Supplementary Information

Apparently improved energy barrier of Dy(III) SMMs by adopting the bridging bipyrimidine ligand

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Experimental Section

Materials and General Characterization. The used ligands (i.e., 4,4'-dimethyl-2,2'-bipyridyl and 2,2'-bipyrimidine) were obtained from J&K Chemical. $Ln^{III}(tfa)_3$ H_2O and $[Ln^{III}(tfpa)_3]_2$ H_2O were prepared based on reported methods.[44-45] X-ray diffraction (XRD) analyses were conducted using a Bruker D8 FOCUS diffractometer. Infrared spectroscopy and elemental analysis were conducted on a PerkinElmer EA 2400 II and a Thermo Scientific Nicolet iS5 instrument, respectively. Magnetic property measurements of prepared complexes were carried out on Quantum Design SQUID VSM magnetometer.

Synthesis of $Ln^{III}(tfa)_3(dmpy)$ (Ln = Gd 1, Dy 2). A solution of 0.1 mmol $Ln(tfa)_3 \cdot 2H_2O$ was initially dispersed uniformly in 25 mL of heptane and refluxed for 1 hour, resulting in solution A. Subsequently, a solution of 0.1 mmol dmpy in 5 mL of CH_2Cl_2 was added to A and stirred vigorously for 3 minutes. Three days later, transparent block-shaped single crystals of $Gd^{III}(tfa)_3(dmpy)$ and $Dy^{III}(tfa)_3(dmpy)$ were obtained through a solvent evaporation process.

For **1**, the Elemental Analytical results of $C_{27}H_{24}F_9GdN_2O_6$ (yield: 57% base on Gd) are C 40.81; H 3.17; N 3.59(%) with calculated results of C 40.50; H 3.02; N 3.50(%). IR analysis result: 1677 (s), 1598 (m), 1527 (s), 1400(s), 1188 (s), 1163(m), 1141 (s), 1009 (m), 927 (m), 795 (w), 584(w) cm^{-1}.

For **2**, the Elemental Analytical results of $C_{27}H_{24}F_9DyN_2O_6$ (yield: 54%) are C 40.40; H 3.17; N 3.53 (%) with calculated results of C 40.24; H 3.03; N 3.48. IR analysis result: 1679 (s), 1597 (m), 1527 (s), 1400(s), 1189 (s), 1163(m), 1141 (s), 1010 (m), 927 (m), 795 (w), 582(w) cm^{-1}.

Synthesis of $Ln^{III}(tfpa)_3(dmpy)$ (Ln = Gd 3, Dy 4). The synthetic methods of $Ln(tfpa)_3(dmpy)$ are similar to $Ln(tfa)_3(dmpy)$.

For **3**, the Elemental Analytical results for $C_{27}H_{24}F_9GdN_2O_6$ (yield: 57% base on Gd) are C 40.81; H 3.17; N 3.59(%) with calculated results of C 40.50; H 3.02; N 3.50. (%) IR analysis result: 1628 (s), 1591 (m), 1502 (m), 1451 (m), 1404(s), 1361 (m), 1184 (s), 1139 (s), 1059 (m), 1003 (m), 942 (m), 801 (m), 732 (m), 601 (m) cm^{-1}.

For **4**, the Elemental Analytical results for $C_{27}H_{24}F_9DyN_2O_6$ (yield: 54%) are C 40.40; H 3.17; N 3.53. (%) with calculated results of C 40.24; H 3.03; N 3.48 (%). IR analysis result: 1628 (s), 1592 (m), 1502 (m), 1451 (m), 1404(s), 1361 (m), 1184 (s), 1139 (s), 1059 (m), 1002 (m), 942 (m), 801 (m), 733 (w), 603 (w) cm^{-1}.

Synthesis of $[Ln^{III}(tfa)_3]_2(bpyd)$ (Ln = Gd 5, Dy 6). A dispersion of $Ln(tfa)_3 \cdot 2H_2O$ (0.1 mmol) in 25 mL of heptane was heated until boiling. Following a 1-hour reflux, a solution containing 0.05 mmol of bpyd in 10 mL of $CHCl_3$ was introduced. The mixture was stirred for an additional 5 minutes and then cooled to room temperature. Through a three-day solvent evaporation process, transparent block-shaped single crystals of compounds **5** and **6** were obtained.

For **5**, empirical formula is $C_{68}H_{42}F_{18}Gd_2N_4O_{12}$ (yield: 38% base on Gd). The elemental analytical measured values are C 46.74; H 2.27; N 3.24 (%) with calculated results of C 46.31; H 2.40; N 3.18. IR analysis result: 3426(w), 1601(s), 1539(m), 1501(s), 1259(s), 1225(s), 1152(s), 811(m), 657(m), 587(w) cm^{-1}.

For **6**, empirical formula is $C_{68}H_{42}F_{18}Dy_2N_4O_{12}$ (yield: 40% base on Dy). The elemental analytical measured values are C 46.51; H 2.30; N 3.20 (%) with calculated results of C 46.13; H 2.38; N 3.16. IR analysis result: 3428(w), 1603(s), 1539(m), 1501(s), 1259(s), 1226(s), 1150(s), 812(m), 657(m), 588(w) cm^{-1}.

Synthesis of [Ln^{III}(tfpa)$_3$]$_2$(bpyd) (Ln = Gd 7, Dy 8). The preparation procedures for [Ln^{III}(tfpa)$_3$]$_2$(bpyd) follow a similar pathway to that of [Ln^{III}(tfa)$_3$]$_2$(bpyd). Initially, Ln(tfpa)$_3$·2H$_2$O (0.1 mmol) was uniformly dispersed in 25 mL of heptane and heated until boiling occurred. Subsequently, the mixture was refluxed for 1 hour, following which a solution containing 0.05 mmol of bpyd in 10 mL of CHCl$_3$ was introduced. The combined mixture was stirred vigorously for an additional 5 minutes before being cool down to room temperature. After standing for three days, transparent block-shaped single crystals of compounds **7** and **8** were obtained through a solvent evaporation method.

For **7**, the Elemental Analytical results for $C_{27}H_{24}F_9GdN_2O_6$ (yield: 57% base on Gd) are C 40.81; H 3.17; N 3.59 (%) with calculated results of C 40.50; H 3.02; N 3.50. (%) IR analysis result: 1601 (m), 1549 (s), 1520 (m), 1464 (s), 1401 (s), 1310(m), 1247 (s), 1191 (s), 1127 (s), 813 (m), 645(w), 575(w) cm^{-1}.

For **8**, the Elemental Analytical results for $C_{27}H_{24}F_9DyN_2O_6$ (yield: 54% base on Dy) are C 40.40; H 3.17; N 3.53. (%) with calculated results of C 40.24; H 3.03; N 3.48. IR analysis result: 1601 (m), 1547 (s), 1520 (m), 1463 (s), 1401 (s), 1310 (m), 1248 (s), 1191 (s), 1127 (s), 812 (m), 645 (w), 577 (w) cm^{-1}.
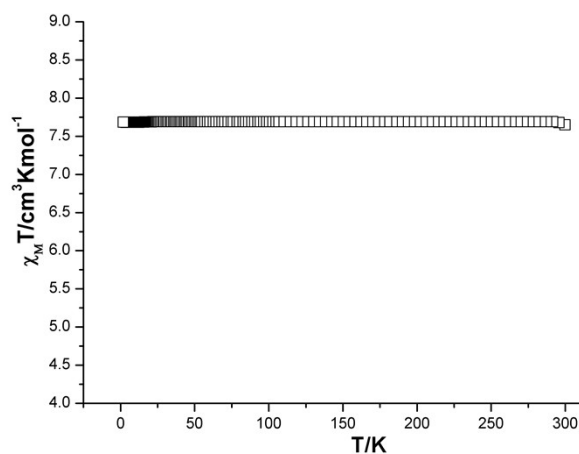
Figure S1 Experimental temperature dependence magnetic susceptibility of complex **1.**
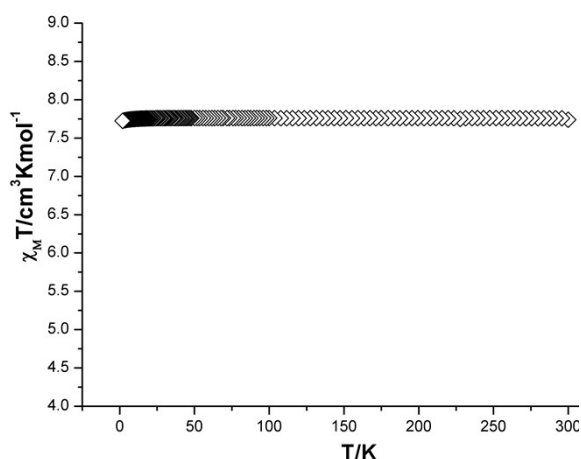
Figure S2 Experimental temperature dependence magnetic susceptibility of complex **3**.

Equation S1

$$\chi_{\mathrm{M}} = \left(\frac{2Ng^2\beta^2}{kT} \right) \times$$

$$\left(\frac{\exp(J/kT) + 5\exp(3J/kT) + 14\exp(6J/kT) + 30\exp(10J/kT) + 55\exp(15J/kT) + 91\exp(21J/kT) + 140\exp(28J/kT)}{1 + 3\exp(J/kT) + 5\exp(3J/kT) + 7\exp(6J/kT) + 9\exp(10J/kT) + 11\exp(15J/kT) + 13\exp(21J/kT) + 15\exp(28J/kT)} \right)$$

Computational details

Both of binuclear complexes **6** and **8** with central symmetrical structure have one type of magnetic center Dy^{III} ion. Complete-active-space self-consistent field (CASSCF) calculations on individual Dy^{III} fragments for **6** and **8** (see Figure S3 for the calculated complete structures of **6** and **8**) on the basis of single-crystal X-ray determined geometry have been carried out with MOLCAS 8.4[S1] program package. Each individual Dy^{III} fragment in **6** and **8** was calculated keeping the experimentally determined structure of the corresponding compound while replacing the neighboring Dy^{III} ion by diamagnetic Lu^{III}.

The basis sets for all atoms are atomic natural orbitals from the MOLCAS ANO-RCC library: ANO-RCC-VTZP for Dy^{III}; VTZ for close N and O; VDZ for distant atoms. The calculations employed the second order Douglas-Kroll-Hess Hamiltonian, where scalar relativistic contractions were taken into account in the basis set and the spin-orbit couplings were handled separately in the restricted active space state interaction (RASSI-SO) procedure. Active electrons in 7 active spaces include all f electrons (CAS(9 in 7) in the CASSCF calculation. To exclude all the doubts, we calculated all the roots in the active space. We have mixed the maximum number of spin-free state which was possible with our hardware (all from 21 sextets, 128 from 224 quadruplets, 130 from 490 doublets for Dy^{II}. SINGLE_ANISO[S2] program was used to obtain the energy levels, g tensors, magnetic axes, *et al.,* based on the above CASSCF/RASSI-SO calculations.
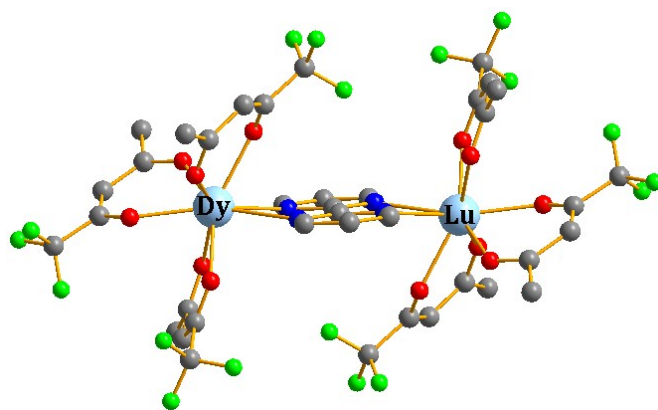
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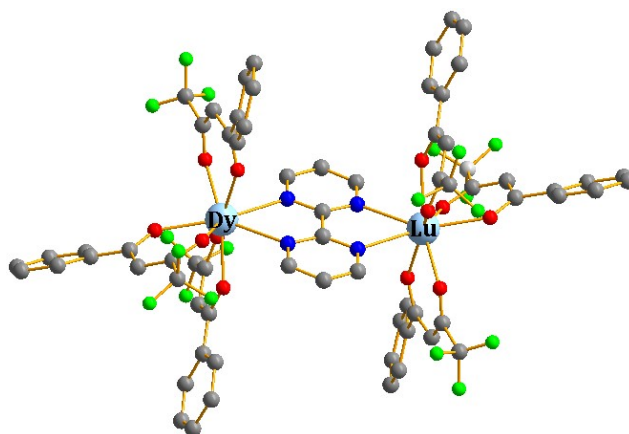
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Figure S3. Calculated complete structures of complexes **6** and **8**; H atoms are omitted.

Table S1. Calculated energy levels (cm^{-1}), g (g_x, g_y, g_z) tensors and predominant m_J values of the lowest eight Kramers doublets (KDs) of individual Dy^{III} fragments for complexes **6** and **8** using CASSCF/RASSI-SO with MOLCAS 8.4.

KDs	6			8		
	E/cm^{-1}	g	m_J	E/cm^{-1}	g	m_J
1	0.0	0.006 0.012 19.499	±15/2	0.0	0.026 0.040 19.339	±15/2
2	126.8	0.297 0.446 16.429	±13/2	124.2	0.617 1.151 15.235	±13/2
3	175.5	1.567 1.804 13.586	±11/2	192.9	1.365 2.030 11.399	±11/2

4	220.5	4.326 5.393 7.338	±7/2	246.7	8.976 6.736 3.038	±5/2
5	266.6	2.044 3.355 11.021	±5/2	285.0	1.680 3.734 12.053	±3/2
6	343.6	0.194 0.288 16.635	±3/2	325.7	0.443 0.650 18.725	±7/2
7	437.9	0.034 0.081 16.372	±1/2	439.3	0.035 0.065 18.026	±1/2
8	497.9	0.017 0.068 18.136	±9/2	562.9	0.009 0.016 19.269	±9/2

Table S2. Wave functions with definite projection of the total moment $| m_J >$ for the lowest two KDs of individual Dy[III] fragments for complexes **6** and **8**.

	E/cm^{-1}	wave functions
6	0.0	94.5%$|\pm15/2>$
	126.8	75%$|\pm13/2>$+10.1%$|\pm11/2>$+7.8%$|\pm9/2>$
8	0.0	90.8%$|\pm15/2>$7.9%$|\pm11/2>$
	124.2	65.9%$|\pm13/2>$+24.1%$|\pm9/2>$

To fit the exchange interactions in complexes **6** and **8**, we took two steps to obtain them. Firstly, we calculated individual Dy[III] fragments using CASSCF/RASSI-SO to obtain the corresponding magnetic properties. Then, the exchange interactions between the magnetic centers were considered within the Lines model,[S3] while the account of the dipole-dipole magnetic couplings were treated exactly. The Lines model is effective and has been successfully used widely in the research field of d and f-elements single-molecule magnets.[S4]

For complexes **6** and **8**, there is only one type of $\tilde{J}$.

The Ising exchange Hamiltonian is:

$$\hat{H}_{exch} = -\tilde{J}\,\hat{\tilde{S}}_{Dy1}\,\hat{\tilde{S}}_{Dy2}$$

(1)

The $\tilde{J}_{total}$ is the parameter of the total magnetic interaction ($\tilde{J}_{total} = \tilde{J}_{dip} + \tilde{J}_{exch}$)

between magnetic center ions. The $\tilde{S}_{Dy} = 1/2$ is the ground pseudospin on the Dy^{III} site. The dipolar magnetic coupling can be calculated exactly, while the exchange coupling constant was fitted through comparison of the computed and measured magnetic susceptibilities using the POLY_ANISO program.[S2]

Table S3. Exchange energies E (cm^{-1}), the energy difference between each exchange doublets Δ_t (cm^{-1}) and the main values of the g_z for the lowest two exchange doublets of **6** and **8**.
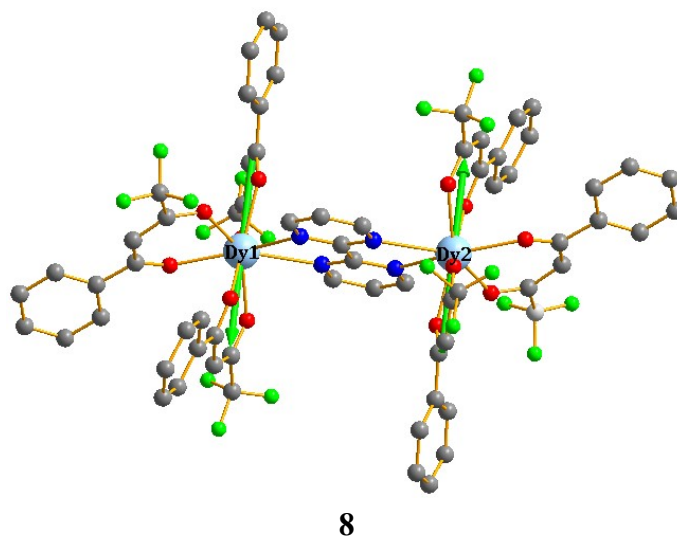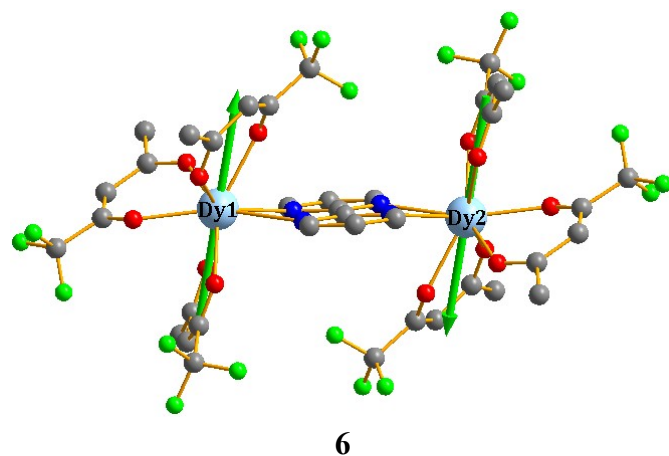
	6			**8**		
	E	Δ_t	g_z	E	Δ_t	g_z
1	0.00	0.61×10^{-6}	0.000	0.00	0.77×10^{-5}	0.000
2	1.42	0.44×10^{-6}	38.998	1.39	0.50×10^{-5}	38.678

6

8
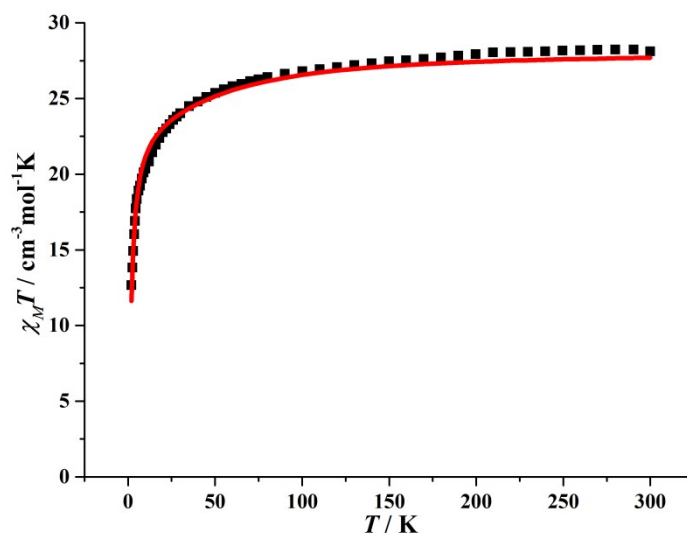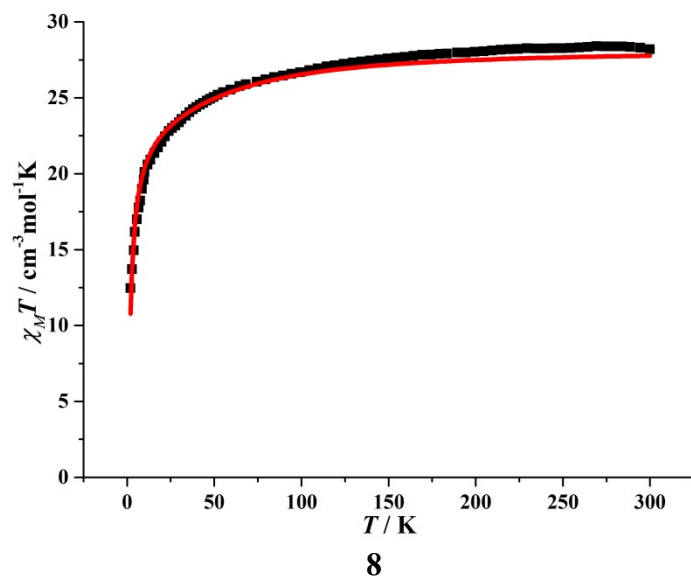
Figure S4. Calculated (red solid line) and experimental (black square dot) data of magnetic susceptibilities of **1** and **2**. The intermolecular interactions zJ' of **1** and **2** were fitted to −0.02 and −0.04 cm^{-1}, respectively.

6

8

Figure S5. Calculated orientations of the local main magnetic axes on Dy^{III} of complexes **6** and **8**.

References:

S1   F. Aquilante, J. Autschbach, R. K. Carlson, L. F. Chibotaru, M. G. Delcey, L. De Vico, I. Fdez. Galván, N. Ferré, L. M. Frutos, L. Gagliardi, M. Garavelli, A. Giussani, C. E. Hoyer, G. Li Manni, H. Lischka, D. Ma, P. Å. Malmqvist, T. Müller, A. Nenov, M. Olivucci, T. B. Pedersen, D. Peng, F. Plasser, B. Pritchard, M. Reiher, I. Rivalta, I. Schapiro, J. Segarra-Martí, M. Stenrup, D. G. Truhlar, L. Ungur, A. Valentini, S. Vancoillie, V. Veryazov, V. P. Vysotskiy, O. Weingart, F. Zapata, R. Lindh, MOLCAS 8: New Capabilities for Multiconfigurational Quantum Chemical Calculations across the Periodic Table, *J. Comput. Chem.*, 2016, **37**, 506.

S2   (a) Chibotaru, L. F.; Ungur, L.; Soncini, A. *Angew. Chem. Int. Ed.*, 2008, **47**, 4126. (b) Ungur, L.; Van den Heuvel, W.; Chibotaru, L. F. *New J. Chem.*, 2009, **33**, 1224. (c) Chibotaru, L. F.; Ungur, L.; Aronica, C.; Elmoll, H.; Pilet, G.; Luneau, D. *J. Am. Chem. Soc.*, 2008, **130**, 12445.

S3   Lines, M. E. *J. Chem. Phys*. **1971**, *55*, 2977.

S4   (a) Mondal, K. C.; Sundt, A.; Lan, Y. H.; Kostakis, G. E.; Waldmann, O.; Ungur, L.; Chibotaru, L. F.; Anson, C. E.; Powell, A. K. *Angew. Chem. Int. Ed*. 2012, **51**, 7550. (b) Langley, S. K.; Wielechowski, D. P.; Vieru, V.; Chilton, N. F.; Moubaraki, B.; Abrahams, B. F.; Chibotaru, L. F.; Murray, K. S. A*ngew. Chem. Int. Ed*. 2013, **52**, 12014.