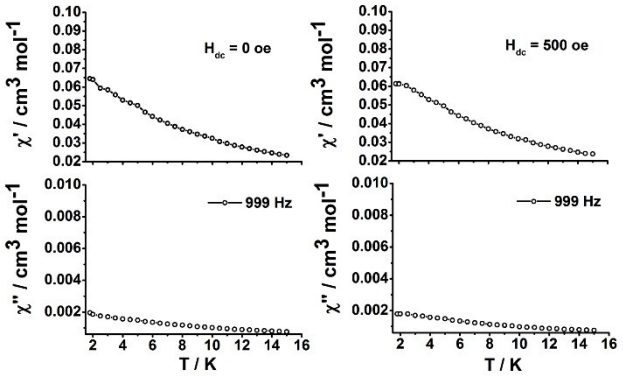

Fig. S5 Temperature-dependent in-phase (χ′) and out-of-phase (χ′′) ac susceptibilities for **2** at the frequency of 999 Hz under H_{dc} = 0 Oe (left) and H_{dc} = 500 Oe (right), respectively.

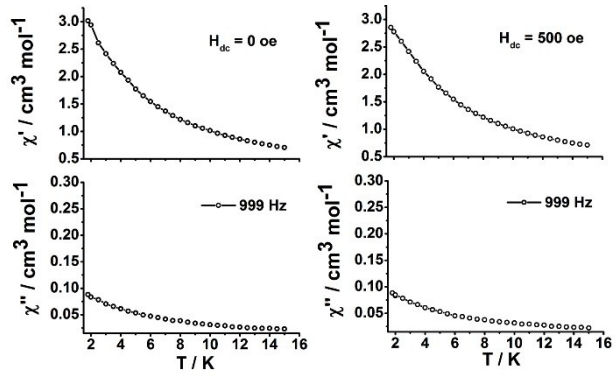

Fig. S6 Temperature-dependent in-phase (χ′) and out-of-phase (χ′′) ac susceptibilities for **3** at the frequency of 999 Hz under H_{dc} = 0 Oe (left) and H_{dc} = 500 Oe (right), respectively.

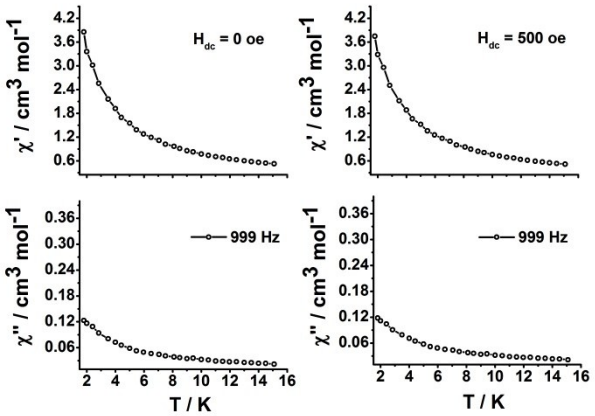

Fig. S7 Temperature-dependent in-phase (χ′) and out-of-phase (χ′′) ac susceptibilities for **4** at the frequency of 999 Hz under H_{dc} = 0 Oe (left) and H_{dc} = 500 Oe (right), respectively.

Table S1 Selected Bond Lengths (Å) and Angles (deg) for Complexes **1**–**4**.

	1	**2**	**3**	**4**
Bond Distances (Å)				
Ln1−O1	2.412 (3)	2.425 (2)	2.387 (2)	2.390 (3)
Ln1−O2	2.480 (3)	2.485 (2)	2.469 (2)	2.473 (2)
Ln1−O4	2.484 (3)	2.488 (2)	2.402 (2)	2.464 (3)
Ln1−O5	2.395 (3)	2.414 (2)	2.467 (2)	2.375 (3)
Ln1−O7	2.466 (3)	2.471 (2)	2.425 (2)	2.444 (3)
Ln1−O8	2.441 (3)	2.447 (2)	2.452 (2)	2.420 (3)
Ln1−O10	2.439 (3)	2.440 (2)	2.453 (2)	2.415 (2)
Ln1−O11	2.465 (2)	2.470 (2)	2.513 (2)	2.452 (2)
Ln1−O12	2.533 (3)	2.537 (2)	2.489 (2)	2.515 (2)
Ln1−O13	2.505 (3)	2.510 (2)	2.424 (2)	2.485 (2)
Bond Angles (deg)				
O1−Ln1−O2	51.99 (10)	52.10 (6)	52.83 (7)	52.37 (9)
O4−Ln1−O5	52.29 (10)	52.37 (7)	52.62 (7)	52.75 (9)
O7−Ln1−O8	52.14 (10)	52.14 (6)	52.72 (7)	52.58 (9)
O10−Ln1−O11	66.11 (8)	66.09 (6)	64.90 (6)	66.50 (8)
O11−Ln1−O12	64.35 (8)	64.53 (6)	64.01 (6)	64.76 (8)
O12−Ln1−O13	63.69 (9)	63.84 (6)	65.92 (6)	64.05 (8)
O10−Ln1−O13	65.48 (9)	65.50 (6)	66.36 (6)	65.84 (8)

Table S2 Parameteres Obtained by Continuous Shape Measure (CShM) Method for Study of Central Ln(III) Coordination Sphere of Complexes **1**–**4**. (The S values indicate the proximity to the selected ideal polyhedron, S = 0 corresponds to the non-distorted polyhedron).

	S_{1Dy}	S_{2Tb}	S_{3Ho}	S_{4Er}
Bicapped square antiprism (JBCSAPR-10, D_{4d})	4.003	3.972	3.872	3.873
Sphenocorona (JSPC-10, C_{2v})	3.043	3.072	2.981	2.959
Tetradecahedron (TD-10, C_{2v})	3.462	3.467	3.479	3.476
Staggered dodecahedron (SDD-10, D_2)	4.389	4.409	4.408	4.411

Table S3 Relaxation Fitting Parameters of the Cole-Cole Plots Based on the Generalized Debye Model[a] for Complex **1** under H_{dc} = 500 Oe in the Temperature Range 2.0–5.5 K.

T / K	χ_s / cm^3 mol^{-1}	χ_T / cm^3 mol^{-1}	ln(τ / s)	α
2.0	2.528	5.350	−3.872	0.21
2.5	2.092	4.330	−4.319	0.14
3.0	1.785	3.637	−4.748	0.10
3.5	1.555	3.141	−5.233	0.07
4.0	1.378	2.754	−5.883	0.05
4.5	1.237	2.449	−6.861	0.03
5.0	1.131	2.204	−8.138	0.02
5.5	0.825	2.100	−9.745	0.01

[a] $\chi_{total}(\omega) = \chi_S + \left[\frac{\chi_T - \chi_S}{1 + (i\omega\tau)^{1-\alpha}}\right]$

Where χ_s is the adiabatic susceptibility, χ_T is the isothermal susceptibility, ω (=2πf) is the angular frequency, τ represents the magnetization relaxation times.