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Electronic Supplementary Material (ESI):

Half-Sandwich Single-Ion Magnets with Metallacrowns

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EXPERIMENTAL SECTION

Materials and Physical Measurements. The ligand quinHA was synthesized as literature described.¹ Metal salts and other reagents were commercially available and used as received without further purification. The C, H, and N microanalyses were carried out with an Elementar Vario-EL CHNS elemental analyzer. X-ray powder diffraction (XRPD) intensities for polycrystalline samples were measured at 293 K on Bruker D8 Advance Diffratometer (Cu-K_{α}, λ = 1.54056 Å) by scanning over the range of 5-50° with step of 0.2°/s. Calculated patterns were generated with Mercury. The luminescence spectra were measured using an Edinburgh Instrument FLS980 Combined Fluorescence Lifetime and Steady State Spectrometer. The steady-state luminescence was excited by unpolarized light from a 450 W xenon CW lamp at 298 K and 15 K. The lifetime measurements were excited by a pulsed µs flash lamp at 298 K. Magnetic susceptibility measurements were performed with a Quantum Design MPMS-XL7 SQUID. Polycrystalline samples were embedded in vaseline to prevent torquing. Data were corrected for the diamagnetic contribution calculated from Pascal constants.

X-ray Structure Determination. Diffraction intensities were collected on a Rigaku R-AXIS SPIDER IP diffractometer with Mo K α radiation ($\lambda = 0.71073$ Å) for complexes **1** and **2** at 150(2) K. The structures were solved by direct methods, and all non-hydrogen atoms were refined anisotropically by least-squares on F^2 using the SHELXTL program suite.² Anisotropic thermal parameters were assigned to all non-hydrogen atoms. The hydrogen atoms attached to carbon, nitrogen and oxygen atoms were placed in idealised positions and refined using a riding model to the atom to which they were attached. The disordered solvent molecules were squeezed³ and reconfirmed by the elemental analysis. CCDC 1055953 (1) and 1055954 (2) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via <u>www.ccdc.cam.ac.uk/conts/retrieving.html</u> (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

Synthesis. Complex 1: A mixture of quinHA (0.13 mmol), $Zn(CF_3SO_3)_2$ (0.13 mmol) and $Yb(CF_3SO_3)_3$ (0.026 mmol) was dissolved in 2 mL dimethylformamide. Under stirring, the solution was dropped with triethylamine (0.26 mmol) and turned yellow. After 20 minutes, 0.5 mL pyridine was added and the mixture was stirred for another 5 minutes. Yellow crystals suitable for X-ray analysis were obtained in several days by slow diffusion of ethyl acetate into the solution above. Elemental analysis calcd (%) for $YbZn_4C_{90}H_{121}N_{21}O_{33}F_9S_3$; C: 39.64, H: 4.47, N: 10.79; found (%): C: 39.49, H: 4.75, N: 11.03.

Complex 2: the procedure was the same as that employed for complex 1, except that pyridine was replaced by isoquinoline. The yellow crystals were obtained by slow diffusion of diethyl ether into the solution. Elemental analysis calcd (%) for $YbZn_4C_{109}H_{130}N_{22}O_{31}F_9S_3$; C: 44.44, H: 4.45, N: 10.46; found (%): C: 44.76, H: 4.42, N: 10.07.

Reference:

- 1. J. Jankolovits, J. W. Kampf and V. L. Pecoraro, Inorg. Chem., 2014, 53, 7534.
- 2. G. M. Sheldrick, Acta Crystallogr., 2008, A64, 112.
- 3. P. van der Sluis and A. L. Spek, Acta Crystallogr., 1990, A46, 194.



Figure S1. Experimental and simulated X-ray powder diffraction (XRPD) patterns for 1 (left) and 2 (right). The peaks marked with * were due to silicon carrier.



Figure S2. The structures of [YbZn₄]³⁺ cation of **1** (left) and **2** (right) viewed along top direction (Yb, olive; Zn, cyan; O, red; N, blue; C, gray). H atoms are omitted for clarity.



Figure S3. The packing arrangement of **1** (a) and **2** (b) viewed along special axes with intermolecular $\pi \cdots \pi$ and $\sigma \cdots \pi$ distances (Å) shown as dashed line. Triflate anions are filled in the interspace. The shortest intermolecular Yb-Yb distances for **1** and **2** are 9.933Å and 13.294 Å, respectively.



Figure S4. The dc field dependence of the relaxation time for **1** (left) and **2** (right) at 1.8K. The solid line is a guide for the eye.



Figure S5. (*left*) The plots of the relaxation time τ *vs. T* on a log-log scale. The red lines are for the best linear fitting. (*right*) The plots of the relaxation time τ *vs. T* only considering the direct and Raman process.



Figure S6. Cole-Cole plots for **1** (*left*) and **2** (*right*) obtained from the ac susceptibility data (600 Oe). The solid lines correspond to the best fit obtained with a generalized Debye model. Cole-Cole plots are quasi-semicircle with $\alpha = 0.01$ -0.12 (**1**) and $\alpha = 0.04$ -0.22 (**2**), indicating a narrow distribution of slow relaxation (K. S. Cole and R. H. Cole, *J. Chem. Phys.*, 1941, **9**, 34).



Figure S7. Emission spectra of the microcrystalline 1 (left) and 2 (right) at 298 K and 40 K.



Figure S8. Emission decay curves for the ${}^{2}F_{5/2} \rightarrow {}^{2}F_{7/2}$ transitions of 1 (*left*) and 2 (*right*).



Figure S9. (*top*) Simulation of the emission spectrum of the ${}^{2}F_{5/2} \rightarrow {}^{2}F_{7/2}$ transition of the microcrystalline 1 at 15 K through a convolution of Gaussian lines ($R^{2} = 0.998$) corresponding to the four Kramers doublets (10207, 10094, 9778, and 9635 cm⁻¹, cyan lines) and two hot transitions (10004 and 9908 cm⁻¹, orange lines). (*bottom*) Energy levels of the ${}^{2}F_{7/2}$ ground state multiplet (gray lines) determined from the (*a*) dc fit ($\Delta = 109 \text{ cm}^{-1}$), (*b*) ac fit ($U_{eff}/k_{B} = 9 \text{ cm}^{-1}$), and (*c*) the luminescence spectrum ($\Delta = 112 \text{ cm}^{-1}$).



Figure S10. Simulation of the emission spectrum of the ${}^{2}F_{5/2} \rightarrow {}^{2}F_{7/2}$ transition of the microcrystalline **2** at 15 K through a convolution of Gaussian lines ($R^{2} = 0.994$) corresponding to the four Kramers doublets (10172, 10003, 9715, and 9532 cm⁻¹, cyan lines) and two hot transitions (9836 cm⁻¹, orange lines).

compound	1	2
Formula	$YbZn_4C_{90}H_{121}N_{21}O_{33}S_3F_9$	$YbZn_4C_{109}H_{130}N_{22}O_{31}S_3F_9$
M_r	2726.90	2946.18
Temp. / K	150	150
Crystal system	tetragonal	monoclinic
Space group	P4/ncc	$P2_{1}/c$
<i>a</i> / Å	23.3111(7)	16.1341(4)
b / Å	23.3111(7)	42.5371(10)
<i>c</i> / Å	19.8660(8)	18.4653(4)
α / Å	90	90
eta / Å	90	93.1310(10)
γ / Å	90	90
$V/\text{\AA}^3$	10795.3(8)	12653.8(5)
Ζ	4	4
ρ_{calcd} . (g/cm ³)	1.620	1.499
μ (mm ⁻¹)	1.871	1.611
F (000)	4484	5376
Reflns obsd $[I \ge 2\sigma(I)]$	4733	18702
GOF on F^2	1.035	0.992
$R_1 [I \ge 2\sigma(I)]^a$	0.0501	0.0683
wR_2 (all data) ^b	0.1471	0.2038
CCDC No.	1055953	1055954
${}^{a}R_{1} = \sum F_{0} - F_{c} / \sum F_{0} $	$. {}^{b} wR_{2} = [\sum w(F_{0}^{2} - F_{c}^{2})^{2}/\sum$	$w(F_0^2)^2]^{1/2}$

 Table S1. Crystallographic Data and Structural Refinements for 1 and 2.

Table S2. Lanthanide geometr	y analysis by	y using Continuous	Shape Measurements	(CShM). ^a
				· /

Complex	*SAP (<i>D</i> _{4d})	TDD (D _{2d})	TP (C _{2v})	
1	0.120	2.644	2.071	
2	0.136	2.235	2.119	

* SAP = square anti-prism; TDD = triangular dodecahedron; TP = biaugmented trigonal prism.

^a (a) S. Alvarez, P. Alemany, D.Casanova, J. Cirera, M. Llunell and D. Avnir, Coord. Chem. Rev., 2005, 249,

1693; (b) D. Casanova, M. Llunell, P. Alemany and S. Alvarez, Chem. Eur. J., 2005, 11, 1479.

Table S3. Structural parameters of the selected lanthanide double-decker with the square anti-prismatic geometry.

Complexes ^a	Yb-O/N ^{<i>b</i>} (Å)	$MAD_{\phi}{}^{c}$ (°)	<i>d</i> _{in} ^{<i>d</i>} (Å)	<i>d</i> _{pp} ^{<i>e</i>} (Å)	Ref.*
Yb(tmtaa)(Htmtaa)	2.44	39.2(2)	2.76	2.93	а
[YbPc ₂]I ₂	2.53	5.1(3)	2.76	3.20	b
Yb(Nc)(OEP)	2.41	0.5(1)	2.82	2.69	С
YbZn ₄ (picHA) ₄ ³⁺	2.37	9.1(1)	2.78	2.58	12d in text
	2.37	2.3(2)	2.87	2.46	12d in toxt
	2.37	1.3(2)	2.87	2.45	120 III text
1	2.39	0.7(1)	2.57	2.49	This work
2	2.35	2.8(1)	2.82	2.48	This work
[Er(POM _a) ₂] ⁹⁻	2.37	2.0(4)	2.86	2.47	16a in text
[Er(POM _b) ₂] ¹³⁻	2.35	2.1(5)	2.86	2.47	16b in text

^{*a*} H₂tmtaa = 5,14-dihydro-6,8,15,17-tetramethyldibenzo[*b*,*i*][1,4,8,11]tetraazacyclotetradecine; Pc is non-integral oxidized phthalocyanine; Nc = 2,3naphthalocyanine; OEP = octaethylporphyrine; YbZn₄(picHA)₄ = [Yb(12-MC_{Zn(II),picHA}-4)(DMF)₄(py)₄](NO₃)₃; YbZn₈(picHA)₈ = Yb(12-MC_{Zn(II),picHA}-4)₂(OH)₃(py)₂; picHA = picoline hydroxamic acid; POM_a = W₅O₁₈; POM_b = θ_2 -SiW₁₁O₃₀. ^{*b*} the average values for bond lengths of Yb-O/N; ^{*c*} MAD = mean absolute deviation, skew angle ϕ for the ideal D_{4d} LF symmetry is 45°. ^{*d*} d_{in} means the average distance between the four neighbouring atoms placed in each square. ^{*e*} d_{pp} means the distance between two centroids from the upper and lower planes respectively.

* (a) Z. Wang, N. Hu, K. Sakata and M. Hashimoto, *J. Chem. Soc., Dalton Tran.*, 1999, 1695; (b) J. Janczak, R. Kubiak and A. Jezierski, *Inorg. Chem.*, 1999, **38**, 2043; (c) Y. Bian, D. Wang, R. Wang, L. Weng, J. Dou, D. Zhao, D. K. P. Ng and J. Jiang, *New J. Chem.*, 2003, **27**, 844.

Table S4. Characteristic parameters (θ and ϕ) of a square anti-prism geometry in 1 and 2.

Angle/o		1	2		Ideal D _{4d} ^a
$\theta 1$	01	60.8(1)	01	61.5(1)	59.76
θ2	O1A	60.8(1)	03	60.5(1)	59.76
θ3	O1B	60.8(1)	05	62.2(2)	59.76
$\theta 4$	O1C	60.8(1)	07	59.6(1)	59.76
θ5	03	54.8(1)	09	55.5(1)	59.76
$\theta 6$	O3A	54.8(1)	O10	55.4(1)	59.76
θ7	O3B	54.8(1)	011	55.7(1)	59.76
$\theta 8$	O3C	54.8(1)	012	55.5(1)	59.76
<i>φ</i> 1	01	45.7(1)	01	48.2 (1)	45
<i>\$</i> \$ \$ \$ \$ \$ \$ \$ \$ \$ \$ \$ \$ \$ \$ \$ \$ \$ \$	O1A	44.3(1)	03	43.0(1)	45
\$ ø 3	O1B	45.7(1)	05	47.5(1)	45
<i>φ</i> 4	O1C	44.3(1)	07	41.3(1)	45

^a E. L. Muetterties and L. J. Guggenberger, J. Am. Chem. Soc., 1974, 96, 1748.

	Energy / cm ⁻¹	Eigenstate
1	0	78.9% ±5/2>+21.1% ±3/2>
	109	97.1% ±7/2>+2.9% ±1/2>
	505	78.9% ±3/2>+21.1% ±7/2>
	600	97.1% ±1/2>+2.9% ±7/2>
2	0	93.4% ±5/2>+6.6% ±3/2>
	116	96.8% ±7/2>+3.2% ±1/2>
	468	96.8% ±1/2>+3.2% ±7/2>
	522	93.5% ±3/2>+6.5% ±5/2>

Table S5. Energy levels and eigenstates for compounds 1 and 2 extracted from the $\chi_m T$ -T and *M*-H data.