

Supporting Information

Nano-sized Chiral [Mn₆Ln₂] Clusters Modeled by Enantiomeric Schiff Base Derivatives: Synthesis, Crystal Structures and Magnetic Properties

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Experimental Sections

Materials and General Methods. All starting materials were obtained commercially and were used without further purification. Elemental analyses (C, H and N) were determined on a Perkin-Elmer 2400 analyzer. The IR spectra were recorded in range of 400–4000 cm⁻¹ on a Nicolet 5DX spectrometer (KBr pellets). Powder X-ray diffraction

(PXRD) data were collected over the 2θ range 5–50° using a X'Pert PRO automated diffractometer at room temperature, with a step size of 0.02° in the 2θ angle. Magnetic susceptibility measurements were carried out in the temperature range of 2–300 K with a magnetic field of 1000 Oe on Quantum Design MPMS XL-7 magnetometer.

Synthesis of **1R** or **1S**

A mixture of *o*-vanillin (0.10 mmol, 15.2 mg), (*R*)-(-)-2-phenylglycinol /(*S*)-(+)-2-phenylglycinol (0.10 mmol, 13.7 mg) was added to a methanolic solution (10 mL) of Mn(OAc)₂·4H₂O (0.2 mmol, 49.0 mg) and Dy(NO₃)₃·6H₂O (0.10 mmol, 45.7 mg) at room temperature. After stirring for 0.5 h, triethylamine (0.43 mL, 0.20 mmol) was added, and the resulting solution was further stirred for 4 h, then filtered and the filtrate was left undisturbed to evaporate slowly. After 7 days, orange needle crystals suitable for single-crystal X-ray diffraction were obtained (yield 48% for **1R** and 45% for **1S** based on Dy). Elemental anal. Calcd (%) for **1R**: C, 46.24, H, 3.99, N, 3.63; found C, 46.33, H, 4.21, N, 3.38. Elemental anal. Calcd (%) for **1S**: C, 46.24, H, 3.99, N, 3.63; found C, 46.31, H, 4.16, N, 3.44. FTIR (KBr pellet, cm⁻¹) for **1R**: 3493(br), 3060(w), 2929(w), 2856(w), 2426(w), 1617(m), 1550(s), 1495(w), 1468(w), 1438(m), 1384(s), 1307(m), 1251(s), 1220(m), 1172(w), 1108(w), 1082(w), 1038(m), 979(w), 927(w), 861(w), 742(m), 705(w), 646(w), 617(w), 586(w), 544(w). FTIR (KBr pellet, cm⁻¹) for **1S**: 3487(br), 3060(w), 2932(w), 2865(w), 2426(w), 1618(m), 1549(s), 1495(w), 1468(w), 1437(m), 1384(s), 1307(m), 1251(s), 1220(m), 1172(w), 1108(w), 1081(w), 1037(m), 979(w), 927(w), 860(w), 742(m), 704(w), 647(w), 616(w), 585(w), 544(w).

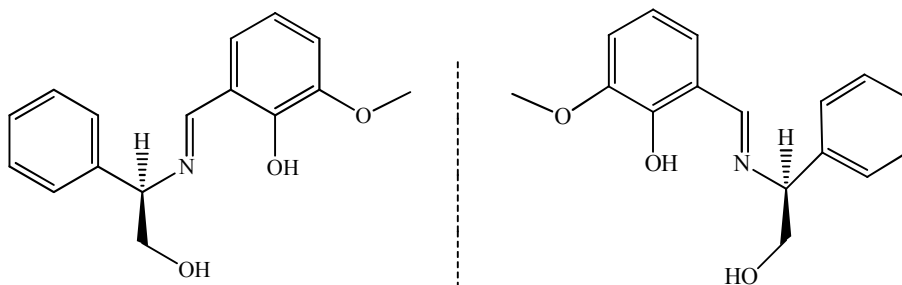
Synthesis of **2R** or **2S**

The procedure for the synthesis of **2** was similar to **1**, except using Gd(NO₃)₃·6H₂O instead of Dy(NO₃)₃·6H₂O, orange needle crystals suitable for single-crystal X-ray diffraction were obtained (yield 51% for **2R** and 47% for **2S** based on Gd). Elemental

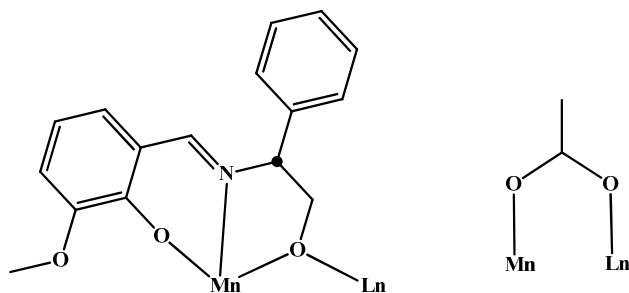
anal. Calcd (%) for **2R**: C, 46.42, H, 4.00, N, 3.64; found C, 46.33, H, 4.17, N, 3.51. Elemental anal. Calcd (%) for **2S**: C, 46.42, H, 4.00, N, 3.64; found C, 46.35, H, 4.15, N, 3.49. FTIR (KBr pellet, cm^{-1}) for **2R**: 3486(br), 3059(w), 2931(w), 2861(w), 2426(w), 1618(m), 1549(s), 1495(w), 1468(w), 1438(m), 1384(s), 1307(m), 1251(s), 1220(m), 1173(w), 1107(w), 1082(w), 1038(m), 979(w), 928(w), 860(w), 742(m), 704(w), 644(w), 616(w), 586(w), 543(w). FTIR (KBr pellet, cm^{-1}) for **2S**: 3485(br), 3060(w), 2930(w), 2860(w), 2426(w), 1617(m), 1549(s), 1495(w), 1468(w), 1438(m), 1384(s), 1307(m), 1251(s), 1220(m), 1173(w), 1108(w), 1081(w), 1037(m), 979(w), 927(w), 860(w), 742(m), 705(w), 645(w), 615(w), 585(w), 542(w).

X-Ray Structural Determination

X-ray diffraction data of the four complexes were collected on Bruker diffractometer MD2 of BL17B beamline of National Center for Protein Sciences Shanghai (NCPSS) at Shanghai Synchrotron Radiation Facility. The *HKL* data were reduced by HKL3000 program. The structures of complexes were solved by direct methods, and the non-hydrogen atoms were located from the trial structure and then refined anisotropically with SHELXTL using a full-matrix leastsquares procedure based on F^2 values. The hydrogen atom positions were fixed geometrically at calculated distances and allowed to ride on the parent atoms. CCDC 1837730–1837733 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.



Scheme S1. Two enantiomeric Schiff base ligands, *R*-H₂L and *S*-H₂L.



Scheme S2. Coordination modes of Ligands *R*-/*S*-H₂L and acetate in this work.

Table S1 Crystal data and structure refinements for **1R**, **1S**, **2R** and **2S**.

Complexes	1R	1S	2R	2S
Formula	C ₁₀₄ H ₁₀₇ Dy ₂ Mn ₆ N ₇ O ₃₇	C ₁₀₄ H ₁₀₇ Dy ₂ Mn ₆ N ₇ O ₃₇	C ₁₀₄ H ₁₀₇ Gd ₂ Mn ₆ N ₇ O ₃₇	C ₁₀₄ H ₁₀₇ Gd ₂ Mn ₆ N ₇ O ₃₇
Formula weight	2684.60	2684.60	2674.10	2674.10
Temp (K)	173(2)	293(2)	293(2)	293(2)
Crystal system	tetragonal	tetragonal	tetragonal	tetragonal
Space group	<i>P</i> 4 ₁	<i>P</i> 4 ₃	<i>P</i> 4 ₁	<i>P</i> 4 ₃
<i>a</i> (Å)	24.788(4)	24.788(4)	24.788(4)	24.788(4)
<i>b</i> (Å)	24.788(4)	24.788(4)	24.788(4)	24.788(4)
<i>c</i> (Å)	22.116(4)	22.116(4)	21.852(4)	22.116(4)
α (deg)	90	90	90	90
β (deg)	90	90	90	90
γ (deg)	90	90	90	90
<i>V</i> (Å ³)	13589(5)	13589(5)	13427(5)	13589(5)
<i>Z</i>	4	4	4	4
<i>D</i> _c (g cm ⁻³)	1.312	1.312	1.323	1.307
<i>M</i> (mm ⁻¹)	1.692	1.692	1.588	1.569
<i>F</i> (000)	5396.0	5396.0	5380.0	5380.0
no. of rflns collected	27819	27815	23649	36699

no. of unique rflns	14263	14257	12137	18465
no. params	1506	1401	1461	1406
GOF	1.035	1.042	1.041	1.107
$R_1,^a wR_2^b [I > 2\sigma(I)]$	0.0423, 0.1143	0.0639, 0.1898	0.0299, 0.0810	0.0794, 0.2343
R_1, wR_2 (all data)	0.0431, 0.1151	0.0647, 0.1913	0.0316, 0.0819	0.0829, 0.2400
Flack parameter	0.358(19)	0.37(3)	0.383(14)	0.42(3)
CCDC	1837730	1837731	1837733	1837732

$$^a R_1 = \sum \|F_o\| - |F_c| / \sum \|F_o\|. \quad ^b wR_2 = [\sum w(F_o^2 - F_c^2) / \sum w(F_o^2)]^{1/2}.$$

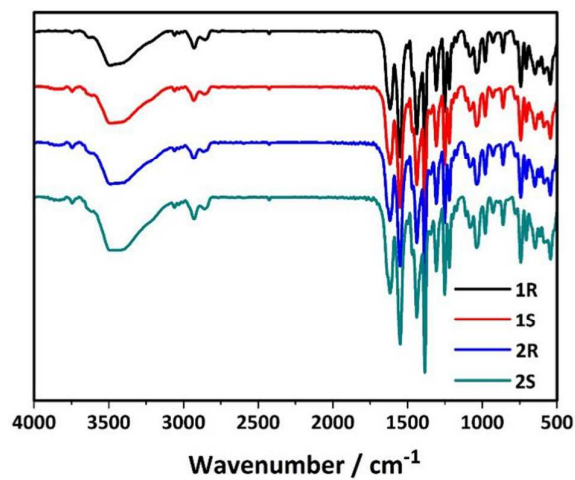


Figure S1. FT-IR spectra of **1R** (black), **1S** (red), **2R** (blue) and **2S** (green).

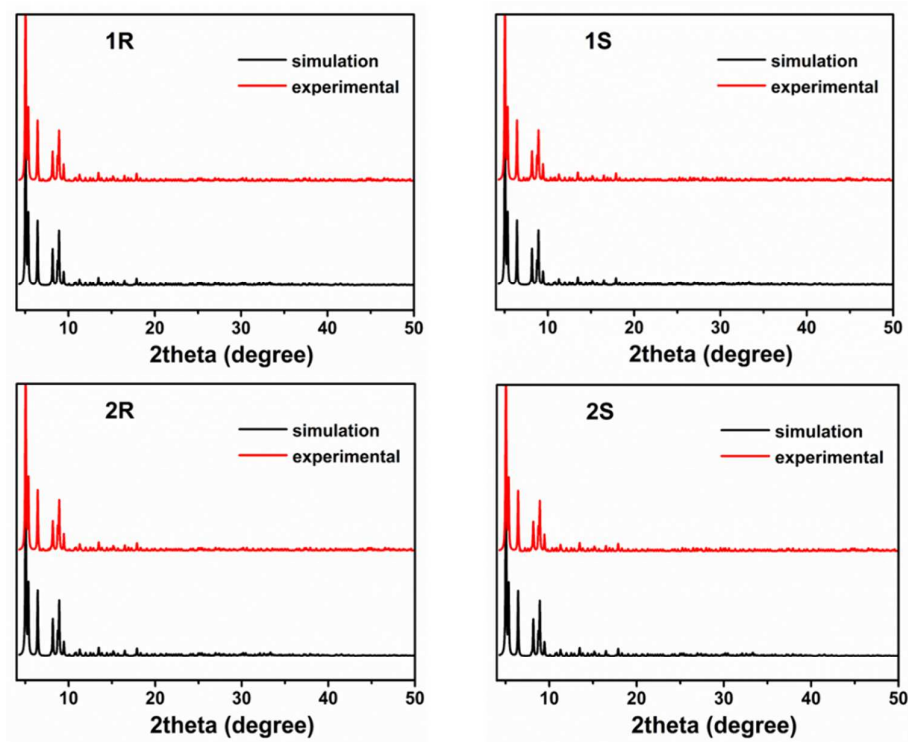


Figure S2. The simulated X-ray powder diffraction patterns (black) and the experimental ones (red) of compounds **1R**, **1S**, **2R** and **2S**. Powder X-ray diffraction (PXRD) of the crystalline samples of complexes **1R**, **1S**, **2R** and **2S** were carried out, and the results are shown in Figure S2. The experimental PXRD patterns are primarily consistent with the the corresponding simulated ones, highlighting the phase purity of the four complexes. Minor inconsistencies in the intensity and shape of the peaks were observed between the experimental and simulation data due to the different orientations of the crystal samples.

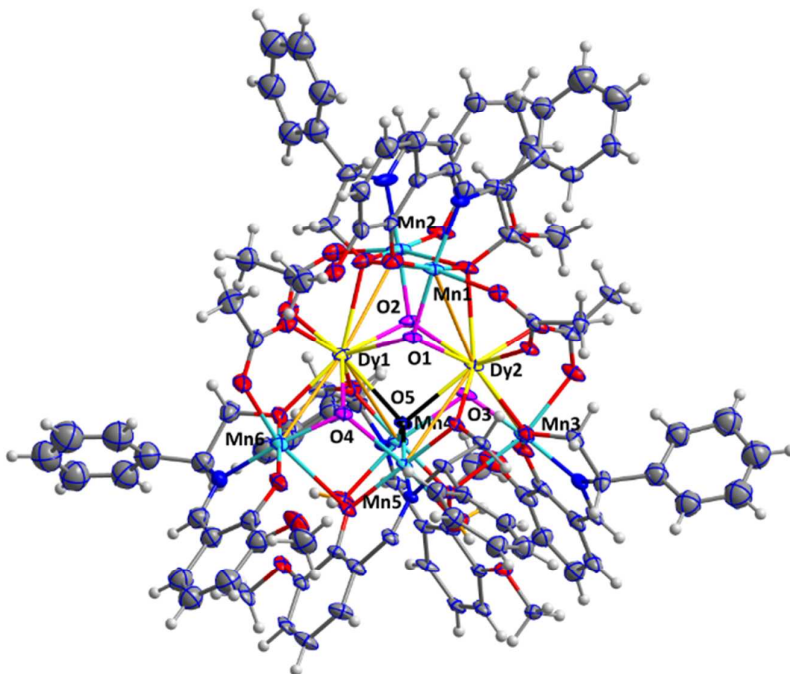


Figure S3. ORTEP representation of compound **1R** with the thermal ellipsoids at 30% probability.

Color code: Dy, yellow; Mn, turquoise; O, red (μ_3 -O, pink; μ_4 -O, black); N, blue; C, gray.

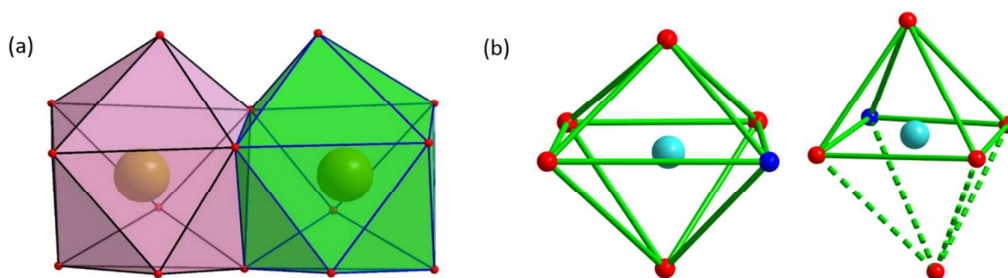


Figure S4. (a) Coordination environment of Dy^{III} ions in compound **1R**. (b) Coordination spheres

around Mn^{III} ions in compound **1R**. The dashed lines represent semi-coordination.

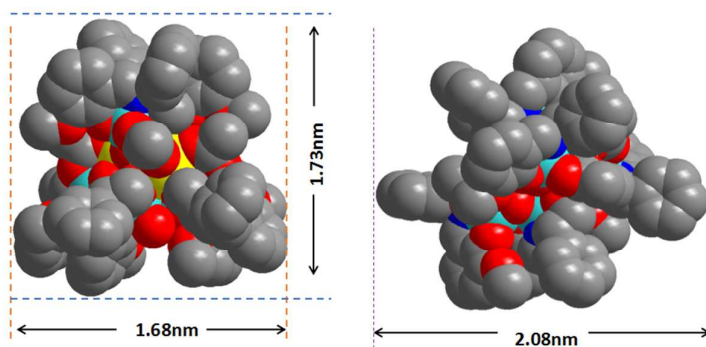


Figure S5. Space-filling representations showing the dimensions and thickness of compound **1R**.

Color code: Dy, yellow; Mn, turquoise; O, red; N, blue; C, gray.

Table S2 Calculating bond valences by using the bond valence sum (BVS) method.

Atom	+2	+3	+4
Mn1	3.31	3.07	3.16
Mn2	3.30	3.06	3.15
Mn3	3.27	3.03	3.12
Mn4	3.31	3.06	3.16
Mn5	3.23	2.99	3.08
Mn6	3.29	3.05	3.14

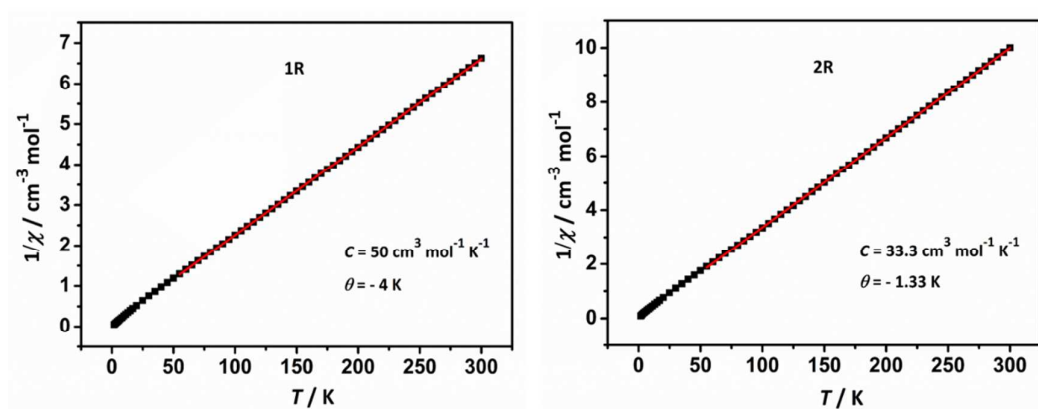


Figure S6. Plots of χ_M^{-1} vs. T for **1R** (left) and **2R** (right) under 1 kOe dc field (The red solid lines represent the best fit to the Curie-Weiss expression).

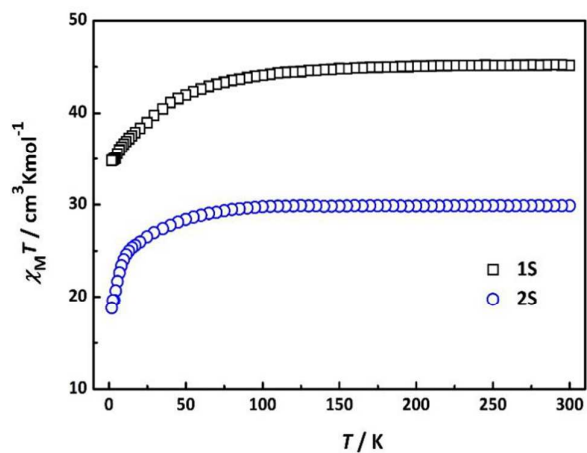


Figure S7. Plots of the temperature dependence of $\chi_M T$ vs. T for **1S** and **2S**.

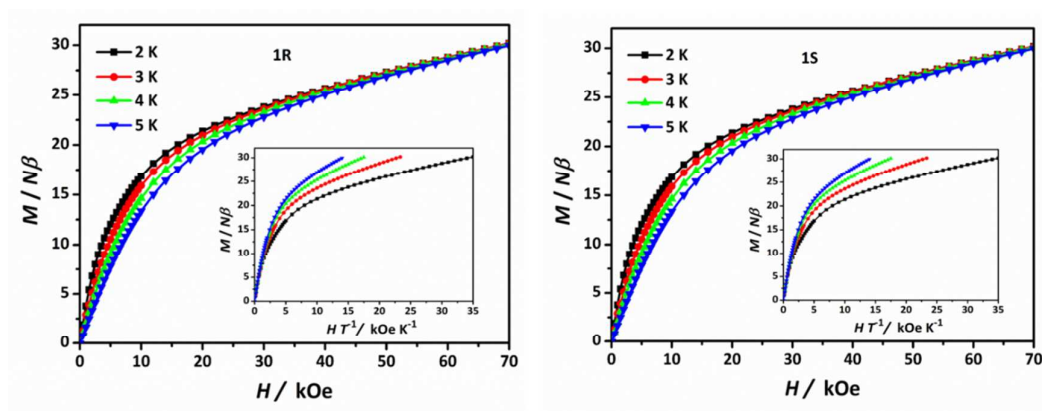


Figure S8. Magnetization curve for compounds **1R** and **1S**. Inset: M vs. H/T plot at different temperatures (2 K, 3 K, 4 K and 5 K).

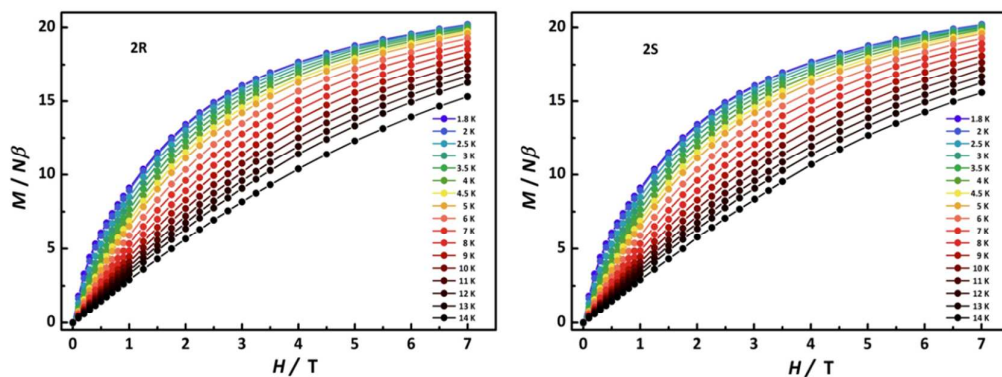


Figure S9. Magnetization curve of applied field in the range of 0–7 T at temperatures between 1.8

and 14 K of complexes **2R** and **2S**.

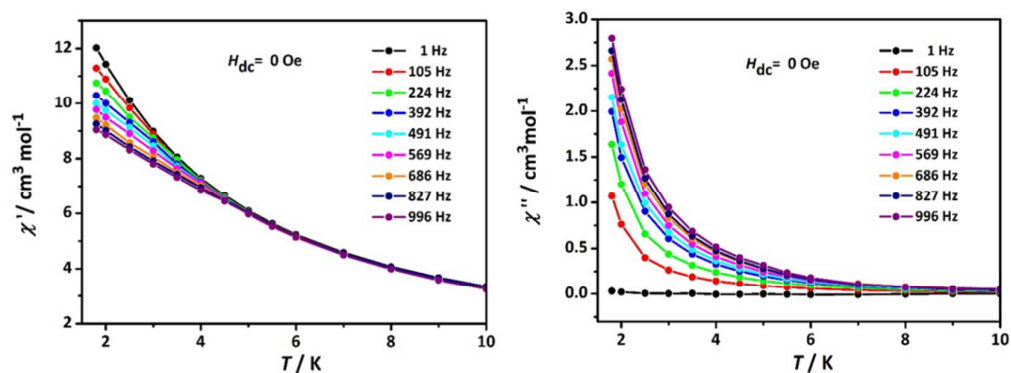


Figure S10. Temperature dependence of the in-phase (χ') (left) and out-of-phase (χ'') (right) ac susceptibility data for **1S** under a zero-dc field.

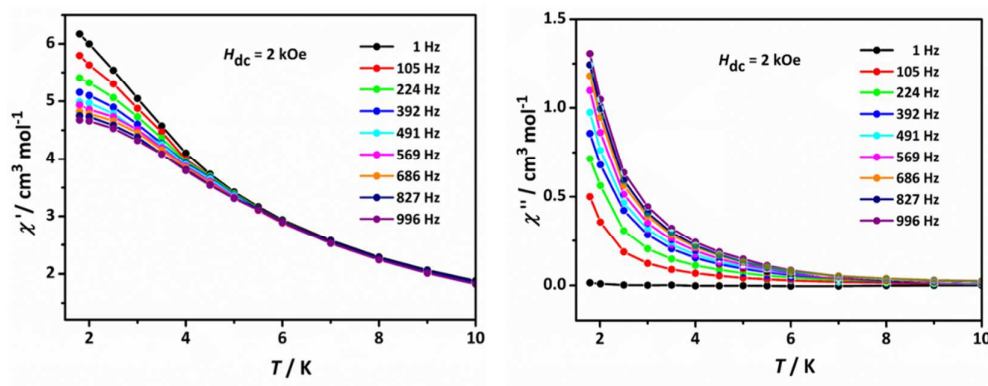


Figure S11. Temperature dependence of the in-phase (χ') (left) and out-of-phase (χ'') (right) ac susceptibility data for **1R** under a 2000 Oe applied dc field.

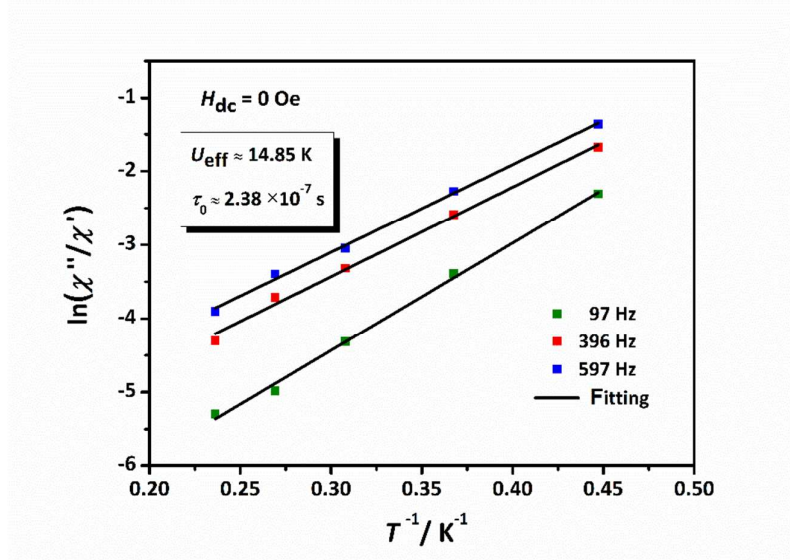


Figure S12 Plot of $\ln(\chi''/\chi')$ versus $1/T$ for **1R** at different frequencies, and the solid lines represent the linear fit with $\ln(\chi''/\chi') = \ln(\omega\tau_0) + E_a/k_B T$.

Magnetic simulation of Genetic Algorithm–Quantum Monte Carlo

In this simulations, we used our program to combine standard genetic Algorithm¹ with Quantum Monte Carlo (QMC). The quantum monte carlo calculation was performed by using of the dirloop_see program of ALPS program². The detailed running procedure were presented in Figure S15³. For genetic algorithm parts, the whole simulation contains 200 generations. Each population contains 30 chromosomes. The value range of J_1 , J_2 and J_3 is set to $[-5, 5] \text{ cm}^{-1}$. The searching accuracy of J are set to $1.0 \times 10^{-5} \text{ cm}^{-1}$. The genetic operations were performed under the crossover probability (P_c) of 0.40 and mutation probability (P_m) with the value of 0.25. For the QMC part, 5×10^6 Monte Carlo steps (MCS) were used for each site, and the first 10% MCS were discarded for thermalization. The detailed information regarding Hamilton operator was presented as eq (S1)

$$H = -J_1 S_{Gd1} S_{Gd2} - J_2 (S_{Mn1} S_{Mn2} + S_{Mn3} S_{Mn4} + S_{Mn5} S_{Mn6}) - J_3 (S_{Gd1} S_{Mn1} + S_{Gd1} S_{Mn2} + S_{Gd1} S_{Mn3} + S_{Gd1} S_{Mn4} + S_{Gd1} S_{Mn5} + S_{Gd2} S_{Mn1} + S_{Gd2} S_{Mn2} + S_{Gd2} S_{Mn4} + S_{Gd2} S_{Mn5} + S_{Gd2} S_{Mn6}) + D_1 (S_{Mn1z}^2 + S_{Mn2z}^2 + S_{Mn4z}^2 + S_{Mn5z}^2) + D_2 (S_{Mn3z}^2 + S_{Mn6z}^2)$$

Eq (S1)

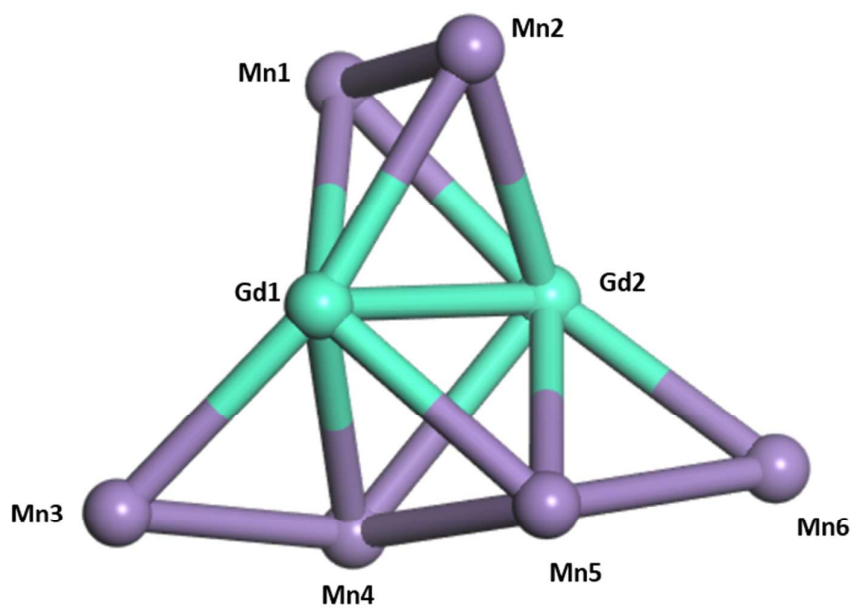


Figure S13. Connecting mode of compound 2R.

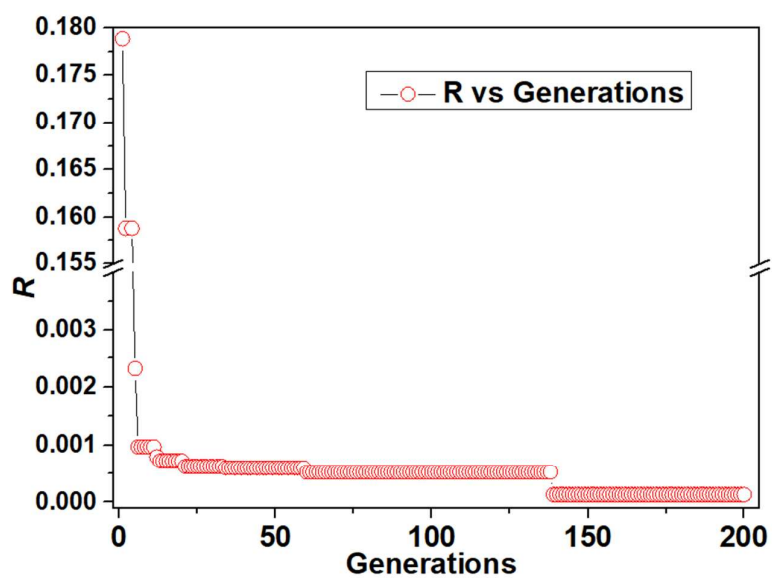


Figure S14 the curve of R vs generations in genetic algorithm searching process.

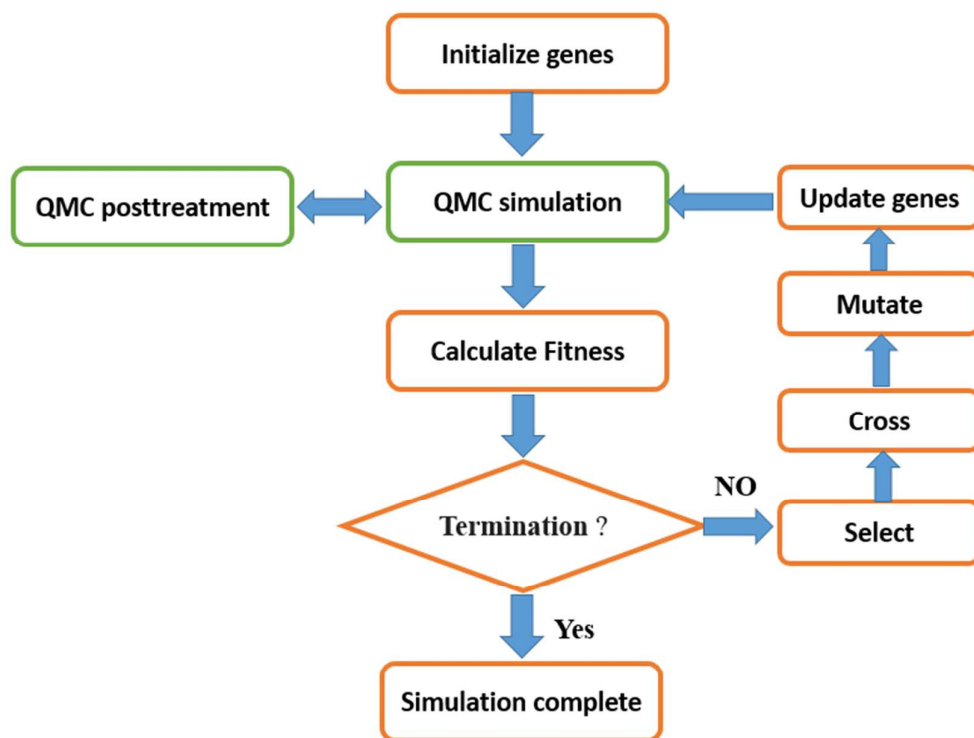


Fig. S15. Running procedure of GAQMC programs with GA part (orange) and QMC part (green) .

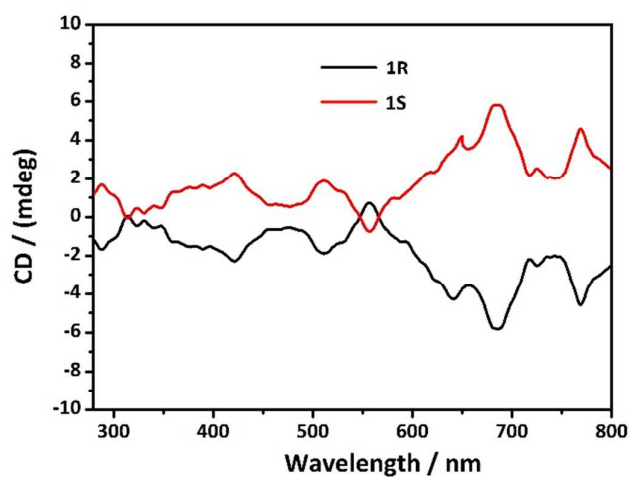


Figure S16. The solid-state CD spectra of **1R** and **1S** in KBr pellet at 298 K.

Reference:

- [1] Holland, J. H. Adaptation in natural and artificial system, Ann Arbor, The University of

Michigan Press, **1975**.

- [2] Albuquerque, A. F.; Alet, F.; Corboz, P.; Dayal, P.; Feiguin, A.; Fuchs, S.; Gamper, L.; Gull, E.; Gürtler, S.; Honecker, A.; Igarashi, R.; Körner, M.; Kozhevnikov, A.; Läuchli, A.; Manmana, S. R.; Matsumoto, M.; McCulloch, I. P.; Michel, F.; Noack, R. M.; Pawłowski, G.; Pollet, L.; Pruschke, T.; Schollwöck, U.; Todo, S.; Trebst, S.; Troyer, M.; Werner, P.; Wessel, S. The ALPS project release 1.3: Open-source software for strongly correlated systems. *J. Magn. Mater.* **2007**, *310*, 1187–1193.
- [3] (a) Zheng, X. Y.; Jiang, Y. H.; Zhuang, G. L.; Liu, D. P.; Liao, H. P.; Kong, X. J.; Long, L. S.; Zheng, L.S. A Gigantic Molecular Wheel of {Gd₁₄₀}: A New Member of the Molecular Wheel Family. *J. Am. Chem. Soc.* **2017**, *139*, 18178–18181. (b) Zheng, X. Y.; Zhang, H.; Wang, Z. X.; Liu, P. X.; Du, M. H.; Han, Y. Z.; Wei, R. J.; Ouyang, Z. W.; Kong, X. J.; Zhuang, G. L.; Long, L.S.; Zheng, L. S. New Insight into Magnetic Interaction in Monodisperse Gd₁₂Fe₁₄ Metal Cluster. *Angew. Chem. Int. Ed.* **2017**, *56*, 11475–11479.