Electronic Supplementary Information

A hexagonal bipyramidal ytterbium complex exhibiting field-induced single-ion magnet behavior

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Table S1. Crystal data and structure refinement for **1-Yb** and **2-Tb**.

	1-Yb	**2-Tb**
Molecular formula	$C_{24}H_{54}N_3O_{11}P_2Yb$	$C_{24}H_{54}N_3O_{11}P_2Tb$
CCDC no	1885763	1885764
Formula weight	795.68	781.56
Temperature	296(2) K	296(2) K
Wavelength / Å	0.71073	0.71073
crystal system	Hexagonal	Hexagonal
Space group	P63/mmc	P63/mmc
a / Å	13.8721(8)	13.9163(14)
b / Å	13.8721(8)	13.9163(14)
c / Å	15.0022(18)	15.107(4)
α / deg	90	90
β / deg	90	90
γ / deg	120	120
V / Å^3	2500.2(4)	2533.7(8)
Z	2	2
D_{calc}, g/cm^3	1.057	1.024
μ / mm^{-1}	1.972	1.496
F (000)	814	804
Goodness-of-fit on F^2	1.165	1.118
Final R indices [$I > 2\sigma(I)$][a]	$R_1 = 0.0756$, $wR_2 = 0.2339$	$R_1 = 0.0763$, $wR_2 = 0.2075$
R indices (all data)[a]	$R_1 = 0.0840$, $wR_2 = 0.2410$	$R_1 = 0.0818$, $wR_2 = 0.2111$

[a] $wR_2 = [\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(Fo^2)^2]]^{1/2}$, $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$.

Table S2 The results of the continuous shape measure (CSM) analyses for **1-Yb** and **2-Tb** SHAPE software.[S1]

CSM	**1-Yb**	**2-Tb**
Hexagonal bipyramid (D_{6h})	0.584	0.637
Cube (O_h)	9.205	9.205

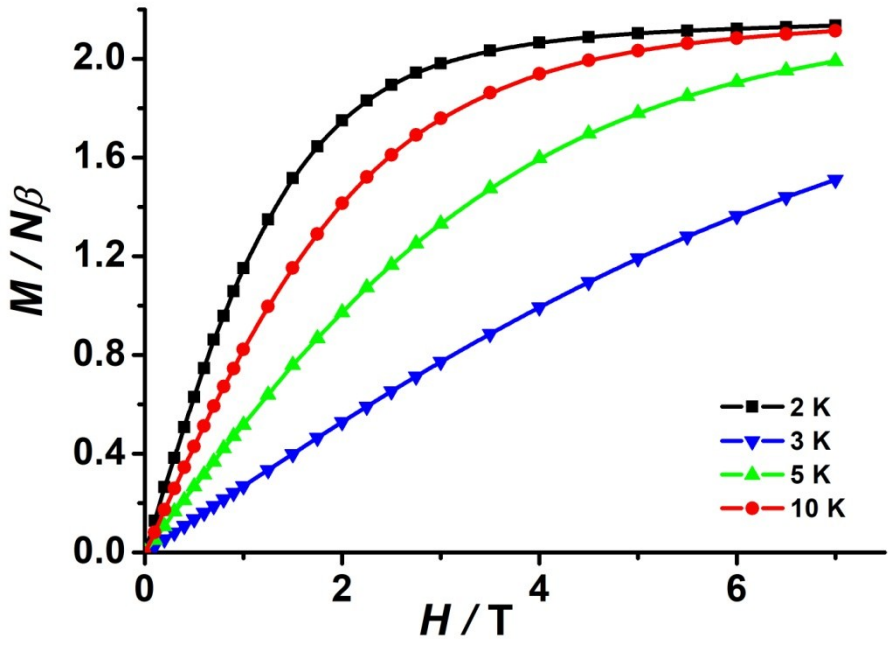


Figure S1 The field-dependence of magnetization at the temperature range of 2-10 K for **1-Yb**. The solid lines are for eye guide.

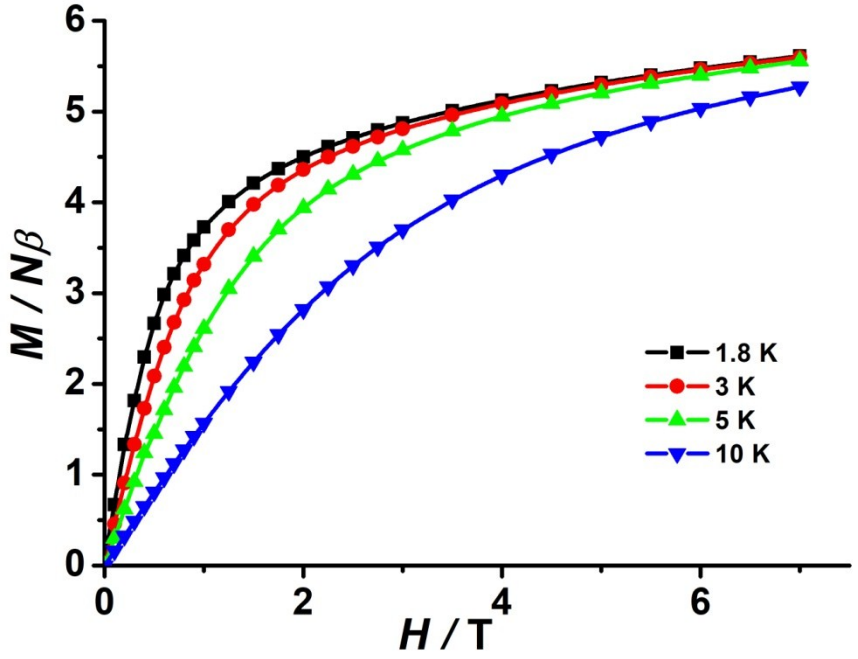


Figure S2 The field-dependence of magnetization at the temperature range of 1.8-10 K for **2-Tb**. The solid lines are for eye guide.

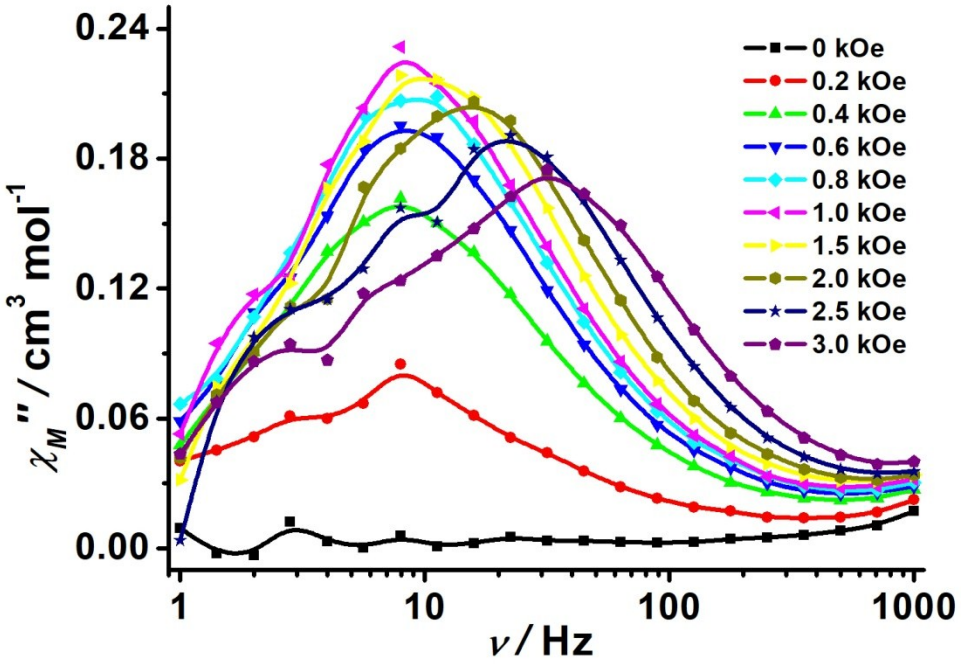


Figure S3 Frequency dependence of out-of-phase (χ_M'') ac susceptibility at 1.8 K under the different applied static fields from 0 to 3.0 kOe for **1-Yb**. The solid lines are for eye guide.

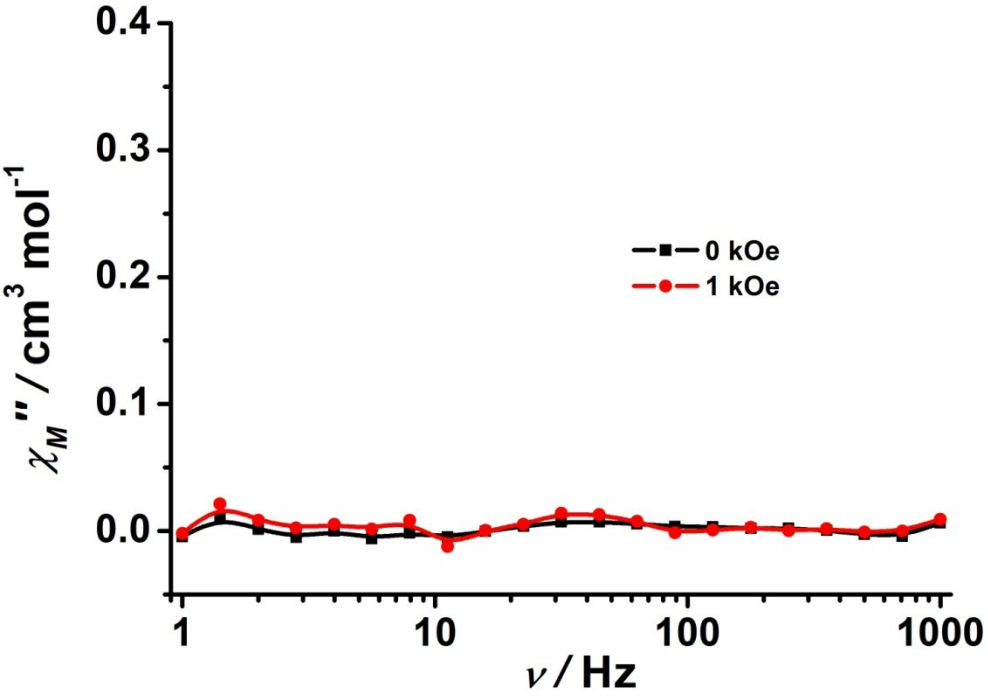


Figure S4 Frequency dependence of out-of-phase (χ_M'') ac susceptibility at 1.8 K under the external field of 0 and 1kOe for **2-Tb**. The solid lines are for eye guide.

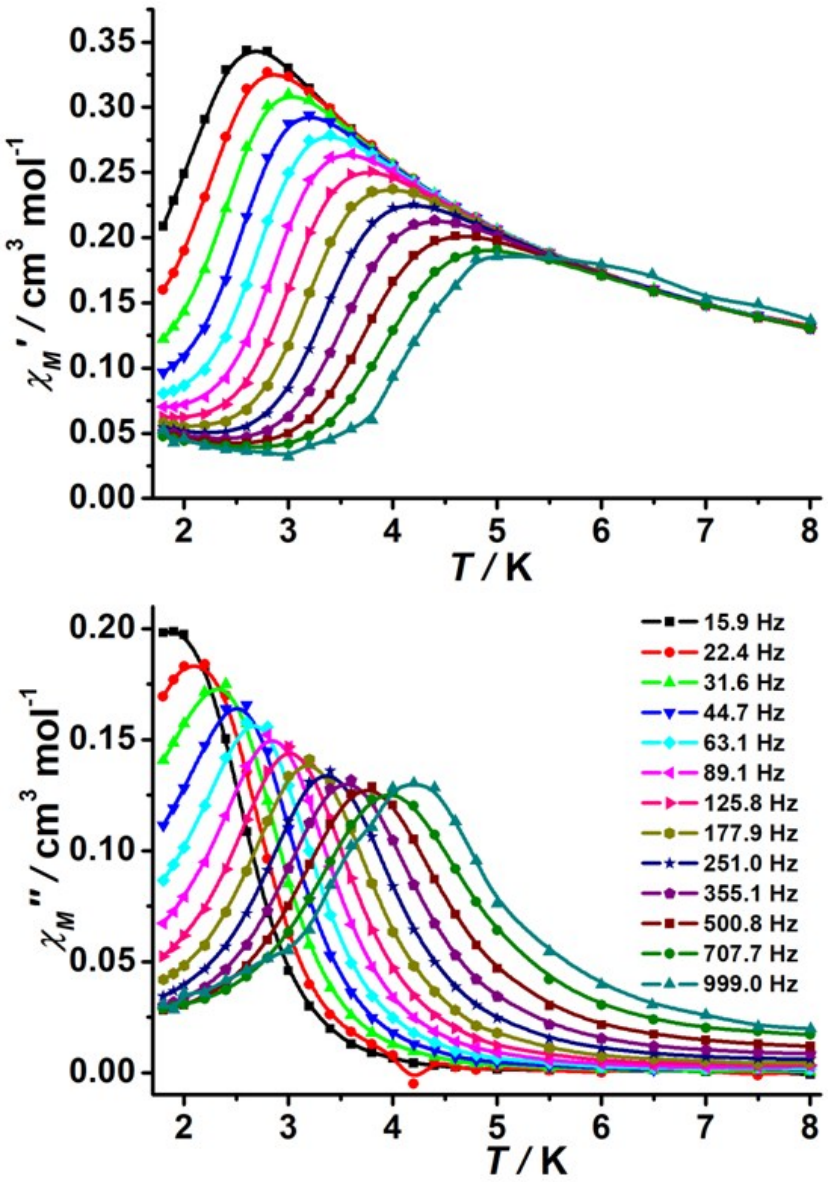


Figure S5 Temperature-dependence of the in-phase and out-of-phase susceptibility between 1 and 1000 Hz under a 1.0 kOe applied dc field.

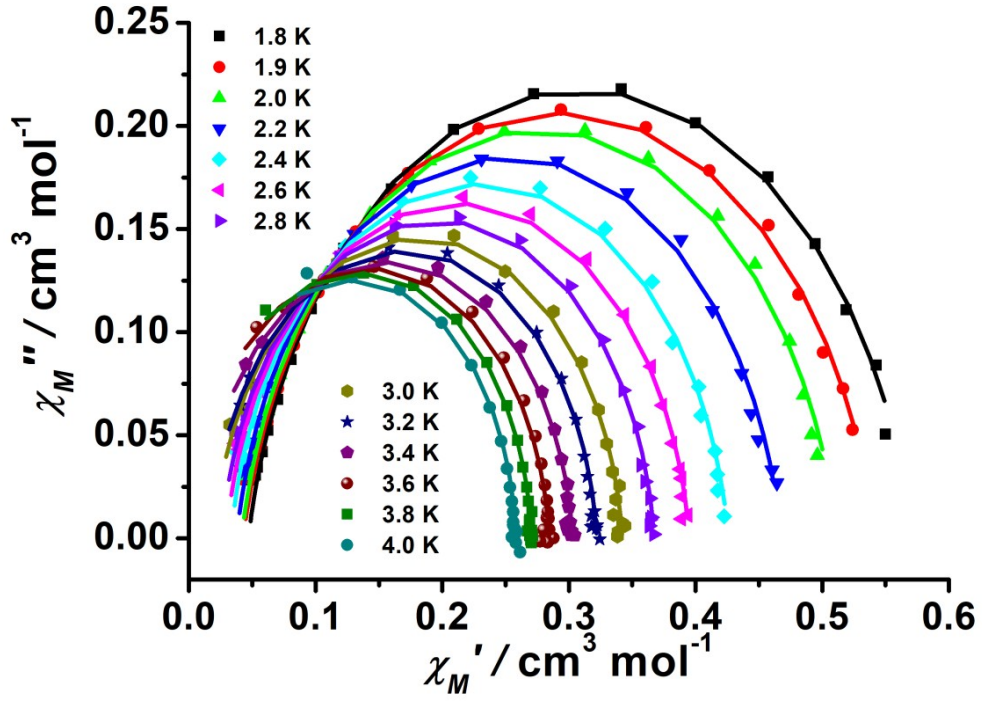


Figure S6 Cole-Cole plot obtained from the ac susceptibility data under a 1.0 kOe dc field in the temperature range of 1.8-4 K for **1-Yb**. Solid lines represent the best fits to a generalized Debye model.

Table S3 The parameters obtained by fitting Cole-Cole plot for **1-Yb**.

T / K	χ_S	χ_T	τ	a
1.8	0.047	0.571	0.0169	0.12
1.9	0.043	0.542	0.0140	0.12
2.0	0.041	0.512	0.0116	0.11
2.2	0.038	0.467	0.0079	0.09
2.4	0.033	0.426	0.0052	0.08
2.6	0.030	0.395	0.0034	0.07
2.8	0.026	0.367	0.0022	0.06
3.0	0.020	0.342	0.0014	0.06
3.2	0.017	0.322	0.0009	0.06
3.4	0.009	0.303	0.0006	0.06
3.6	~0	0.284	0.0004	0.05
3.8	~0	0.270	0.0003	0.03
4.0	~0	0.257	0.0002	0.02

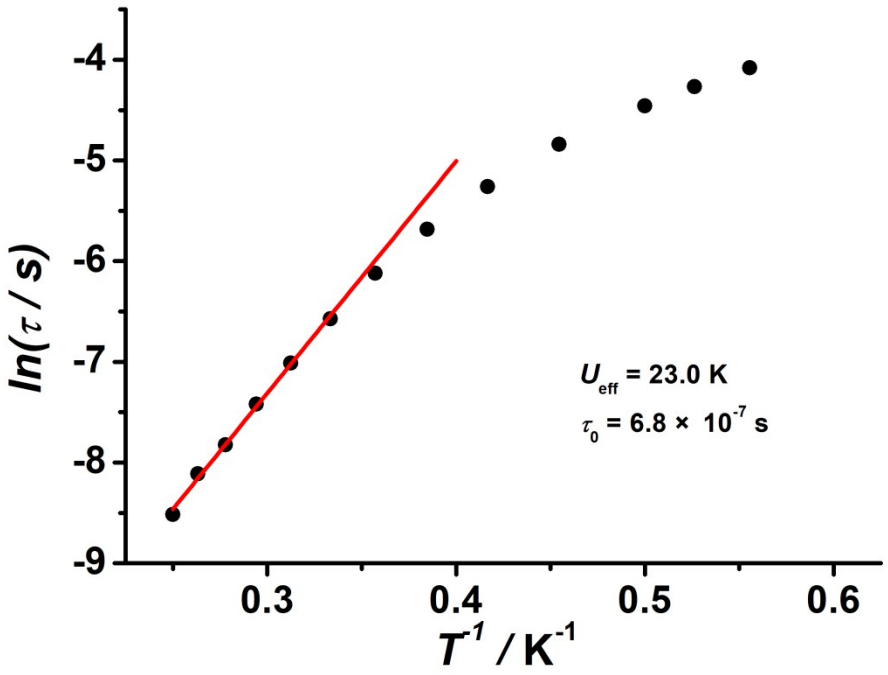


Figure S7 Relaxation time of the magnetization *ln(τ)* vs T^{-1} plots for **1-Yb**. The solid lines represent Arrhenius fits.

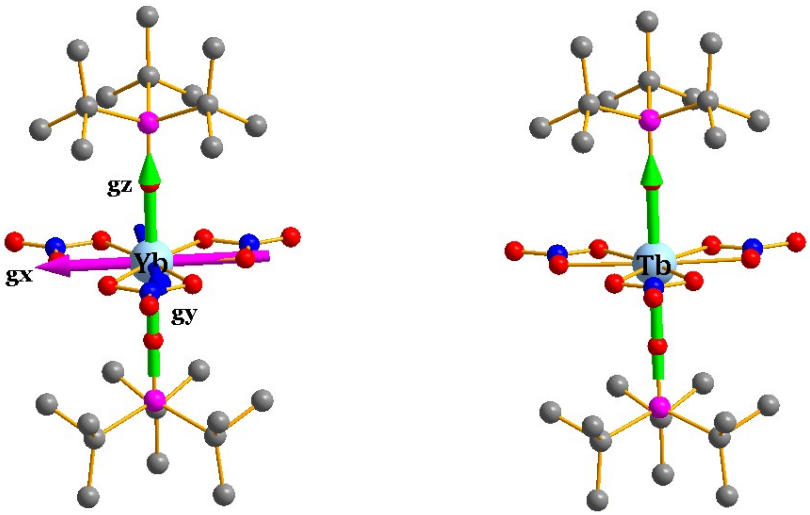
Table S4 Wave functions with definite projection of the total moment | m_J > for the lowest two spin-orbit doublets of **1-Yb** and **2-Tb** using CASSCF/RASSI with MOLCAS 8.2.

1-Yb	0.0	8%|−1/2>+92%|+1/2>
	0.0	92%|−1/2>+8%|+1/2>
	233.0	15%|−5/2>+85%|+7/2>
	233.0	15%|+5/2>+85%|−7/2>
2-Tb	0.0	50%|−5>+50%|+5>
	0.5	50%|−5>+50%|+5>
	36.8	50%|−4>+50%|+4>
	37.0	50%|−4>+50%|+4>

Table S5. Calculated energy levels (cm^{-1}), ***g*** (g_x, g_y, g_z) tensors and m_J values of the lowest seven or four spin-orbit states of **1-Yb** and **2-Tb** using CASSCF/RASSI with MOLCAS 8.2.

	1-Yb			**2-Tb**		
	E/cm^{-1}	***g***	m_J	E/cm^{-1}	***g***	m_J
1	0.0	4.575 4.553 1.171	±1/2	0.0 0.5	0.000 0.000 15.023	±5

2	233.0	2.177 2.213 5.940	±7/2	36.8 37.0	0.000 0.000 11.681	±4
3	267.9	0.009 0.031 3.454	±3/2	143.2 167.8	0.000 0.000 0.066	−3 +6
4	525.2	2.154 2.158 3.664	±5/2	168.3 209.7	0.000 0.000 0.133	−6 +3
5				346.6 346.7	0.000 0.000 5.307	±2
6				481.1 491.6	0.000 0.000 2.558	±1
7				544.1		0



1-Yb **2-Tb**

Figure S8 Calculated orientations of the local magnetic axes in the ground spin-orbit states on Yb^{III} and Tb^{III} ions of **1-Yb** and **2-Tb**.

References

S1 a) D. Casanova, M. Llunell, P. Alemany, S. Alvarez, *Chem. -Eur. J.* **2005**, *11*, 1479; b) S. Alvarez, P. Alemany, D. Casanova, J. Cirera, M. Llunell, D. Avnir, *Coord. Chem. Rev.* **2005**, *249*, 1693.