Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers. This journal is © the Partner Organisations 2020

Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Electronic Supplementary Information

Orientation Mapping of Rabi Frequencies in a Rare-Earth Molecular Qudit

Yu-Hui Fang,‡^a Zheng Liu,‡^a Ye-Xin Wang,^a Shen Zhou,^{*b,d} Shang-Da Jiang^{*a,b} and Song Gao^{a,b,c}

^{*a.*} Beijing National Laboratory of Molecular Science, Beijing Key Laboratory of Magnetoelectric Materials and Devices, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China.

^{b.} School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510640, China.3

^{c.} Beijing Academy of Quantum Information Sciences, West Bld.#3, No.10 Xibeiwang East Rd., Haidian District, Beijing 100193, China.

^{*d.*} College of Aerospace Science and Engineering, National University of Defence Technology, Changsha 410000, P. R. China.

‡ These authors contributed equally.

Emails: zhoushen@nudt.edu.cn, jiangsd@pku.edu.cn

Content of Supplementary Information

Figure S1. CW EPR spectra.	2
Table S1. The parameters of CW EPR simulation.	3
Figure S2. T_1 and T_M curves.	4
Figure S3. FFT spectra of $T_{\rm M}$ curves.	5
Table S2. Data of T_1 and T m.	5
Table S3. T_1 and T_M versus temperature.	5
Table S4. T_1 and T_M versus B_1 field.	6
Figure S4. Rabi oscillations and FFT spectra.	6
SI 1. Rabi frequency calculation.	7



Figure S1. (a) CW EPR spectrum (black) measured at room temperature and its simulation (red) for the powder sample. The parameters and explanations are noted in Table S1. (b) Angle-dependent CW EPR spectra measured at 10K from $\theta = 0^{\circ}$ (parallel), through $\theta = 90^{\circ}$ (perpendicular) to $\theta = 180^{\circ}$ (parallel) and (c) its simulation.

Table S1. Parameters of CW EPR simulation from the best fits at 10 K. Compared to

10) K	room temperature		
$g_{ }$	1.995	$ $ $g_{ }$	1.986	
g $_{\perp}$	1.985	g_{\perp}	1.985	
B_2^0 (MHz)	554.7	B_2^0 (MHz)	485.3*	
B_4^0 (MHz)	-1.02	B_4^0 (MHz)	-0.78*	
B_{6}^{0} (MHz)	2.0×10^{-3}	B_{6}^{0} (MHz)	-8.4 × 10 ⁻⁴	
B_4^4 (MHz)	0.20	B_4^4 (MHz)	0.042	
B_{6}^{4} (MHz)	0.063	B_{6}^{4} (MHz)	0.049	
		B_{6}^{-4} (MHz)	0**	

the parameters measured at room temperature in the right columns,¹ the zero-field splitting parameters change as the temperature decreases.

* The B_2^0 and the B_4^0 cited in the literature is 970.6 MHz and -7.8 MHz, exactly two and ten times larger than the parameters used in Figure S1(b), respectively. We consider there are typos in the literature, as 970.6 MHz -7.8 MHz will not fit the experimental data demonstrated in the literature.

**The B_{6}^{-4} cited in the literature is 0.018 MHz, which is different from what is reported here. We report $B_{6}^{-4} = 0$ MHz, because in D_4 symmetry the Steven's operator B_{6}^{-4} of [NEt₄][Gd{Pt(SAc)₄}] is vanished.



Figure S2. T_1 (a) and T_M (b) curves measured at selected B_0 field positions as each transition marked in Figure 2b in parallel direction, and T_1 (c) and T_M (d) curves measured as each transition marked in Figure 2c in perpendicular direction.



Figure S2. FFT spectra of $T_{\rm M}$ curves in Figure S2 in parallel direction (a) and perpendicular direction (b), with linear fitting showing the Larmor precession frequency of ¹H being 41.5 MHz/T.

	1						
R/G	T /us	T /us	Transitio	R/G	T /us	T/us	Transitio
<i>D</i> ₀ /u	$1_{1}/\mu^{3}$	$M/\mu S$	n	<i>D</i> ₀ /u	$1_{1}/\mu s$	I_{M}	n
		n di avalan				mallal	
	perpe	ndicular			pa	rallel	
1860	170.4	0.81		0	277 5	0.58	
1000	170.т	0.01	$ 1\rangle \leftrightarrow 2\rangle$	0	211.5	0.50	7)↔ 8)
2240	156.6	0.86	2⟩↔ 3⟩	730	182.9	0.64	6)↔ 7)
			., .,				1, 1,
2670	130.3	1 04	121 () 141	1960	160.6	0.63	
2070	150.5	1.01	3)↔ 4)	1700	100.0	0.05	5}↔ 6}
2145	100.0	1 1 1		2415	172 (0.00	
3145	180.0	1.11	4⟩↔ 5⟩	3415	1/3.6	0.68	4)↔ 5)
3635	189.8	1.09	15\4-16\	4800	203.8	0.86	13\41
			13/(/ 10/				[]/, /[]/
4110	100.2	1.00		5075	1047	0.05	
4110	180.3	1.08	6⟩↔ 7⟩	3833	194./	0.85	2⟩↔ 3⟩
5410	225.5	0.99	17\⇔18\	6385	240.9	0.87	1\↔ 2)
			1,1,1,101				-/、/ -/

Table S2. Spin relaxation times measured for different transitions.

* All results measured at 10 K.

Table S3. Spin relaxation times measured at different temperatures.

	T/K $T_1/\mu s$ $T_M/\mu s$ Transition T/K $T_1/\mu s$ $T_M/\mu s$ Transitio
--	--

				-			
perpendicular					parallel		
5	209.2	1.07	measured at	5	123.5	0.44	measured at
7	220.8	1.25	3145 G,	7	140.8	0.42	3415 G,
10	192.0	1.21	corresponding	10	154.4	0.44	corresponding
15	86.6	1.17	to the	15	91.5	0.44	to the
20	38.3	1.01		20	44.5	0.42	
25	17.0	0.65	4⟩↔ 5⟩	25	24.1	0.25	4⟩↔ 5⟩
25	17.2	0.65	transition	25	24.1	0.35	transition

Table S4. $T_{\rm M}$ measured with different numbers of inversion recovery pulses (CPMG dynamic decoupling measurement).

	1 0	,			
CPMG pulse numbers	T _M /μs	Transition	CPMG pulse numbers	T _M /μs	Transition
	perpendicu	ılar		parallel	
1 2 4 8	1.14 1.68 2.60 3.97	measured at 3145 G, corresponding to the	1 2 4 8	0.51 0.70 1.12 1.92	measured at 3415 G, corresponding to the
16 32 64 128	5.98 8.77 12.07 16.80	$ 4\rangle \leftrightarrow 5\rangle$ transition	32 64	3.38 5.07 9.75	$ 4\rangle \leftrightarrow 5\rangle$ transition



Figure S4. (a) Rabi oscillations measured at 10 K for the crystal sample at different transitions in parallel direction(blue) and (b) their FFT result. (c) Rabi oscillations measured in perpendicular (purple) and (d) their FFT result.

SI 1. Rabi frequency calculation

The total Hamiltonian of the system is

$$\hat{H}_{tot} = \hat{H} + \hat{H}_1(t)$$

 \hat{H} is given by eq. (1) in the text. It is time-independent and expressed in the molecular frame therein. $\hat{H}_1(t)$ describes the interaction of the system with the microwave pulse. With the rotating wave approximation, it is

$$\hat{H}_{1}(t) = \mu_{B}B_{1}(\cos(\omega t + \phi) \quad \sin(\omega t + \phi)) \begin{pmatrix} g_{xx} & g_{xy} \\ g_{yx} & g_{yy} \end{pmatrix} \begin{pmatrix} \hat{S}_{x} \\ \hat{S}_{y} \end{pmatrix}.$$

If \hat{H} commutes with \hat{S}_z , i.e. is diagonal when using the eigenstates of \hat{S}_z as the basis set,

and the *z*-axis of the molecular frame coincided with that of the lab frame, the Rabi frequencies could be calculated simply by eq. (2). However, the rotation of the sample and the crystal field splitting make the Hamiltonian not diagonalized. To interpret the Rabi cycles in this case and calculate the Rabi frequencies, we first diagonalize the matrix (we use letters without the cap to denote matrices) in the lab frame, as

$$H_{diag} = U^{\dagger} H U_{J}$$

where *U* is a unitary transformation accounting for both the rotation and the crystal field terms, and H_{diag} defines the energy levels between which the Rabi oscillations occur. A Rabi oscillation occurs when $\omega = H_{diag,ii} - H_{diag,jj}$. In this condition, we can describe the system in a rotating frame with an angular frequency of ω . In the rotating frame, the total Hamiltonian becomes

$$\hat{H}_{rot} = e^{i\omega t\hat{S}_z} (\hat{H} + \hat{H}_1) e^{-i\omega t\hat{S}_z} + i\hbar \frac{\partial e^{i\omega t\hat{S}_z}}{\partial t} e^{-i\omega t\hat{S}_z},$$

making the contribution of the microwave pulse time-independent.

By the basis set with which \hat{H} is represented diagonally, one can derive a complicated matrix H_{rot} representing \hat{H}_{rot} . Fortunately, it can be simplified in two steps, (i) the time

dependence brought about by
$$e^{i\omega tS_z}He^{-i\omega tS_z}$$
 and $i\hbar \frac{\partial e^{i\omega tS_z}}{\partial t}e^{-i\omega tS_z}$ are of much higher
frequency than ω and therefore can be neglected using the rotating wave approximation,
(ii) $H_{rot,ik}$, $H_{rot,ki}$, $H_{rot,jk}$ and $H_{rot,kj}$, where $k \neq i,j$, are all negligible, therefore the two
levels in which the Rabi oscillation occurs can be considered as isolated. Diagonalizing
 $\begin{pmatrix} H_{rot,ii} & H_{rot,ij} \\ H_{rot,ji} & H_{rot,jj} \end{pmatrix}$

gives eigenvalues E + and E -. The Rabi frequency is

$$\Omega_{Rabi} = \frac{E_{+} - E_{-}}{\hbar}$$

1 M. A. Sørensen, H. Weihe, M. G. Vinum, J. S. Mortensen, L. H. Doerrer, J. Bendix, Imposing high-symmetry and tuneable geometry on lanthanide centres with chelating Pt and Pd metalloligands, *Chem. Sci.*, 2017, **8**, 3566-3575.