Supporting Information

Angular-Resolved Rabi Oscillations of Orthorhombic Spins in a Co(II) Molecular Qubit

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Table S1. Crystallographic data

$Zn_{0.994}Co_{0.006}$	
Molecular formula	$C_{16}H_{26}N_4O_8Zn$
Molecule weight	467
Crystal system	Orthorhombic
Space group	*Pccn*
a, Å	15.2423
b, Å	9.3278
c, Å	13.0916
α, °	90
β, °	90
γ, °	90
V, Å^3	1864.33
Z	1

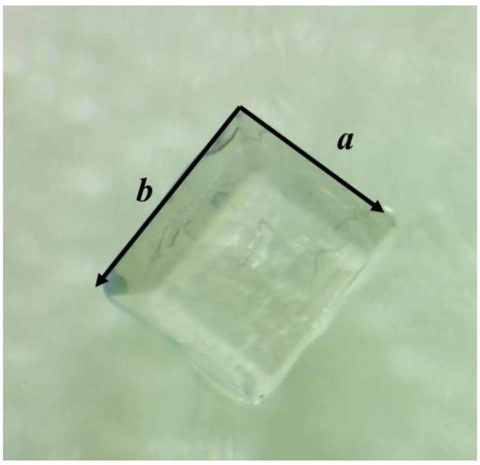

Fig.S1. (a) The result of face indexing showing on a physical crystal. The markings represent crystallographic ***a***-axis and ***b***-axis respectively.

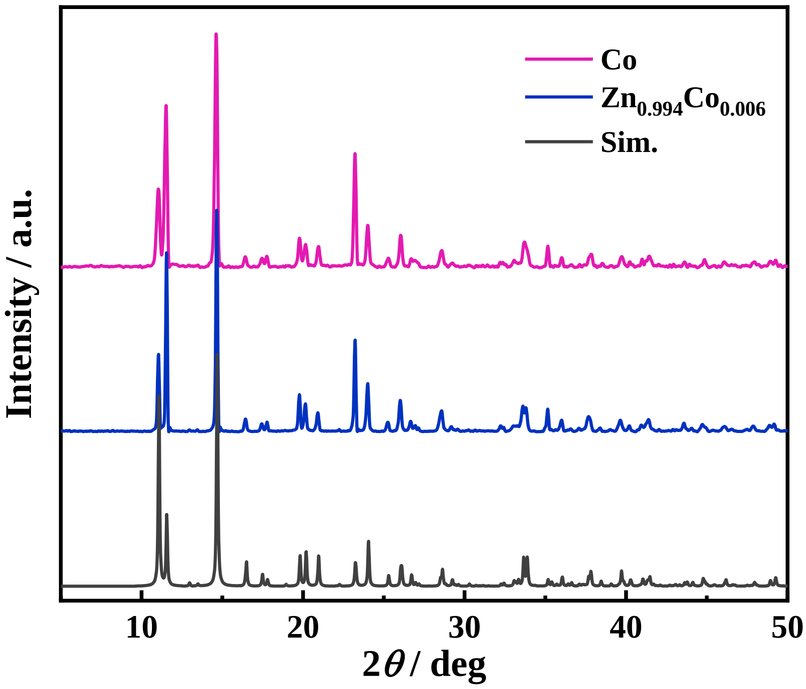

Fig.S2. Powder X-ray diffraction (PXRD) patterns of Co(H_2dota) (**Co**) and $Zn_{0.994}Co_{0.006}$(H_2dota) (**$Zn_{0.994}Co_{0.006}$**). The simulated pattern (**Sim.**) is also shown for comparison.

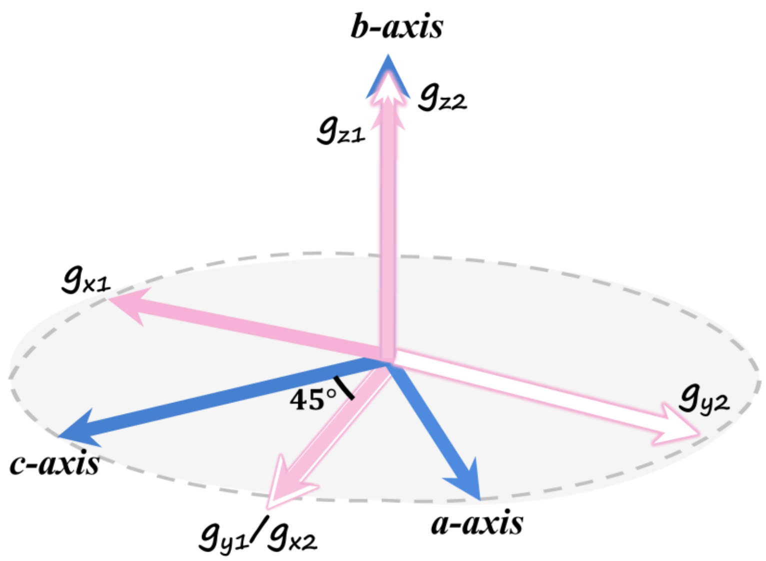

Fig.S3. Relative position between the crystal frame (***a***-axis, ***b***-axis, ***c***-axis) and tensor frames of two magnetically inequivalent Co(II) sites. The Euler transformations from the crystal frame to tensor frame of Co-1 and Co-2 are $\bar{\bar{R}}_1(-90° \ -90° \ -45°), \bar{\bar{R}}_2(-90° \ -90° \ 45°)$ respectively.

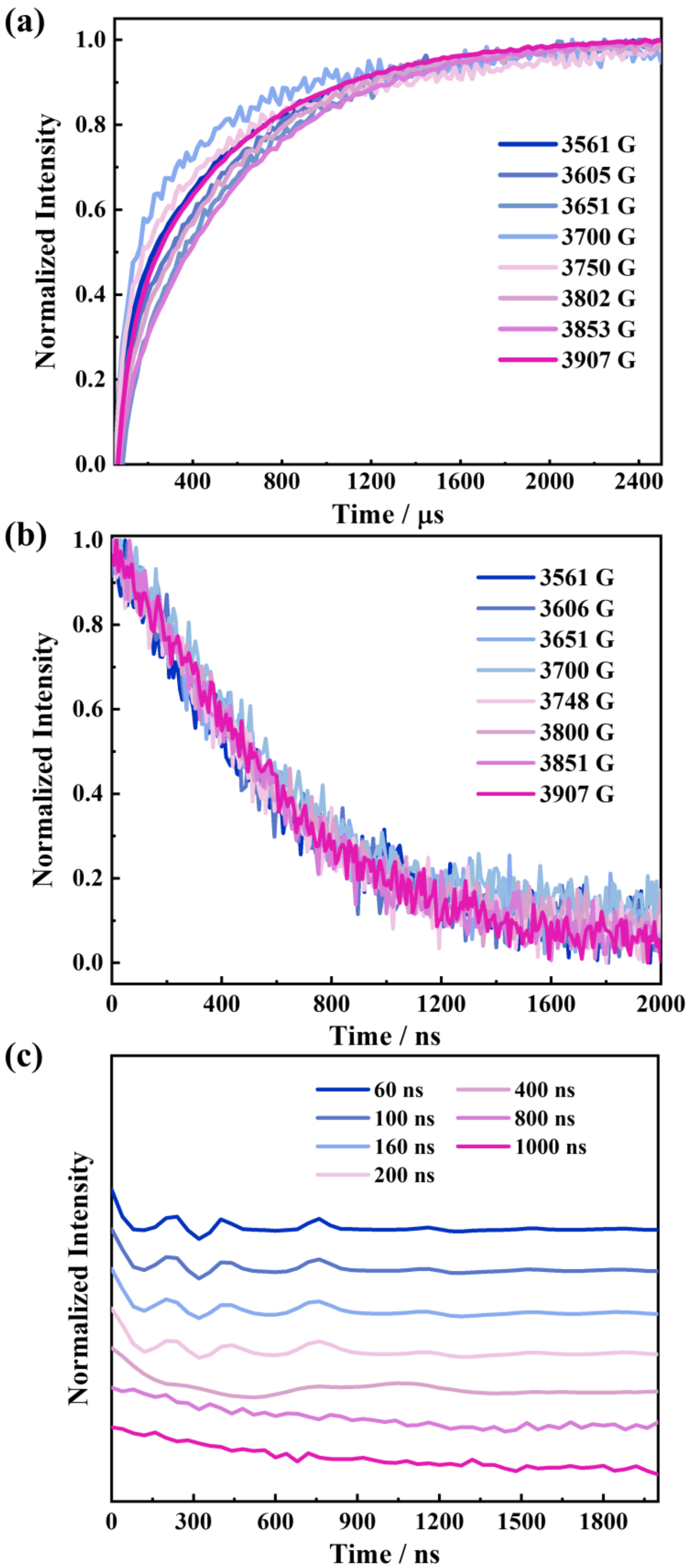

Fig.S4. T_1 (a) and T_m (b) curves at 5 K when $B_0 \parallel \boldsymbol{b}$. (c) T_m curves measured by different pulse lengths at 5 K by AWG and variation of ESEEM observed.

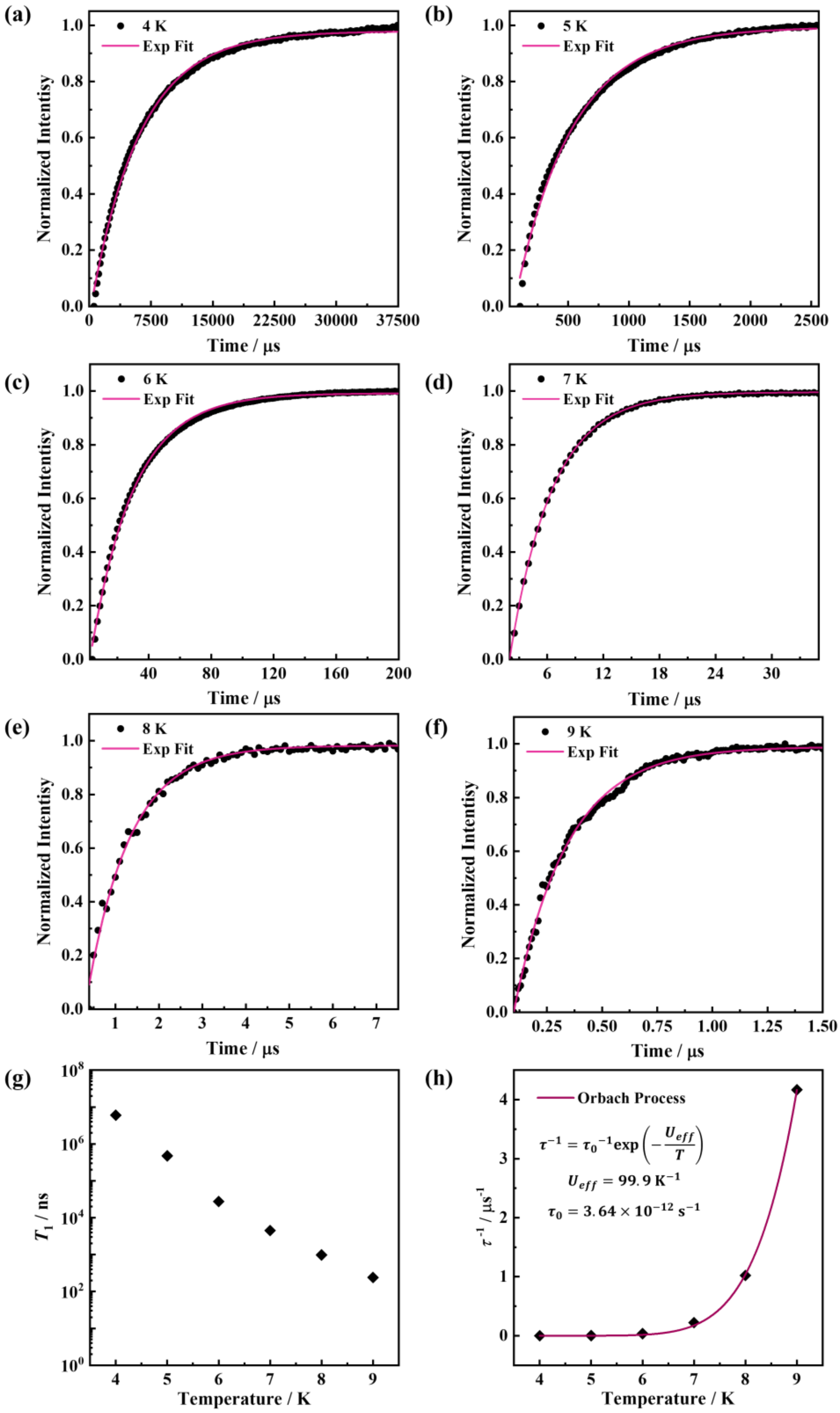

Fig.S5. (a)-(f) T_1 data (black point) measured at different temperatures at 3907 G and individual exponential fitting curves (wine line). (g) Temperature dependence of T_1 at 3907 G. (h) Fitting the spin relaxation mechanism.

Table S2. T_1 and T_m data at 5 K when $B_0 \parallel \boldsymbol{b}$.

B_0 / G	T_1 / µs	T_m / ns
3561	479.96	576.67
3606	498.94	563.50
3651	489.18	588.81
3700	444.07	600.69
3750	450.15	567.71
3802	490.17	606.86
3853	502.49	586.31
3907	475.27	664.97

Table S3. T_1 data between 4-9 K at 3907 G.

T / K	T_1 / µs
4	5995.39
5	475.27
6	27.45
7	4.51
8	0.98
9	0.24

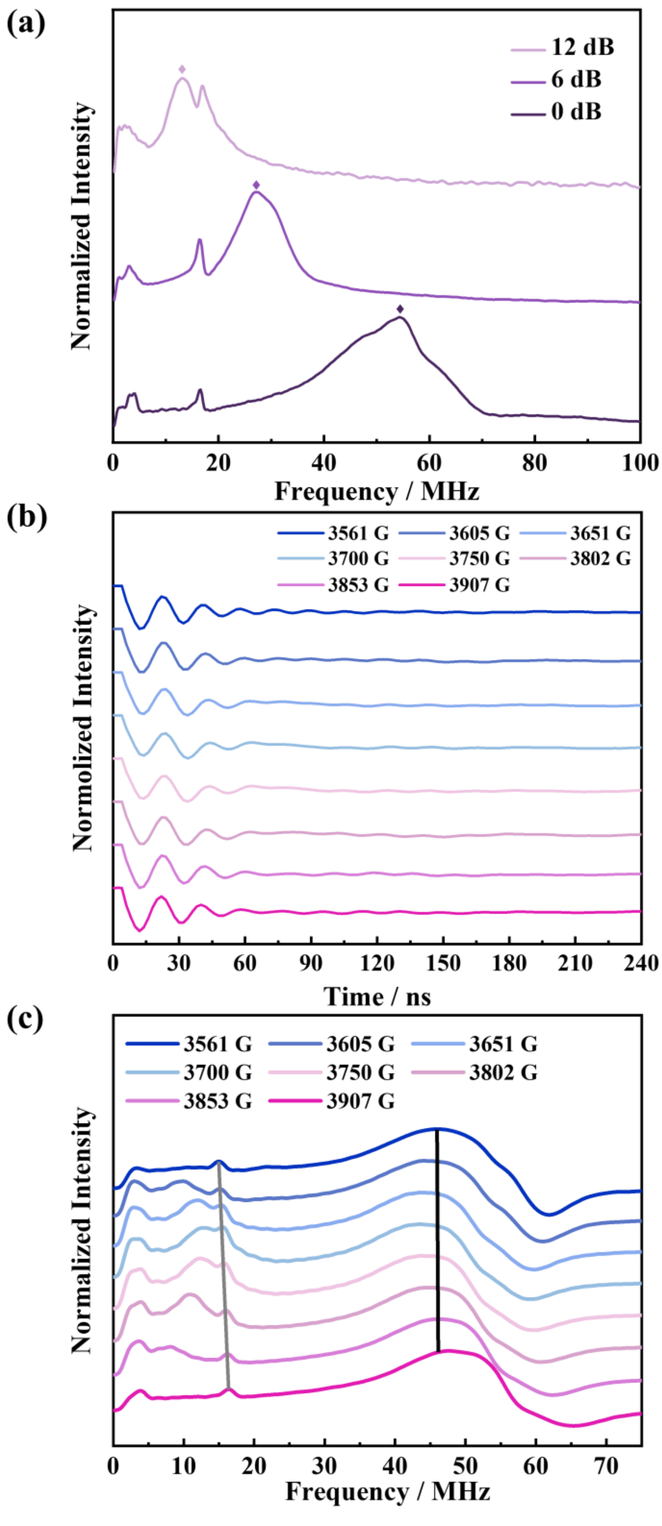

Fig.S6. (a) FFT of Rabi oscillations measured at 3907 G by a range of attenuation settings. (b) Rabi oscillations of the single crystal sample measured at different fields when $B_0 \parallel \boldsymbol{b}, B_1 \parallel \boldsymbol{a}$ at 5 K, 0 dB. (c) FFT of (b). Black and grey solid lines correspond to Rabi frequencies and ^{1}H Larmor frequencies respectively.

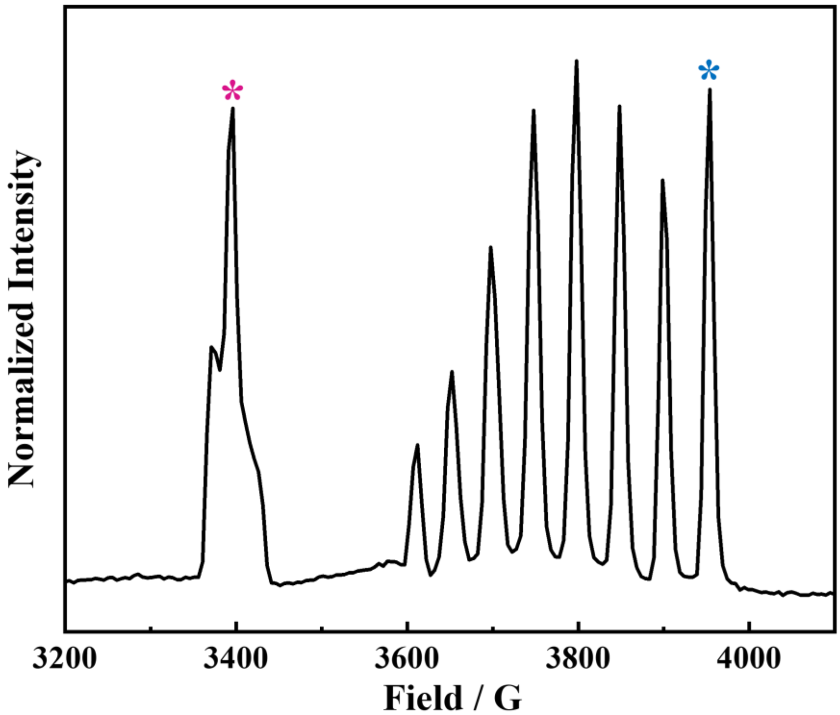

Fig.S7. EDFS of $\mathbf{Zn_{0.994}Co_{0.006}}$ with internal standard TEMPO at 5 K, 0 dB when $B_0 \parallel \boldsymbol{b}$. The absolute values of experimental B_1 and g_{eff} are calibrated by the peak with wine mark. The Rabi oscillations of $\mathbf{Zn_{0.994}Co_{0.006}}$ without specific description of B_0 field in Fig.S8-9 are measured on the transition with blue mark.

$$B_1 = \frac{\Omega_{TEMPO}}{\mu_B g_{TEMPO}} \qquad \textbf{(Eq. S1 − 1)}$$

$$g_{eff} = \frac{g_{TEMPO}}{\Omega_{TEMPO}} * \Omega_{Sample} \qquad \textbf{(Eq. S1 − 2)}$$

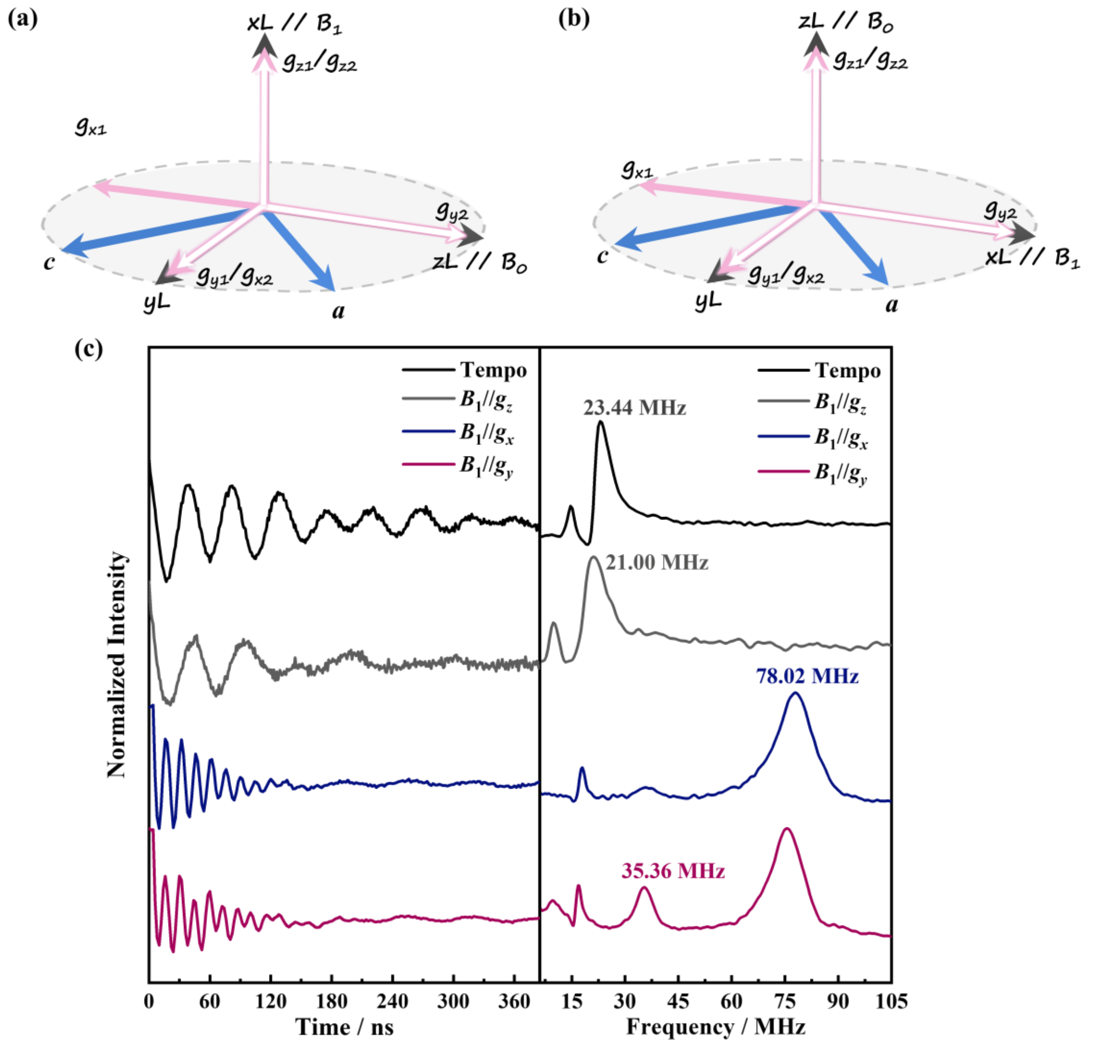

Fig.S8. Sketch of relative position between the lab frame and tensor frames in anisotropic Rabi oscillation experiments, depicting the case $B_1 \parallel g_z$ (a) and $B_1 \parallel g_{x,y}$(b) respectively. The pink frame and white frame represent the tensor frames for Co-1 and Co-2 respectively. *x*L, *y*L, *z*L represent the lab frame (dark grey). *z*L is along the static magnetic field B_0, *x*L is along microwave magnetic field B_1. The blue frame represents crystal frame but ***b***-axis is omitted. (c) Left: Rabi oscillations of internal standard TEMPO and $\mathbf{Zn_{0.994}Co_{0.006}}$ crystal when $B_1 \parallel g_z$, g_x, g_y respectively. Right: FFT of Rabi oscillations shown on the left.

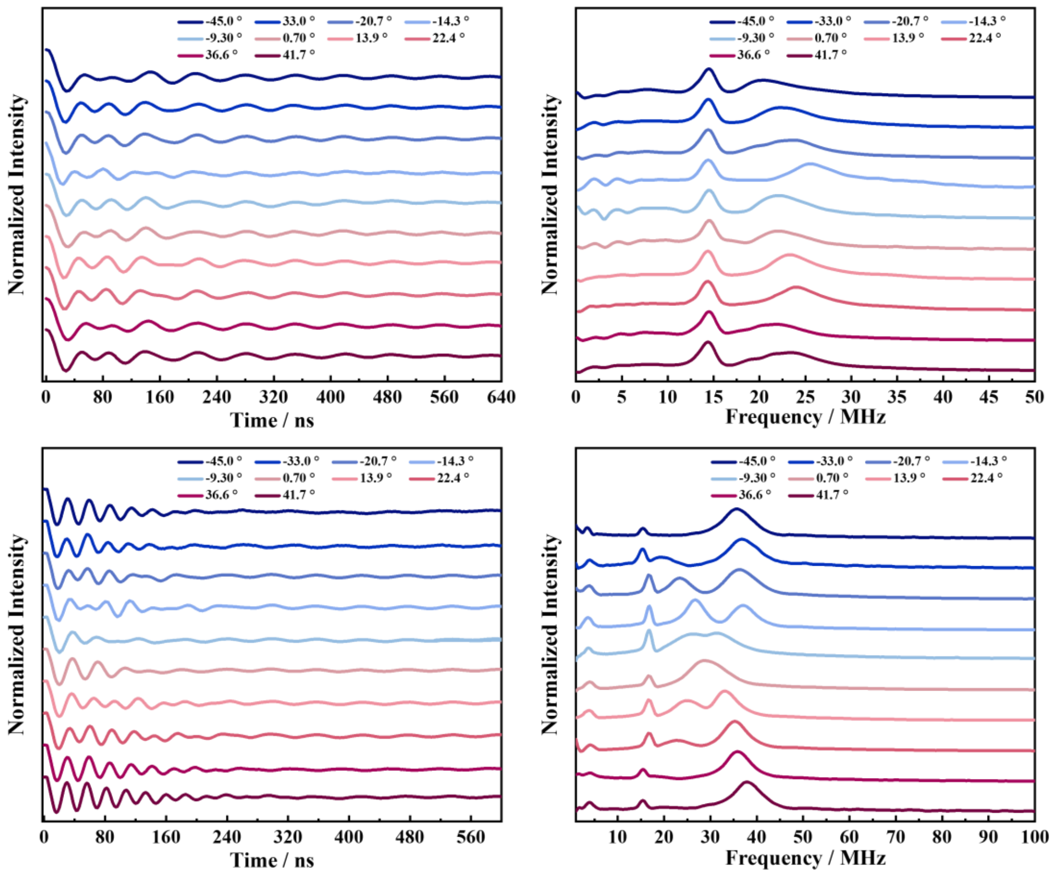

Fig.S9. Anisotropic Rabi oscillation experiments with internal standard. (a) Rabi oscillations of TEMPO measured with variable rotation angle α at 5 K, 0 dB. (b) FFT of (a). (c) Rabi oscillations of $\mathbf{Zn_{0.994}Co_{0.006}}$ measured with variable rotation angle α at 5 K, 6 dB. (d) FFT of (c).

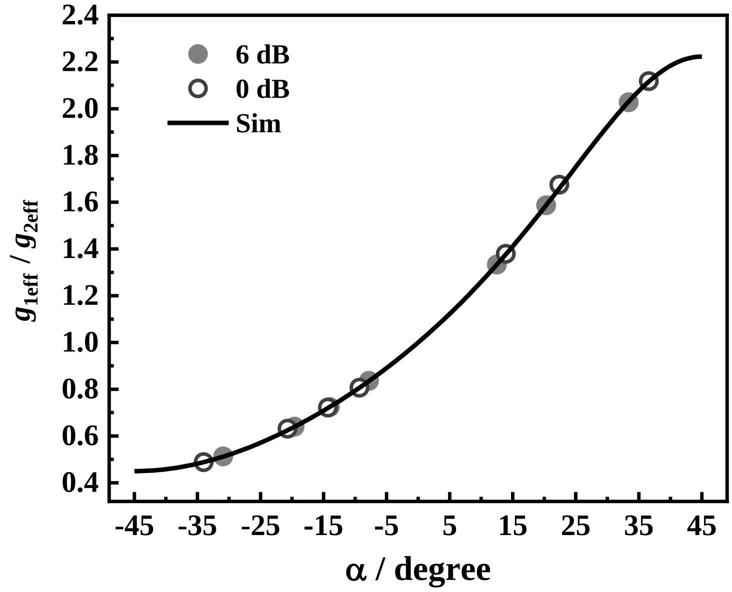

Fig.S10. Calibration of experimental rotation angle α. The black line is the calculated variation of g_{1eff}/g_{2eff} with α. Matching the ratio of two Rabi frequencies in Fig.4c (0 dB, open circle) and Fig.S9d (6 dB, grey circle) to calibrate experimental α.

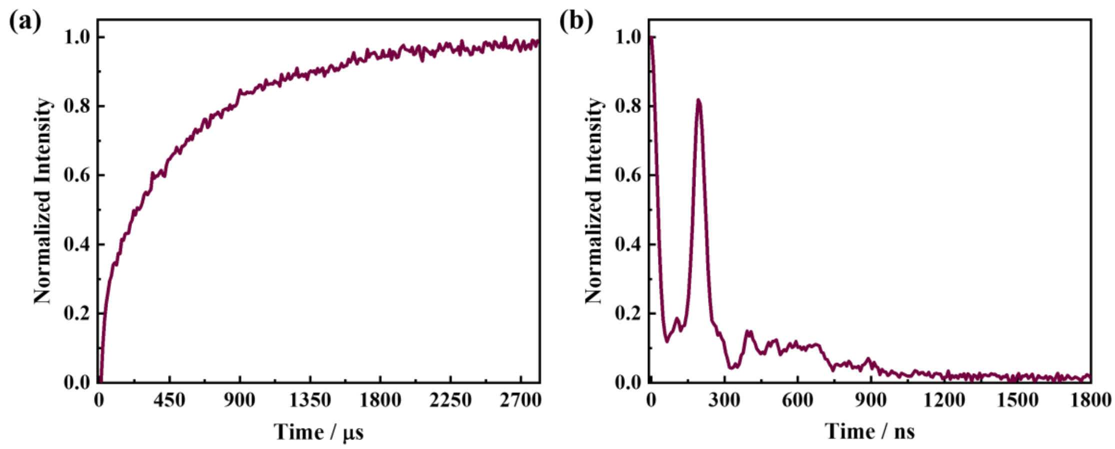

Fig.S11. T_1 (a) and T_m (b) curves at 5 K when B_0 is along g_y direction ($\pi/2$ = 16 ns, τ = 260 ns). Modelling the curves with single exponential function as T_1 = 457.67 μs and T_M = 283 ns.

SI 2 Theoretical analysis of anisotropic Rabi oscillation (I)

Considering a $S=\frac{1}{2}$ system with

$$\hat{H}_0=\mu_B\vec{B}\bar{\bar{g}}\hat{S}.$$

Based on the model shown in Fig.4a, i.e. $B_0 \parallel g_z$, g tensor should be expressed in lab frame as

$$\bar{\bar{g}}=\bar{\bar{R}}(\beta,0,0)\begin{pmatrix} g_x & 0 & 0 \\ 0 & g_y & 0 \\ 0 & 0 & g_z \end{pmatrix}\bar{\bar{R}}^{\dagger}(\beta,0,0)=\begin{pmatrix} g_{xx} & g_{xy} & 0 \\ g_{yx} & g_{yy} & 0 \\ 0 & 0 & g_{zz} \end{pmatrix},$$

where $\bar{\bar{R}}(\beta,0,0)$ and $\bar{\bar{R}}^{\dagger}(\beta,0,0)$ represent the Euler rotation matrixes and

$$g_{zz}=g_z$$

$$g_{xx}(\beta)=g_x\cos\beta^2+g_y\sin\beta^2 \qquad \textbf{(Eq. S2}-\textbf{1)}$$

$$g_{xy}(\beta)=\left(g_y-g_x\right)\cos\beta\sin\beta \qquad \textbf{(Eq. S2}-\textbf{2)}$$

The total Hamilton of the system is

$$\hat{H}=\hat{H}_0+\hat{H}_1(t,\beta),$$

where

$$\hat{H}_0=\mu_B B_0 g_z\hat{S}_z \quad (\omega_0=\mu_B B_0 g_z),$$

$$\hat{H}_1(t,\beta)=\mu_B B_1(\cos(\omega_{mw}t+\phi) \quad 0)\begin{pmatrix} g_{xx}(\beta) & g_{xy}(\beta) \\ g_{yx}(\beta) & g_{yy}(\beta) \end{pmatrix}\begin{pmatrix} \hat{s}_x \\ \hat{s}_y \end{pmatrix}.$$

We describe the system in a rotating frame with the microwave frequency ω_{mw}, the total Hamilton becomes

$$\hat{H}_{rot}=\hat{R}_z\left(\hat{H}-\omega_{mw}\hat{S}_z\right)\hat{R}_z^{\dagger}=\exp\left(i\omega_{mw}t\hat{S}_z\right)\left(\hat{H}-\omega_{mw}\hat{S}_z\right)\exp\left(-i\omega_{mw}t\hat{S}_z\right).$$

So

$$\hat{H}_{rot}=\frac{1}{2}\begin{pmatrix} \omega_0-\omega_{mw} & \mu_B B_1\cos(\omega t+\phi)\left(g_{xx}(\beta)-g_{xy}(\beta)i\right)e^{i\omega t} \\ \mu_B B_1\cos(\omega t+\phi)\left(g_{xx}(\beta)+g_{xy}(\beta)i\right)e^{-i\omega t} & -(\omega_0-\omega_{mw}) \end{pmatrix}.$$

Base on Euler's formula,

$$\hat{H}_{rot}=\frac{1}{2}\begin{pmatrix} \omega_0-\omega_{mw} & \mu_B B_1\left(g_{xx}(\beta)-g_{xy}(\beta)i\right)\left[e^{-i\phi}+e^{i(2\omega t+\phi)}\right] \\ \mu_B B_1\left(g_{xx}(\beta)+g_{xy}(\beta)i\right)\left[e^{i\phi}+e^{-i(2\omega t+\phi)}\right] & -(\omega_0-\omega_{mw}) \end{pmatrix}.$$

The terms $e^{\pm i(2\omega t+\phi)}$ can be neglected using the rotating wave approximation. Finally, in the resonance condition, $\omega_0 = \omega_{mw}$, and the total Hamilton can be expressed as

$$\hat{H}_{rot} = \frac{\mu_B B_1}{2}\begin{pmatrix} 0 & \left(g_{xx}(\beta) - g_{xy}(\beta)i\right)e^{-i\phi} \\ \left(g_{xx}(\beta) + g_{xy}(\beta)i\right)e^{i\phi} & 0 \end{pmatrix}.$$

For a general notation,

$$\hat{H}_{rot} = \mu_B B_1\left[A(\beta,\ \phi)\hat{S}_x + B(\beta,\ \phi)\hat{S}_y\right], \qquad (\mathbf{Eq. S3-1})$$

where

$$A(\beta,\ \phi) = g_{xx}(\beta)\, cos\, \phi - g_{xy}(\beta)\, sin\, \phi\,, \qquad (\mathbf{Eq. S3-2})$$

$$B(\beta,\ \phi) = g_{xx}(\beta)\, sin\, \phi + g_{xy}(\beta)\, cos\, \phi\,. \qquad (\mathbf{Eq. S3-3})$$

Therefore, the rotation of spin in Bloch sphere will be determined by:

$$g_{eff}(\beta) = \sqrt{A^2 + B^2} = \sqrt{g_{xx}(\beta)^2 + g_{xy}(\beta)^2}, \qquad (\mathbf{Eq. S4-1})$$

$$\Phi(\beta, \phi) = tan^{-1}\left(\frac{B}{A}\right). \qquad (\mathbf{Eq. S4-2})$$

$g_{eff}(\alpha)$ decides the nutation rate:

$$\Omega_{rabi}(\beta) = \mu_B B_1\sqrt{g_{xx}(\beta)^2 + g_{xy}(\beta)^2}.$$

SI 3 Theoretical analysis of anisotropic Rabi oscillation (II)

Considering a $S=\frac{1}{2}$ system with

$$\hat{H}_0 = \mu_B \vec{B}\bar{\bar{g}}\hat{S}.$$

Considering a model analogue to Fig.S8, i.e. B_1 coincides with a certain principal axis of the $\bar{\bar{g}}$ but B_0 does not. $\bar{\bar{g}}$ should be expressed in lab frame as

$$\bar{\bar{g}} = \begin{pmatrix} g_{xx} & 0 & 0 \\ 0 & g_{yy} & g_{yz} \\ 0 & g_{zy} & g_{zz} \end{pmatrix}.$$

The static magnetic field Hamilton is

$$\hat{H}_0 = \mu_B (0 \quad 0 \quad B_0) \begin{pmatrix} g_{xx} & 0 & 0 \\ 0 & g_{yy} & g_{yz} \\ 0 & g_{zy} & g_{zz} \end{pmatrix} \begin{pmatrix} \hat{s}_x \\ \hat{s}_y \\ \hat{s}_z \end{pmatrix} = \mu_B B_0 (g_{zy}\hat{s}_y + g_{zz}\hat{S}_z).$$

Diagonalize $\hat{H}_0$ and acquire the unitary transformation U and Larmor frequency as following

$$\hat{H}_0{}' = U\hat{H}_0 U^{\dagger},$$

$$\omega_0 = \mu_B B_0 \sqrt{g_{zy}{}^2 + g_{zz}{}^2}.$$

Time dependent microwave Hamiltonian can be expressed as

$$\hat{H}_1(t) = \mu_B g_{xx} B_1 \, cos(\omega t + \phi)\, \hat{S}_x.$$

Unitary transformation U will be used to rotate $\hat{H}_1(t)$ to eigen basis,

$$\hat{H}_1{}'(t) = U\hat{H}_1 U^{\dagger}.$$

The total Hamilton of the system is

$$\hat{H} = \hat{H}_0{}' + \hat{H}_1{}'(t).$$

We describe the system in a rotating frame with the microwave frequency ω_{mw}, the total Hamilton becomes

$$\hat{H}_{rot} = \hat{R}_z\big(\hat{H} - \omega_{mw}\hat{S}_z\big)\hat{R}_z^{\dagger},$$

where

$$\hat{R}_z = \exp\big(i\omega_{mw} t \hat{S}_z\big).$$

So

$$\hat{H}_{rot} = \frac{1}{2}\begin{pmatrix} \omega_0 - \omega_{mw} & \mu_B B_1 g_{xx}\, cos(\omega t + \phi)\, e^{i\omega t} \\ \mu_B B_1 g_{xx}\, cos(\omega t + \phi)\, e^{-i\omega t} & -(\omega_0 - \omega_{mw}) \end{pmatrix}.$$

Base on Euler's formula,

$$\hat{H}_{rot} = \frac{1}{2}\begin{pmatrix} \omega_0 - \omega_{mw} & \mu_B B_1 g_{xx}\left[e^{-i\phi} + e^{i(2\omega t+\phi)}\right] \\ \mu_B B_1 g_{xx}\left[e^{i\phi} + e^{-i(2\omega t+\phi)}\right] & -(\omega_0 - \omega_{mw}) \end{pmatrix}.$$

The terms $e^{\pm i(2\omega t+\phi)}$ can be neglected using the rotating wave approximation. Finally, in the resonance condition, $\omega_0 = \omega_{mw}$, and the total Hamilton can be expressed as

$$\hat{H}_{rot} = \frac{1}{2}\begin{pmatrix} 0 & \mu_B B_1 g_{xx} e^{-i\phi} \\ \mu_B B_1 g_{xx} e^{i\phi} & 0 \end{pmatrix}.$$

Diagonalize $\hat{H}_{rot}$ and Rabi frequency is therefore determined as

$$\Omega_{rabi} = \mu_B B_1 g_{xx}.$$

In our case shown in Fig.S8a, $g_{xx} = g_z$, so Rabi frequency is expressed as

$$\Omega_{Rabi} = g_z \mu_B B_1.$$