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Electronic Supplementary Information

New Sandwich-Type Lanthanide Complexes Based on Closed-Macrocyclic Schiff base and Phthalocyanine Molecules

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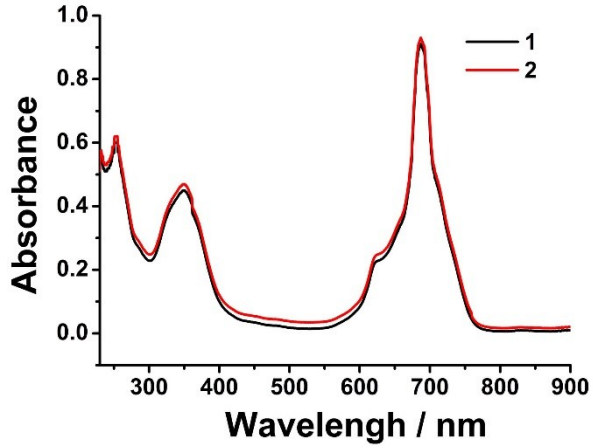

Fig. S1 UV-Vis absorption spectra for complexes **1** and **2** in CH_2Cl_2 (c = 5 × 10^{-5} M).

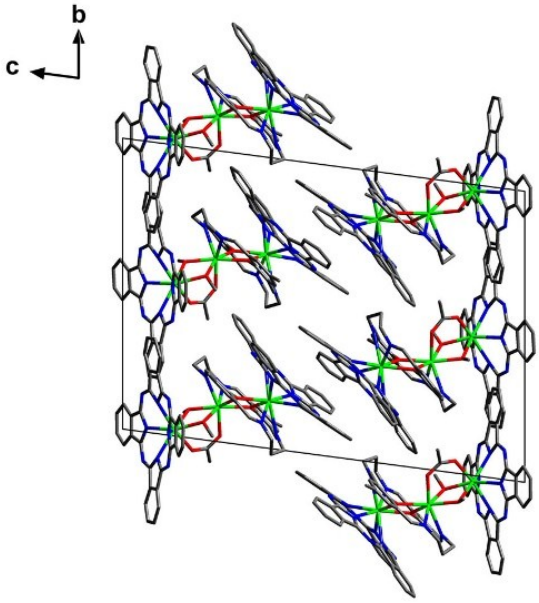

Fig. S2 Crystal packing of lanthanide complexes with hydrogen atoms omitted for clarity. (Ln (Ln = Dy for **1**, and Er for **2**), green; N, blue; O, red; and C grey.)

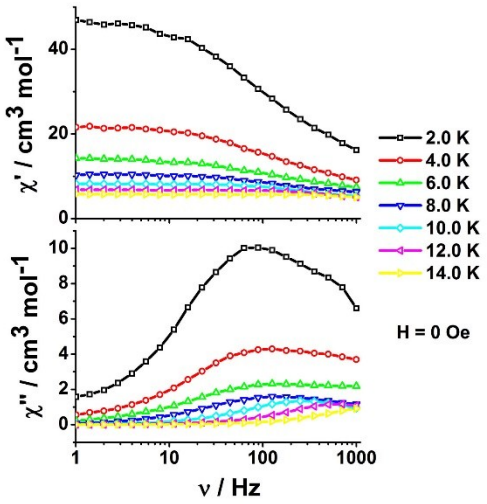

Fig. S3 Frequency-dependent in-phase (χ') and out-of-phase (χ'') ac susceptibilities from 2 to 14 K for **1** at H_{dc} = 0 Oe.

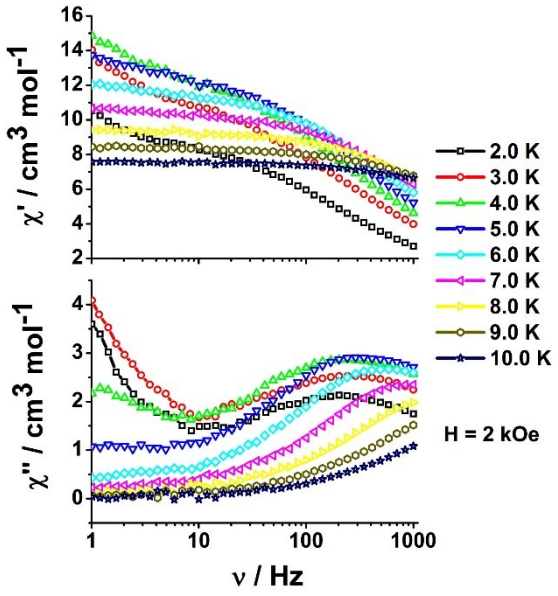

Fig. S4 Frequency-dependent in-phase (χ') and out-of-phase (χ'') ac susceptibilities from 2 to 10 K for **1** at H_{dc} = 2 kOe.

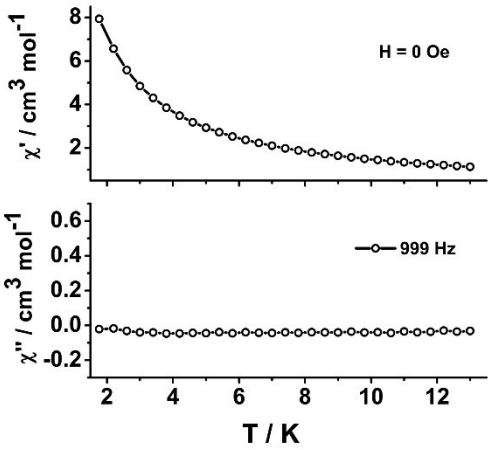

Fig. S5 Temperature-dependent in-phase (χ′) and out-of-phase (χ′′) ac susceptibilities for **2** at the frequency of 999 Hz under H_{dc} = 0 Oe.

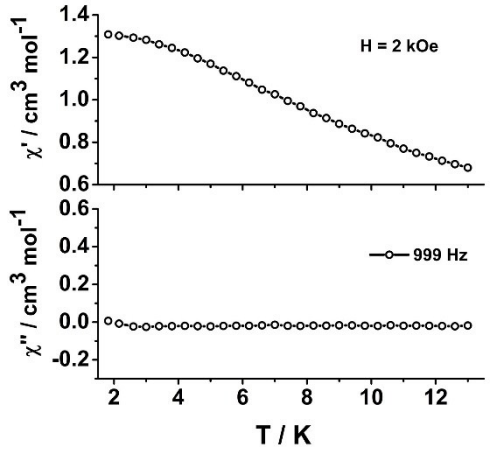

Fig. S6 Temperature-dependent in-phase (χ′) and out-of-phase (χ′′) ac susceptibilities for **2** at the frequency of 999 Hz under H_{dc} = 2 kOe.

Table S1 Selected Bond Lengths (Å) and Angles (°) for Complex 1.

Bond Lengths (Å)					
Dy1A—O5A	2.219 (4)	Dy3A—O5A	2.282 (4)	Dy2B—O1C	2.347 (4)
Dy1A—O4A	2.268 (4)	Dy3A—O4A	2.325 (4)	Dy2B—N3J	2.397 (5)
Dy1A—O1B	2.306 (4)	Dy3A—O3A	2.349 (4)	Dy2B—N3K	2.416 (5)
Dy1A—O2A	2.322 (5)	Dy3A—N3H	2.359 (5)	Dy2B—N3L	2.432 (5)
Dy1A—O1A	2.346 (4)	Dy3A—N3E	2.361 (5)	Dy2B—N3I	2.442 (5)
Dy1A—N2B	2.476 (5)	Dy3A—N3F	2.367 (5)	Dy2B—N2C	2.558 (5)
Dy1A—N1B	2.544 (5)	Dy3A—N3G	2.373 (5)	Dy2B—N1C	2.598 (6)
Dy2A—O1A	2.338 (4)	Dy1B—O5B	2.222 (4)	Dy3B—O4B	2.298 (4)
Dy2A—O1B	2.369 (4)	Dy1B—O4B	2.277 (5)	Dy3B—O5B	2.301 (4)
Dy2A—N3D	2.400 (5)	Dy1B—O2B	2.322 (5)	Dy3B—O3B	2.339 (5)
Dy2A—N3A	2.409 (5)	Dy1B—O1C	2.322 (4)	Dy3B—N3M	2.370 (5)
Dy2A—N3C	2.417 (5)	Dy1B—O1D	2.349 (4)	Dy3B—N3N	2.373 (5)
Dy2A—N3B	2.425 (5)	Dy1B—N1D	2.501 (6)	Dy3B—N3O	2.374 (5)
Dy2A—N1A	2.567 (5)	Dy1B—N2D	2.520 (5)	Dy3B—N3P	2.376 (5)
Dy2A—N2A	2.601 (5)	Dy2B—O1D	2.346 (4)		
Bond Angles (°)					
O5A—Dy1A—O2A	84.72 (17)	O5A—Dy3A—O3A	81.65 (16)	N2C—Dy2B—N1C	76.34 (17)
O4A—Dy1A—O2A	79.28 (16)	O4A—Dy3A—O3A	78.03 (15)	N3L—Dy2B—N3I	69.70 (17)
O5A—Dy1A—O4A	75.14 (15)	N3E—Dy3A—N3F	72.15 (17)	N3J—Dy2B—N3K	70.84 (17)
N2B—Dy1A—N1B	77.93 (18)	N3H—Dy3A—N3G	72.64 (16)	O4B—Dy3B—O5B	71.62 (15)
O1B—Dy1A—O1A	68.19 (14)	O5B—Dy1B—O4B	73.46 (15)	O4B—Dy3B—O3B	80.41 (17)
N1A—Dy2A—N2A	75.03 (17)	O5B—Dy1B—O2B	82.22 (17)	O5B—Dy3B—O3B	78.99 (16)
O1A—Dy2A—O1B	67.28 (14)	O4B—Dy1B—O2B	82.44 (18)	N3M—Dy3B—N3N	72.73 (17)
N3C—Dy2A—N3B	70.20 (17)	O1C—Dy1B—O1D	68.33 (15)	N3O—Dy3B—N3P	71.97 (16)
N3D—Dy2A—N3A	70.90 (18)	N1D—Dy1B—N2D	76.93 (18)		
O5A—Dy3A—O4A	72.85 (15)	O1D—Dy2B—O1C	67.96 (15)		

Table S2 Selected Bond Lengths (Å) and Angles (°) for Complex 2.

Bond Lengths (Å)					
Er1A—O5A	2.205 (5)	Er3A—O5A	2.263 (5)	Er2B—O1C	2.347 (5)
Er1A—O4A	2.260 (5)	Er3A—O4A	2.315 (5)	Er2B—N3J	2.389 (6)
Er1A—O2A	2.294 (5)	Er3A—O3A	2.328 (5)	Er2B—N3K	2.403 (6)
Er1A—O1B	2.304 (5)	Er3A—N3E	2.334 (6)	Er2B—N3I	2.413 (6)
Er1A—O1A	2.336 (5)	Er3A—N3H	2.341 (6)	Er2B—N3L	2.420 (6)
Er1A—N2B	2.442 (6)	Er3A—N3G	2.343 (6)	Er2B—N2C	2.544 (6)
Er1A—N1B	2.514 (6)	Er3A—N3F	2.354 (6)	Er2B—N1C	2.586 (6)
Er2A—O1A	2.330 (5)	Er1B—O5B	2.212 (5)	Er3B—O4B	2.271 (5)
Er2A—O1B	2.352 (5)	Er1B—O4B	2.266 (5)	Er3B—O5B	2.272 (5)
Er2A—N3D	2.392 (6)	Er1B—O2B	2.296 (6)	Er3B—O3B	2.317 (5)
Er2A—N3B	2.398 (6)	Er1B—O1C	2.311 (5)	Er3B—N3M	2.344 (6)
Er2A—N3A	2.401 (6)	Er1B—O1D	2.333 (5)	Er3B—N3O	2.351 (6)
Er2A—N3C	2.402 (6)	Er1B—N1D	2.481 (6)	Er3B—N3N	2.353 (6)
Er2A—N1A	2.553 (6)	Er1B—N2D	2.497 (7)	Er3B—N3P	2.356 (6)
Er2A—N2A	2.588 (6)	Er2B—O1D	2.338 (5)		
Bond Angles (°)					
O5A—Er1A—O2A	84.57 (19)	O5A—Er3A—O3A	81.72 (18)	N2C—Er2B—N1C	76.20 (2)
O4A—Er1A—O2A	79.27 (18)	O4A—Er3A—O3A	77.86 (17)	N3I—Er2B—N3L	70.40 (2)
O5A—Er1A—O4A	75.60 (17)	N3E—Er3A—N3F	72.90 (2)	N3J—Er2B—N3K	70.60 (2)
N2B—Er1A—N1B	77.80 (2)	N3H—Er3A—N3G	73.10 (2)	O4B—Er3B—O5B	72.13 (18)
O1B—Er1A—O1A	68.32 (16)	O5B—Er1B—O4B	73.33 (18)	O4B—Er3B—O3B	80.70 (2)
N1A—Er2A—N2A	75.30 (2)	O5B—Er1B—O2B	82.20 (2)	O5B—Er3B—O3B	78.85 (19)
O1A—Er2A—O1B	67.63 (17)	O4B—Er1B—O2B	82.40 (2)	N3M—Er3B—N3N	73.00 (2)
N3B—Er2A—N3C	70.50 (2)	O1C—Er1B—O1D	68.99 (17)	N3O—Er3B—N3P	72.40 (2)
N3D—Er2A—N3A	71.30 (2)	N1D—Er1B—N2D	77.30 (2)		
O5A—Er3A—O4A	73.43 (16)	O1D—Er2B—O1C	68.32 (17)		

Table S3 Parameters Obtained by Continuous Shape Measure (CShM) Method for Study of Central Dy(III) Coordination Sphere of Complex 1. (The S values indicate the proximity to the selected ideal polyhedron, S = 0 corresponds to the non-distorted polyhedron).

	S_{Dy1A}	S_{Dy2A}	S_{Dy3A}	S_{Dy1B}	S_{Dy2B}	S_{Dy3B}
Capped octahedron (COC-7, C_{3v})	1.592	--	1.989	1.127	--	1.351
Capped trigonal prism (CTPR-7, C_{2v})	0.654	--	1.035	2.086	--	1.108
Pentagonal bipyramid (PBPY-7, D_{5h})	6.330	--	7.068	7.392	--	7.137
Cube (CU-8, O_h)	--	9.466	--	--	10.010	--
Square antiprism (SAPR-8, D_{4d})	--	0.728	--	--	0.706	--
Triangular dodecahedron (TDD-8, D_{2d})	--	2.660	--	--	2.741	--

Table S4 Parameters Obtained by Continuous Shape Measure (CShM) Method for Study of Central Er(III) Coordination Sphere of Complex 2. (The S values indicate the proximity to the selected ideal polyhedron, S = 0 corresponds to the non-distorted polyhedron).

	S_{Er1A}	S_{Er2A}	S_{Er3A}	S_{Er1B}	S_{Er2B}	S_{Er3B}
Capped octahedron (COC-7, C_{3v})	1.518	--	1.900	1.025	--	1.224
Capped trigonal prism (CTPR-7, C_{2v})	0.615	--	0.941	2.100	--	1.015
Pentagonal bipyramid (PBPY-7, D_{5h})	6.404	--	10.901	7.421	--	10.657
Cube (CU-8, O_h)	--	9.704	--	--	10.175	--
Square antiprism (SAPR-8, D_{4d})	--	0.616	--	--	0.591	--
Triangular dodecahedron (TDD-8, D_{2d})	--	2.701	--	--	2.655	--

Table S5 Relaxation Fitting Parameters of the Cole-Cole Plots Based on the Generalized Debye Model[a] for Complex 1 at H_{dc} = 0 Oe in the Temperature Range of 2–14 K.

T / K	χ_S / cm^3 mol^{-1}	χ_T / cm^3 mol^{-1}	ln(τ / s)	α
2	10.27	48.05	−6.60	0.37
4	5.28	22.38	−6.98	0.39
6	4.74	14.57	−7.17	0.33
8	4.70	10.50	−7.29	0.28
10	4.76	8.20	−7.46	0.16
12	4.04	6.77	−8.34	0.10
14	3.56	5.75	−9.19	0.06

[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.

Table S6 Relaxation Fitting Parameters of the Cole-Cole Plots Based on the Extended Debye Model[b] for Complex 1 at H_{dc} = 2 kOe in the Temperature Range of 2–10 K.

T / K	χ_S / cm^3 mol^{-1}	χ_T / cm^3 mol^{-1}	ln(τ_1 / s)	α_1	ln(τ_2 / s)	α_2	β
2	0.30	20.89	−7.24	0.44	−0.71	0.08	0.57
3	0.27	22.44	−7.38	0.49	−1.06	0.09	0.47
4	0.45	17.49	−7.46	0.48	−1.55	0.06	0.23
5	1.26	14.84	−7.74	0.42	−1.86	0.10	0.13
6	1.75	12.38	−8.10	0.29	−2.18	0.12	0.33
7	2.16	10.82	−8.69	0.34	−2.60	0.15	0.05
8	1.55	9.51	−9.48	0.35	−2.78	0.30	0.02
9	0.87	8.46	−10.57	0.39	−3.05	0.11	0.01
10	0.28	7.59	−11.02	0.36	−3.26	0.15	0.01

[b] $$\chi_{total}(\omega) = \chi_S + (\chi_T - \chi_S) \times \left[\frac{\beta}{1 + (i\omega\tau_1)^{1-\alpha_1}} + \frac{1-\beta}{1 + (i\omega\tau_2)^{1-\alpha_2}} \right]$$

Where χ_s is the adiabatic susceptibility, χ_T is the isothermal susceptibility, ω (=2πf) is the angular frequency, τ_1 (high-frequency part) and τ_2 (low-frequency part) represent the magnetization relaxation times, β is the weight of the relaxation process.