

Supporting Information

Prediction of the Quantized Axis of Rare-Earth Ions: the Electrostatic Model with Displaced Point Charges

List of Supporting Information

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SI1 Calculation details for average radius of 2p orbitals

The radial part of 2p orbitals of neutral C, N and O atoms can be expressed as

$$R_{21}(r) = \frac{(Z/a_0)^{3/2}}{2\sqrt{6}} \cdot \frac{2Zr}{na_0} \cdot \text{Exp}\left(-\frac{Zr}{na_0}\right)$$

where a_0 is the Bohr radius (taken as 0.529 Å), n is the principal quantum number of the atomic orbital (taken as 2 for 2p), and Z is the effective nuclear charge which can be calculated according to the modified Slater's rules. For neutral atoms of C, N and O, the effective nuclear charge are reported to be 3.09, 3.75 and 4.42, respectively.

The average radius are calculated as

$$\bar{r} = \int_{r=0}^{+\infty} [R_{21}(r)]^2 \cdot r \cdot r^2 dr$$

The integration results for C, N and O lead to the value of 0.856 Å, 0.705 Å and 0.598 Å.

SI2 Calculation details for [CuTb]₂ complex

Table S2.1 Calculation details for [CuTb]₂ complex^a

Ln ³⁺	^{2S+1} L _J	M	c ₂	c ₄	c ₆
^b Tb ³⁺	⁷ F ₆	± 6	$-\frac{\sqrt{5}}{6\sqrt{\pi}}$	$\frac{3}{22\sqrt{\pi}}$	$-\frac{5}{66\sqrt{13\pi}}$
	^c Q _n	^d r _{disp} (Å)	x (Å)	y (Å)	z (Å)
O	-1	0.598	-0.159	2.377	-0.136
O	-1	0.598	-1.961	0.792	-1.014
N	-1	0.705	1.168	0.287	-2.062
N	1	0	1.587	1.214	-2.633
N	-1	0	1.937	2.087	-3.331
N	-1	0.705	1.396	-1.863	0.468
N	1	0.705	1.391	-2.682	1.308
N	-1	0	1.436	-3.498	2.150
N	-1	0	-1.637	-1.425	1.219
N	1	0.705	-2.281	-2.336	0.675
N	-1	0.705	-2.846	-3.203	0.150
N	-1	0	-0.086	0.382	2.353
N	1	0	0.531	1.307	2.917
N	-1	0	1.133	2.195	3.373
Cu	2	0	-1.925	2.704	-0.777
Tb	3	0	-1.700	-0.912	3.587
Cu	2	0	0.173	-3.591	4.537
N	-1	0	-3.121	0.902	3.036
N	1	0	-3.073	1.765	2.236
N	-1	0	-3.099	2.650	1.485
N	-1	0	-2.965	-1.053	5.623
N	1	0	-3.236	-1.966	6.256
N	-1	0	-3.606	-2.911	6.849
O	-1	0	-1.553	-3.232	3.766

^a The structure can be found in *Chem. Comm.* **2015**, DOI: 10.1039/C5CC03089G;

^b The central ion is considered located at (0 0 0);

^c The charges are analyzed by valence bond resonate structure. Chemical neutral charges are assumed as no contribution to the potential, and therefore are not reported here;

^d Only the atoms which directly coordinated with the central ion are considered as displaced charges.

SI3 Calculation details for Dy/ β -diketonate complex

Table S3.1 Calculation details for Dy/ β -diketonate complex

Ln^{3+}	$2S+1L_J$	M	c_2	c_4	c_6
Dy^{3+}	${}^6H_{15/2}$	$\pm 15/2$	$-\frac{\sqrt{5}}{6\sqrt{\pi}}$	$-\frac{2}{11\sqrt{\pi}}$	$\frac{25}{66\sqrt{13\pi}}$
	Q_n	$r_{\text{disp}} (\text{\AA})$	$x (\text{\AA})$	$y (\text{\AA})$	$z (\text{\AA})$
O	-1/3	0.598	-1.798	-1.172	0.850
O	-1/3	0.598	0.822	-1.936	0.938
O	-1/3	0.598	-0.933	1.611	1.320
O	-1/3	0.598	1.690	0.763	1.449
O	-1/3	0.598	-1.675	0.854	-1.397
O	-1/3	0.598	0.906	1.793	-1.177

SI4 Calculation results and details for Er³⁺ equatorially coordinated complex

Table S4.1 Calculation details for Er³⁺ equatorially coordinated complex^a

Ln ³⁺	^{2S+1} L _J	M	c ₂	c ₄	c ₆
Er ³⁺	⁴ I _{15/2}	± 15/2	$\frac{2}{6\sqrt{5}\sqrt{\pi}}$	$\frac{3}{22\sqrt{\pi}}$	$\frac{25}{33\sqrt{13\pi}}$
	Q _n	r _{disp} (Å)	^b x (Å)	y (Å)	z (Å)
N	-1	0.705	-2.107	0.450	0.041
N	-1	0.705	0.661	2.073	0.041
N	-1	0.705	1.139	-1.915	0.041

^a The structure can be found in *J. Am. Chem. Soc.*, **2014**, *136*, 4484;

^b In order to plot the potential surface clearly, the molecular axial direction is rotated to be coincide with the Cartesian z axis.

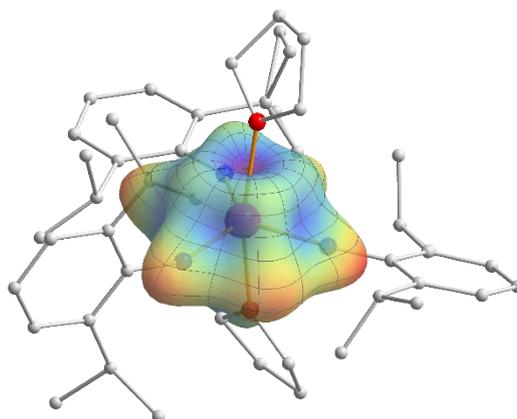


Figure S4.1 The potential energy surface for a single Er³⁺ describing the crystal field interaction with various orientations of the quantized axis of the Ising limit state. Blue and red part represents lower and higher energy. The Cartesian z axis is selected as the molecular axial direction for clarity.

SI5 Calculation details for Er³⁺ double decker complex

Table S5.1 Calculation details for Cp*ErCOT complex^a

Ln ³⁺	^{2S+1} L _J	M	c ₂	c ₄	c ₆
Er ³⁺	⁴ I _{15/2}	± 15/2	$\frac{2}{6\sqrt{5}\sqrt{\pi}}$	$\frac{3}{22\sqrt{\pi}}$	$\frac{25}{33\sqrt{13\pi}}$
	Q _n	^b r _{disp} (Å)	^c x (Å)	y (Å)	z (Å)
C	-0.20	0.856	0.952	-0.709	2.285
C	-0.20	0.856	0.952	0.709	2.285
C	-0.20	0.856	-0.352	-1.150	2.251
C	-0.20	0.856	-0.352	1.150	2.251
C	0.20	0.856	-1.199	0.000	2.240
C	-0.25	0.856	1.592	0.000	-1.793
C	-0.25	0.856	-1.549	-1.161	-1.490
C	-0.25	0.856	-1.549	1.161	-1.490
C	-0.25	0.856	0.855	-1.341	-1.762
C	-0.25	0.856	0.855	1.341	-1.762
C	-0.25	0.856	-2.133	0.000	-1.381
C	-0.25	0.856	-0.358	-1.793	-1.615
C	-0.25	0.856	-0.358	1.793	-1.615

^a The structure can be found in *J. Am. Chem. Soc.*, **2011**, *133*, 4730;

^b The charges are displaced along the normal of the aromatic plane, rather than the ligand-ion direction (see the main article).

^c In order to plot the potential surface clearly, the molecular axial direction is rotated to be coincide with the Cartesian z axis.