

Electronic Supplementary Information

The sandwich-type triple-decker lanthanide complex with mixed phthalocyanine and schiff base ligands

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Experimental Section

General Methods

All the reagents were commercially available and used without further purification. The half-sandwich complex [Dy(Pc)(acac)] and chiral Schiff base ligand H₂L were prepared according to the published procedure.^{1,2} Elemental analyses for C, H and N were performed on a Perkin-Elmer 240C analyzer. Melting points were determined with a X-4 digital micro melting point apparatus and were uncorrected. Infrared spectra were recorded on a Vector22 Bruker Spectrophotometer with KBr pellets in the 400–4000 cm⁻¹ region. UV–vis spectra were obtained on a UV–3100 spectrophotometer. Magnetic susceptibilities for polycrystalline sample were measured with the use of a Quantum Design MPMS-SQUID-VSM magnetometer in the temperature range 1.8–300 K. Field dependences of magnetization were measured using Quantum Design MPMS-SQUID-VSM system in an applied field up to 70 kOe.

Synthetic Procedure

Procedure for preparation of [(Pc)₂Dy₂(L)(H₂O)]·2CHCl₃·H₂O (1)

The half-sandwich complex [Dy(Pc)(acac)] (30.96 mg, 0.04 mmol) and chiral Schiff base ligand H₂L (11.57 mg, 0.02 mmol) were mixed in 10 mL of CHCl₃/CH₃OH (v/v=2:1). The resulted mixture was stirred for about 1 h at room temperature, sealed in 20 mL Teflon-lined stainless steel autoclave, and heated at 80 °C for 24 h. Blue block-shaped crystals were collected by filtration after slow evaporation of the resulting solution for several days. Yield: 38%. M. p. > 300 °C. Anal. Calcd for C₉₄H₅₈Br₂Cl₆Dy₂N₁₈O₄ (%): C, 51.29; H, 2.66; N, 11.45. Found: C, 51.42; H, 2.89; N, 11.63. IR (KBr, cm⁻¹): 3410(m), 3054(s), 1620(m), 1475(m), 1401(m), 1324(m), 1164(s), 1070(m), 879(s), 822(s), 733(m), 633(s). UV–vis (CH₂Cl₂, λ_{max}/ nm, [log (ε / dm³ mol⁻¹ cm⁻¹) in parentheses]): 341(4.35), 618(4.07), 671(4.59), 683(4.61).

X-ray Crystallography

The crystal structure was determined on a Siemens (Bruker) SMART CCD diffractometer using monochromated Mo Kα radiation (λ = 0.71073 Å) at 291 K. Cell parameters were retrieved using SMART software and refined using SAINT³ on all observed reflections. Data was collected using a narrow-frame method with scan widths of 0.30° in ω and an exposure time of 10 s / frame. The highly redundant data sets were reduced using SAINT³

and corrected for Lorentz and polarization effects. Absorption correction was applied using SADABS⁴ supplied by Bruker. Structures were solved by direct methods using the program SHELXL-97.⁵ The positions of the metal atoms and their first coordination spheres were located from direct-methods *E* maps, other non-hydrogen atoms were found in alternating difference Fourier syntheses and least-squares refinement cycles and, during the final cycles, refined anisotropically. Hydrogen atoms were placed in calculated positions and refined as riding atoms with a uniform value of U_{iso} . CCDC reference number 929606 (**1**).

Table S1. Selected bond lengths (Å) and angles (°) for complex **1**

Bond Distances(Å)			
Dy(1)-O(1)	2.379(3)	Dy(1)-N(7)	2.376(5)
Dy(1)-O(2)	2.382(3)	Dy(1)-N(9)	2.591(4)
Dy(2)-O(1)	2.376(3)	Dy(1)-N(10)	2.619(4)
Dy(2)-O(2)	2.397(4)	Dy(2)-N(11)	2.266(5)
Dy(2)-O(1W)	2.435(3)	Dy(2)-N(13)	2.368(5)
Dy(1)-N(1)	2.419(4)	Dy(2)-N(15)	2.369(4)
Dy(1)-N(3)	2.391(4)	Dy(2)-N(17)	2.361(4)
Dy(1)-N(5)	2.404(4)		
Bond Angles(°)			
N(7)-Dy(1)-O(1)	152.42(14)	N(3)-Dy(1)-N(10)	85.95(14)
N(7)-Dy(1)-O(2)	85.82(13)	N(5)-Dy(1)-N(10)	152.36(13)
O(1)-Dy(1)-O(2)	71.99(12)	N(1)-Dy(1)-N(10)	79.16(14)
N(7)-Dy(1)-N(3)	111.12(14)	N(9)-Dy(1)-N(10)	62.22(13)
O(1)-Dy(1)-N(3)	81.26(13)	N(11)-Dy(2)-N(17)	73.88(16)
O(2)-Dy(1)-N(3)	145.27(13)	N(11)-Dy(2)-N(13)	74.33(16)
N(7)-Dy(1)-N(5)	71.06(15)	N(17)-Dy(2)-N(13)	113.06(15)
O(1)-Dy(1)-N(5)	90.65(13)	N(11)-Dy(2)-N(15)	115.15(15)
O(2)-Dy(1)-N(5)	85.70(13)	N(17)-Dy(2)-N(15)	71.83(14)
N(3)-Dy(1)-N(5)	72.63(14)	N(13)-Dy(2)-N(15)	71.22(15)
N(7)-Dy(1)-N(1)	69.50(15)	N(11)-Dy(2)-O(1)	89.20(14)
O(1)-Dy(1)-N(1)	137.46(14)	N(17)-Dy(2)-O(1)	148.45(13)
O(2)-Dy(1)-N(1)	144.90(13)	N(13)-Dy(2)-O(1)	86.58(13)
N(3)-Dy(1)-N(1)	69.26(14)	N(15)-Dy(2)-O(1)	139.60(12)
N(5)-Dy(1)-N(1)	108.05(14)	N(11)-Dy(2)-O(2)	95.63(14)
N(7)-Dy(1)-N(9)	81.26(14)	N(17)-Dy(2)-O(2)	83.38(13)
O(1)-Dy(1)-N(9)	105.03(12)	N(13)-Dy(2)-O(2)	156.44(14)

O(2)-Dy(1)-N(9)	69.44(12)	N(15)-Dy(2)-O(2)	131.78(14)
N(3)-Dy(1)-N(9)	140.83(14)	O(1)-Dy(2)-O(2)	71.77(12)
N(5)-Dy(1)-N(9)	144.02(14)	N(11)-Dy(2)-O(1W)	166.45(14)
N(1)-Dy(1)-N(9)	82.07(13)	N(17)-Dy(2)-O(1W)	119.50(14)
N(7)-Dy(1)-N(10)	134.66(13)	N(13)-Dy(2)-O(1W)	100.39(13)
O(1)-Dy(1)-N(10)	68.52(12)	N(15)-Dy(2)-O(1W)	73.67(13)
O(2)-Dy(1)-N(10)	103.75(13)	O(1)-Dy(2)-O(1W)	77.93(12)
Dy(2)-O(1)-Dy(1)	108.48(14)	O(2)-Dy(2)-O(1W)	84.45(12)
Dy(1)-O(2)-Dy(2)	107.71(14)		

Table S2. Relaxation fitting parameters based on the extended Debye model^a from 2.0 K to 3.8 K for **1**

T / K	$\chi_s / \text{cm}^3 \text{mol}^{-1}$	$\chi_T / \text{cm}^3 \text{mol}^{-1}$	$\ln(\tau_1 / \text{s})$	α_1	$\ln(\tau_2 / \text{s})$	α_2	β
2.0	0.53	10.36	-1.27	0.09	-6.64	0.42	0.40
2.4	0.76	9.72	-1.62	0.12	-7.03	0.35	0.37
2.6	0.89	9.53	-1.66	0.20	-7.25	0.31	0.38
2.8	0.84	9.23	-1.73	0.22	-7.44	0.31	0.34
3.0	0.87	8.61	-1.85	0.22	-7.65	0.30	0.30
3.2	0.94	8.18	-1.92	0.23	-7.85	0.29	0.27
3.4	0.92	7.78	-1.99	0.27	-8.08	0.30	0.24
3.6	0.81	7.27	-2.06	0.21	-8.33	0.33	0.17
3.8	0.86	6.91	-2.13	0.17	-8.53	0.34	0.14

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

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

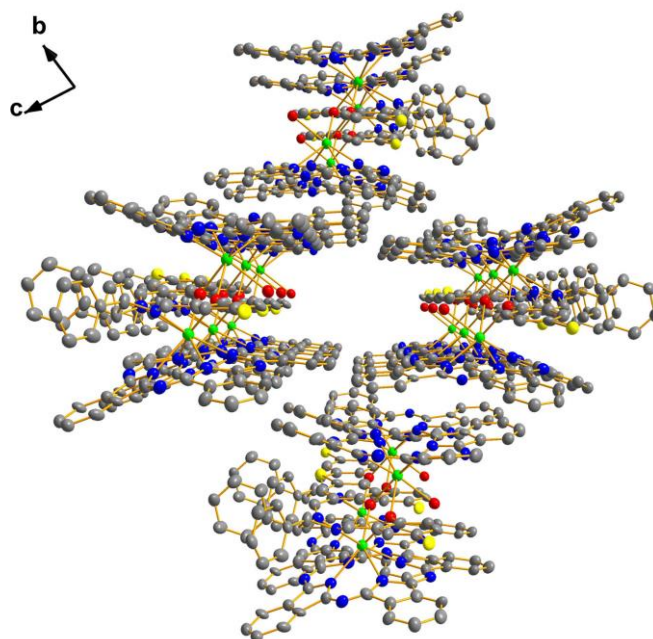


Figure S1. Crystal packing of complex **1**. Hydrogen atoms and solvent molecule are omitted for clarity [Dy(III) green, N blue, O red, Br yellow and C grey].

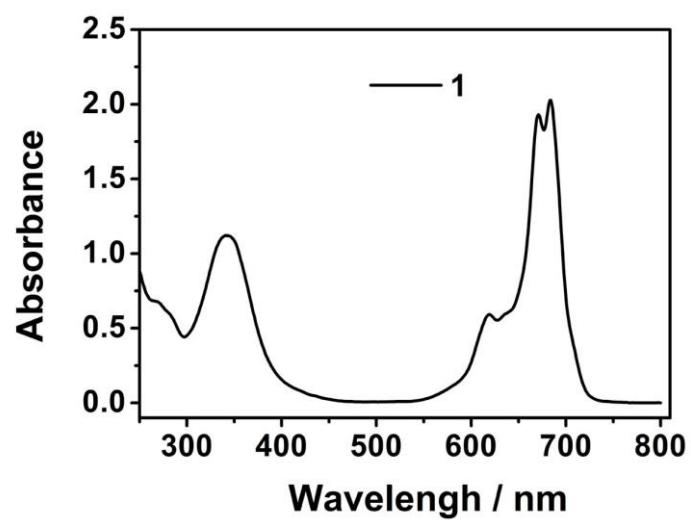


Figure S2. UV-Vis absorption spectra for **1** in CH_2Cl_2 (1×10^{-5} M).

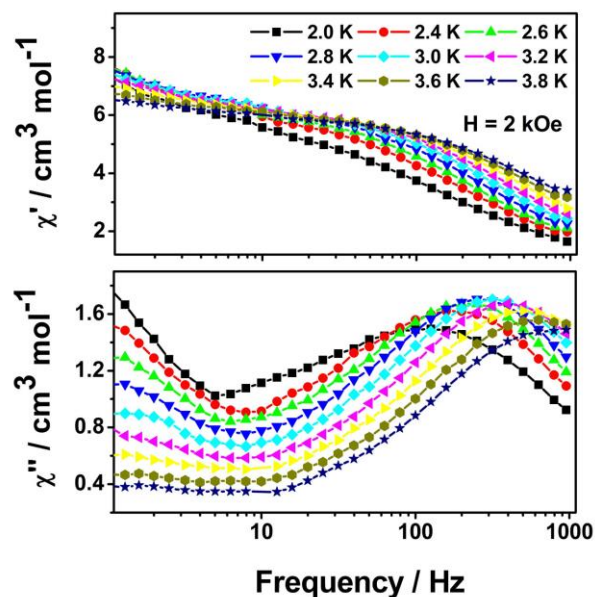


Figure S3. Frequency dependence of the in-phase (χ') and out-of-phase (χ'') for **1** from 2.0 to 3.8 K at a 2 kOe dc field. The solid lines are guides only.

References

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