Electronic supporting Information for

Structural and spectroscopic investigations of nine-coordinate redox active lanthanide complexes with a pincer O,N,O ligand

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Content :

1. Figures

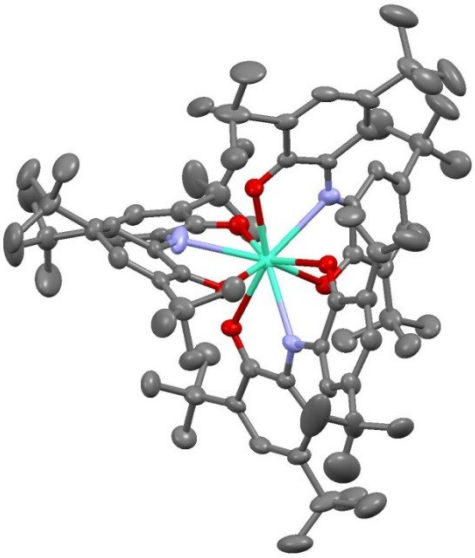

Fig. S1 X-Ray crystal structure of **GdL_3**

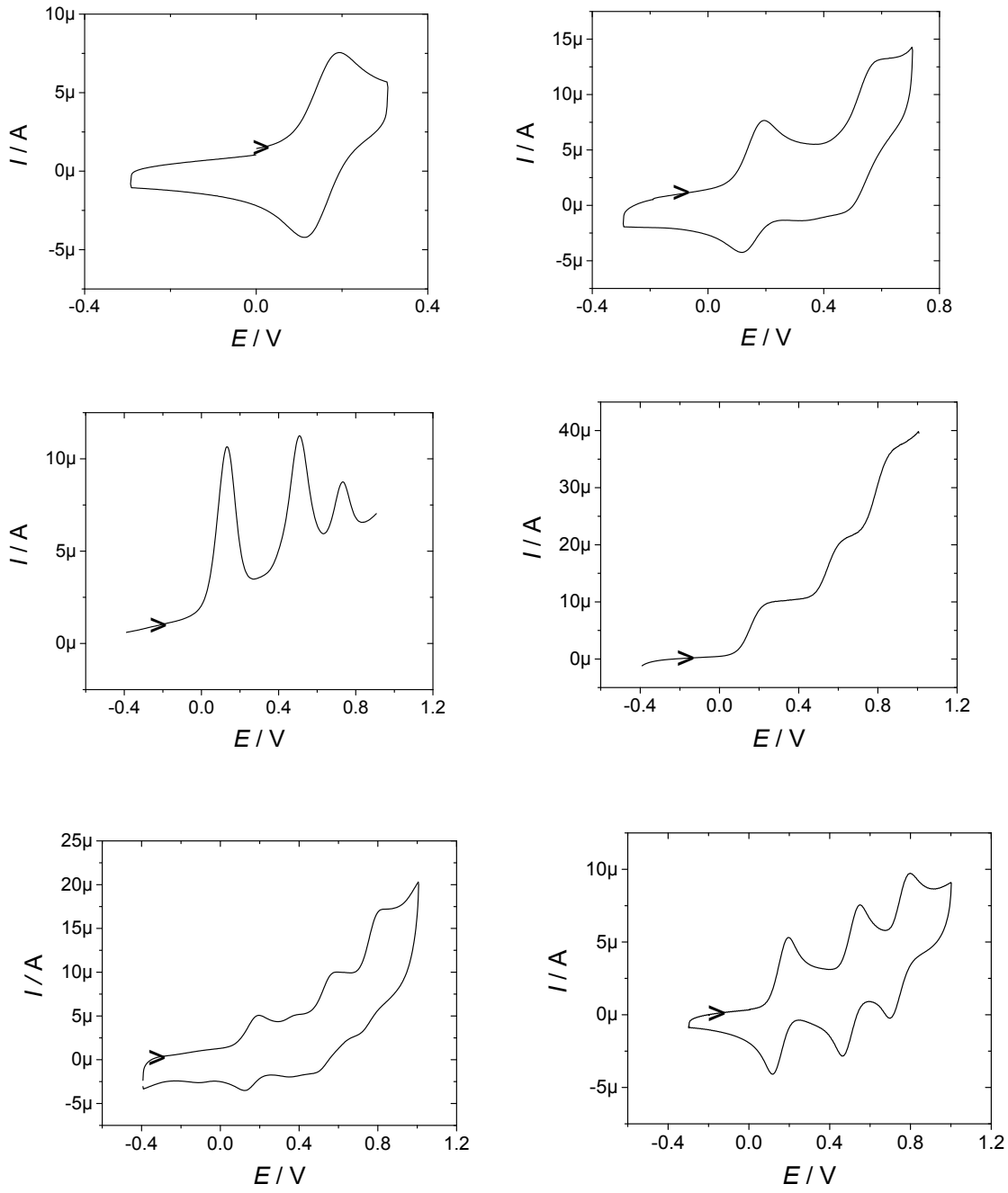

Fig. S2 Electrochemical behaviour of of **GdL_3** at a carbon electrode in oxidation. Top: CV curves (scan rate = 0.1 V/sec). Middle left: DPV curve (pulse amplitude = 0.05 V). Middle right: Voltammetry curve at the RDE (500 rpm, scan rate = 0.05 V/sec). Bottom: CV curve (scan rate = 0.1 V/sec). Left: 298K; Right: 233 K. The potentials are referenced vs. the Fc^+/Fc redox couple. Curves recorded with 0.5 mM CH_2Cl_2 solution (containing 0.1 M TBAP as supporting electrolyte). *T* = 298 K except bottom curve right.

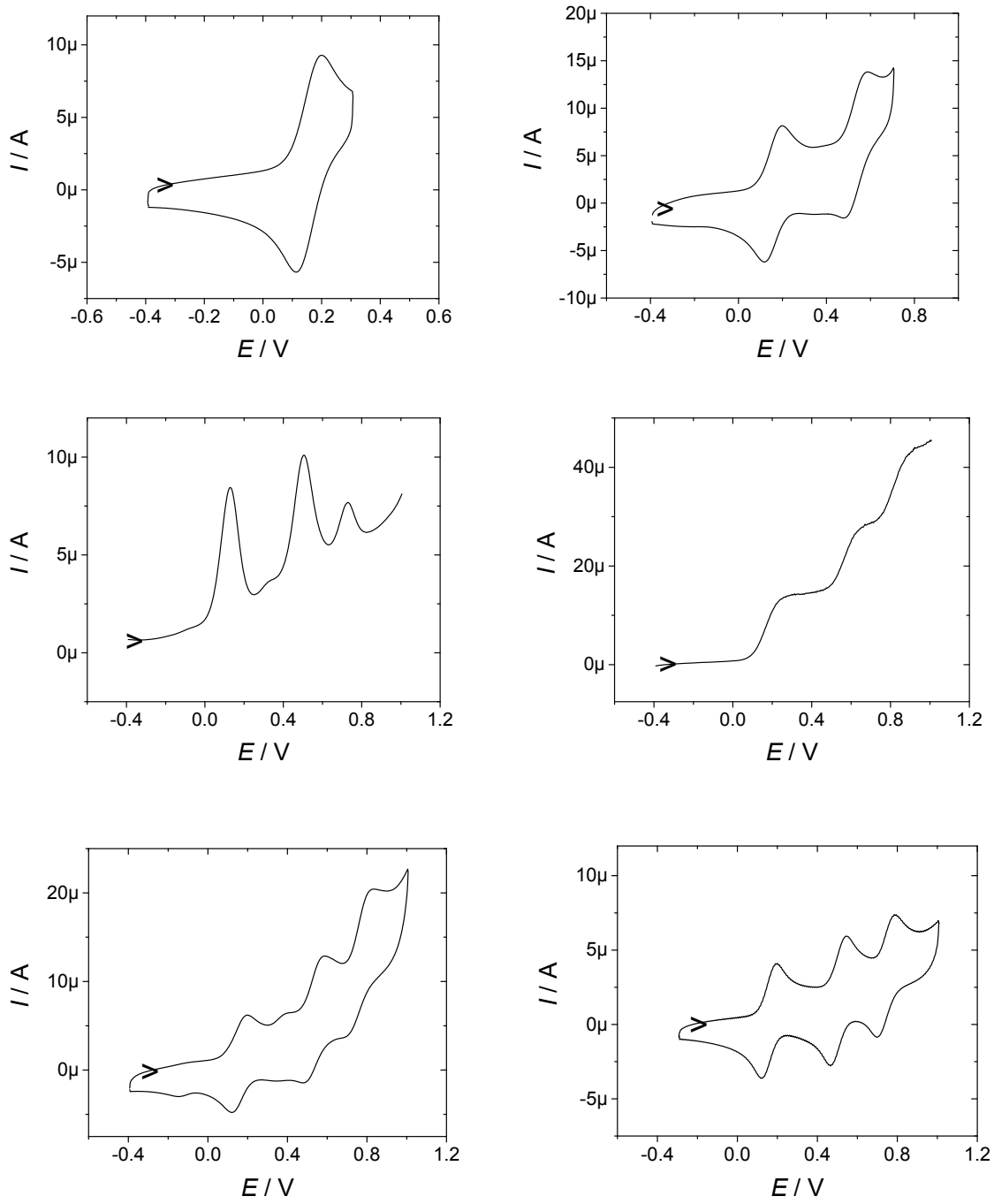

Fig. S3 Electrochemical behaviour of of **EuL_3** at a carbon electrode in oxidation. Top: CV curves (scan rate = 0.1 V/sec). Middle: Voltammetry curve at the RDE (500 rpm, scan rate = 0.05 V/sec). Bottom: CV curves of **EuL_3^+** and **EuL_3** (scan rate = 0.1 V/sec). Left: 298K; Right: 233 K. The potentials are referenced vs. the Fc^+/Fc redox couple. Curves recorded with 0.5 mM CH_2Cl_2 solution (containing 0.1 M TBAP as supporting electrolyte). *T* = 298 K except bottom curve.

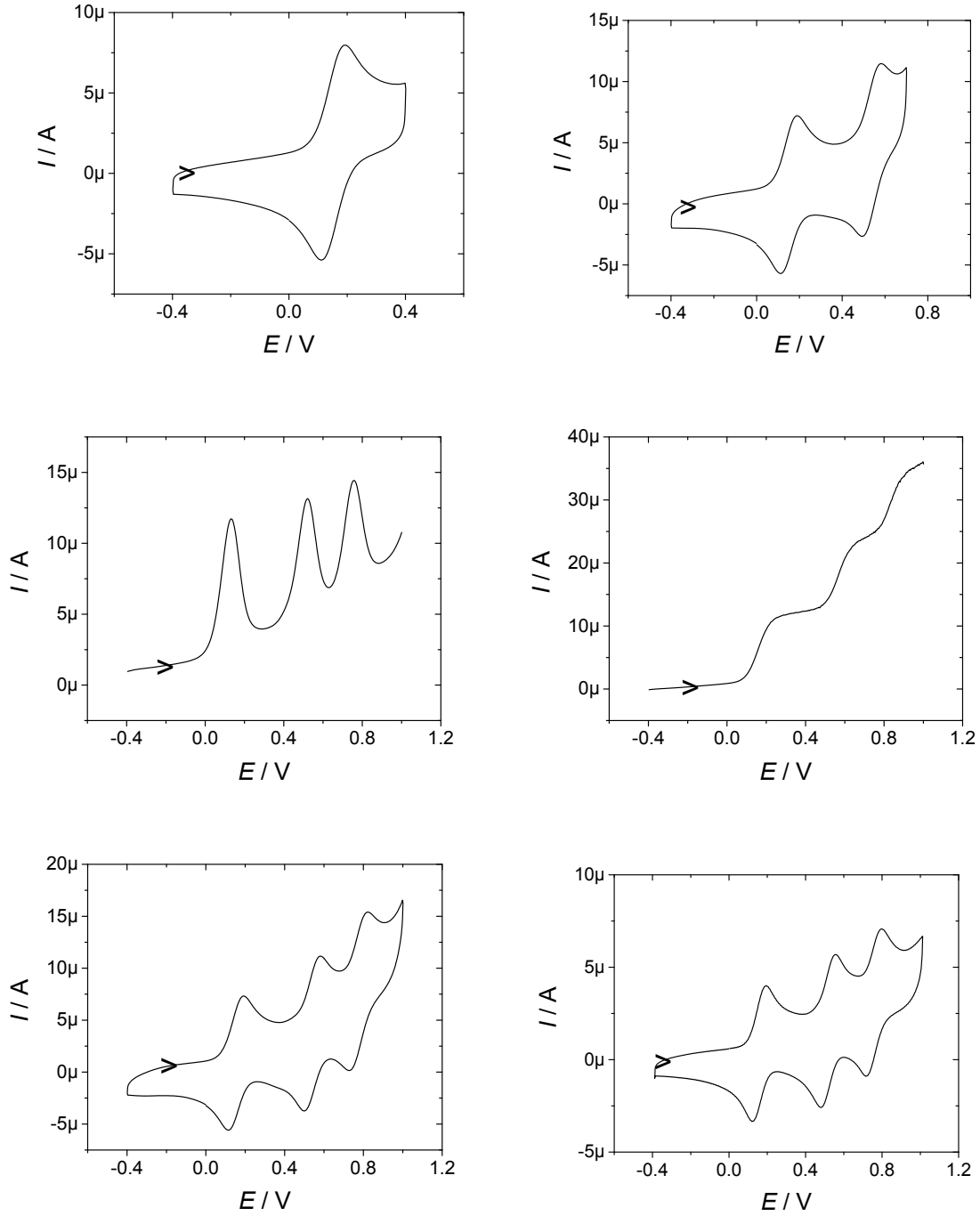

Fig. S4 Electrochemical behaviour of **YbL_3** at a carbon electrode in oxidation. Top: CV curves (scan rate = 0.1 V/sec). Middle left: DPV curve (pulse amplitude = 0.05 V). Middle right: Voltammetry curve at the RDE (500 rpm, scan rate = 0.05 V/sec). Bottom: CV curve (scan rate = 0.1 V/sec); Left: 298 K; Right: 233 K. The potentials are referenced vs. the Fc^+/Fc redox couple. 0.5 mM CH_2Cl_2 solution (containing 0.1 M TBAP as supporting electrolyte). *T* = 298 K except bottom curve right.

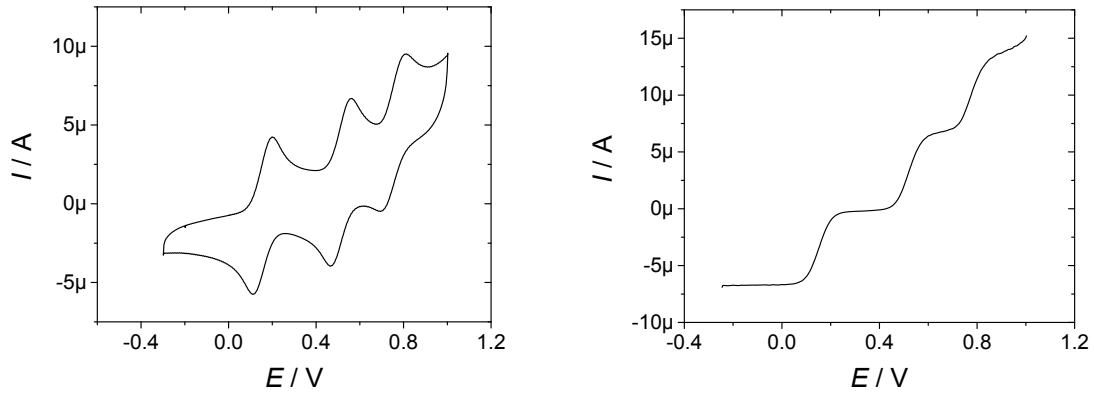

Fig. S5 Electrochemical behaviour of $\mathbf{GdL_3}$ after exhaustive electrolysis at 0.3 V (electrochemically generated $\mathbf{GdL_3^+}$) at a carbon electrode. Left: CV curves (scan rate = 0.1 V/sec). Right: Voltammetry curve at the RDE (500 rpm, scan rate = 0.05 V/sec). The potentials are referenced vs. the Fc^+/Fc redox couple. 0.5 mM CH_2Cl_2 solution (containing 0.1 M TBAP as supporting electrolyte). T = 233 K.

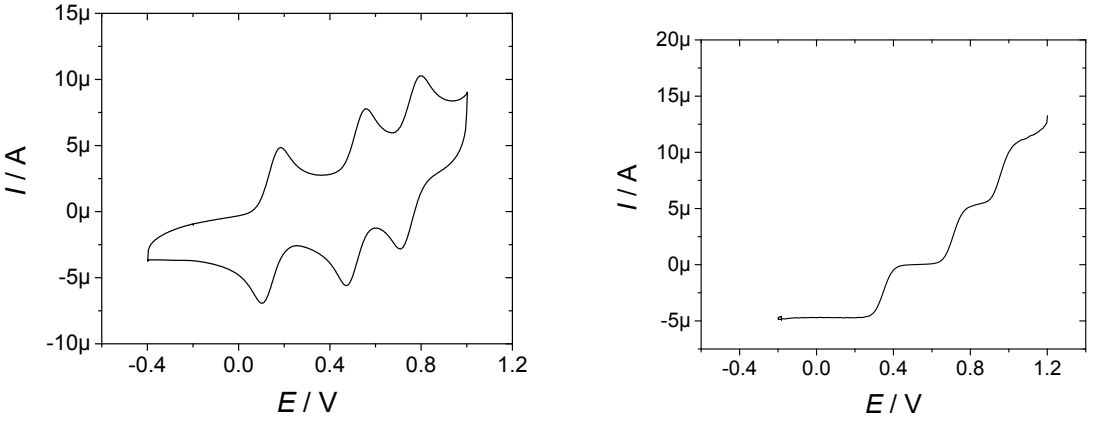

Fig. S6 Electrochemical behaviour of $\mathbf{EuL_3}$ after exhaustive electrolysis at 0.3 V (electrochemically generated $\mathbf{EuL_3^+}$) at a carbon electrode. Left: CV curves (scan rate = 0.1 V/sec). Right: Voltammetry curve at the RDE (500 rpm, scan rate = 0.05 V/sec). The potentials are referenced vs. the Fc^+/Fc redox couple. 0.5 mM CH_2Cl_2 solution (containing 0.1 M TBAP as supporting electrolyte). T = 233 K.

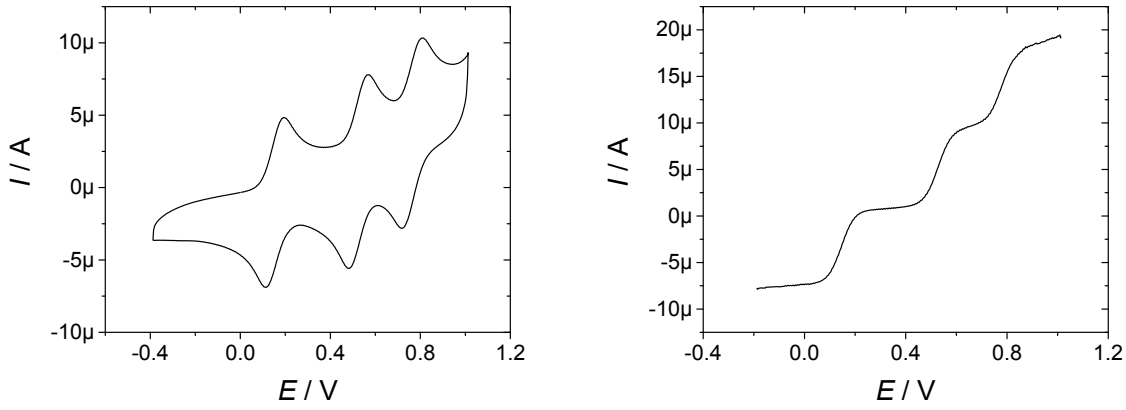

Fig. S7 Electrochemical behaviour of **YbL_3** after exhaustive electrolysis at 0.3 V (electrochemically generated **YbL_3^+**) at a carbon electrode. Left: CV curves (scan rate = 0.1 V/sec). Right: Voltammetry curve at the RDE (500 rpm, scan rate = 0.05 V/sec). The potentials are referenced vs. the Fc^+/Fc redox couple. 0.5 mM CH_2Cl_2 solution (containing 0.1 M TBAP as supporting electrolyte). *T* = 233 K.

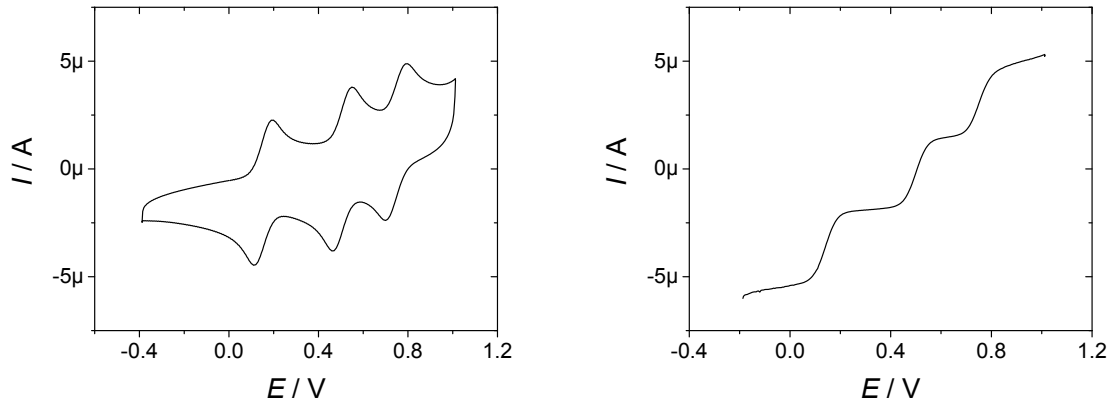

Fig. S8 Electrochemical behaviour of **YbL_3** after exhaustive electrolysis at 0.7 V at a carbon electrode. Left: CV curves (scan rate = 0.1 V/sec). Right: Voltammetry curve at the RDE (500 rpm, scan rate = 0.05 V/sec). The potentials are referenced vs. the Fc^+/Fc redox couple. 0.5 mM CH_2Cl_2 solution (containing 0.1 M TBAP as supporting electrolyte). *T* = 233 K.

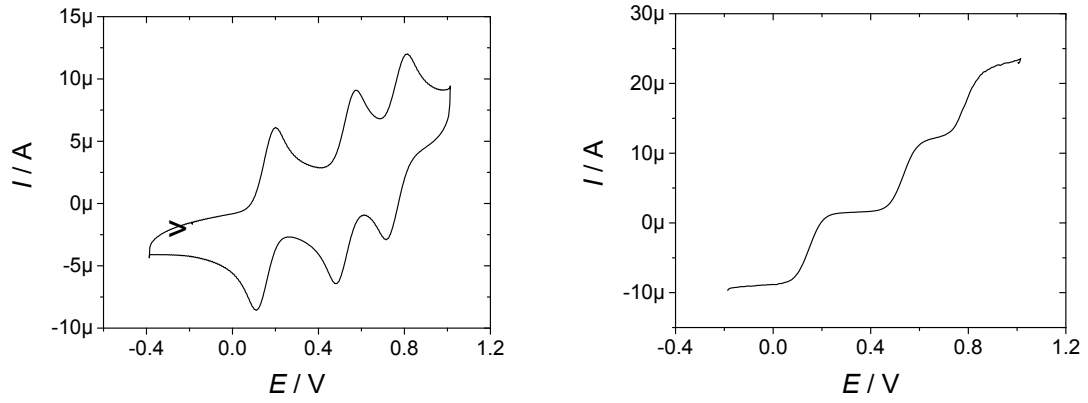

Fig. S9 Electrochemical behaviour of **LuL_3** after exhaustive electrolysis at 0.3 V (electrochemically generated **LuL_3^+**) at a carbon electrode. Left: CV curves (scan rate = 0.1 V/sec). Right: Voltammetry curve at the RDE (500 rpm, scan rate = 0.05 V/sec). The potentials are referenced vs. the Fc^+/Fc redox couple. 0.5 mM CH_2Cl_2 solution (containing 0.1 M TBAP as supporting electrolyte). *T* = 233 K.

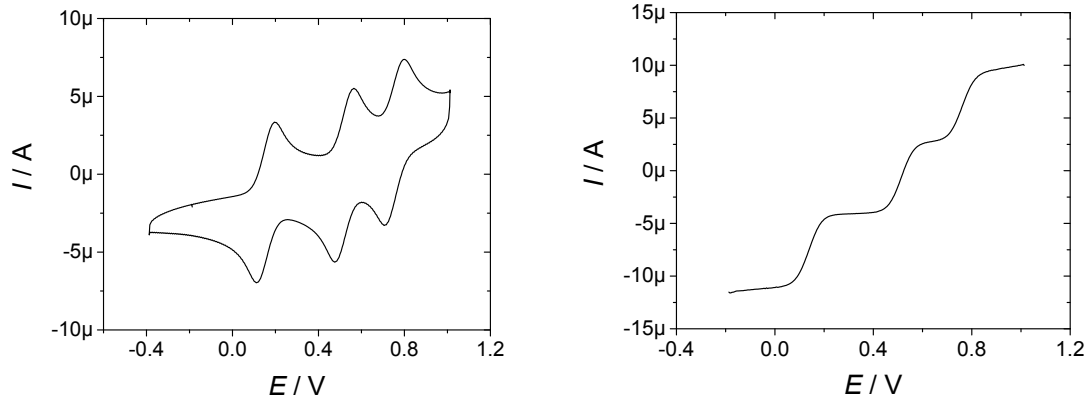

Fig. S10 Electrochemical behaviour of **LuL_3** after exhaustive electrolysis at 0.7 V at a carbon electrode. Left: CV curves (scan rate = 0.1 V/sec). Right: Voltammetry curve at the RDE (500 rpm, scan rate = 0.05 V/sec). The potentials are referenced vs. the Fc^+/Fc redox couple. 0.5 mM CH_2Cl_2 solution (containing 0.1 M TBAP as supporting electrolyte). *T* = 233 K.

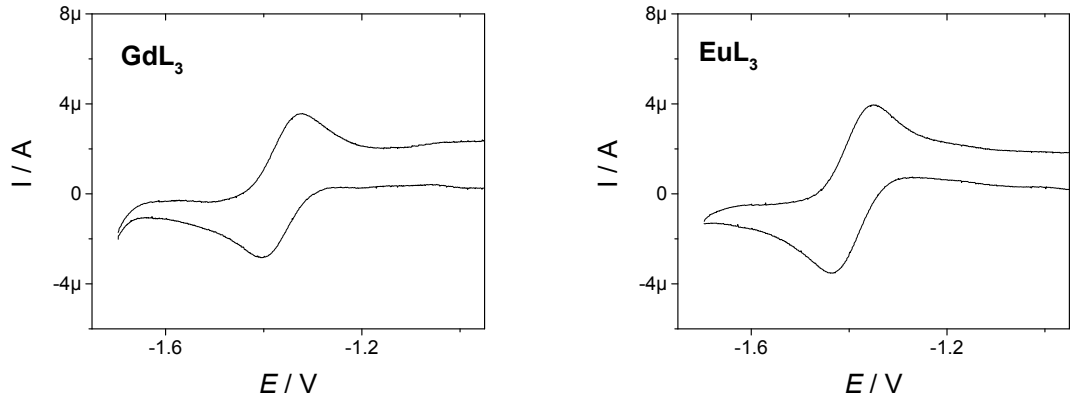

Fig. S11 Cyclic voltammetry curves of 0.5 mM CH_2Cl_2 solutions (containing 0.1 M TBAP as supporting electrolyte) of the complexes at a carbon electrode in reduction (in the glove box). The potentials are referenced vs. the Fc^+/Fc redox couple. *T* = 298 K, scan rate = 0.1 V/sec.

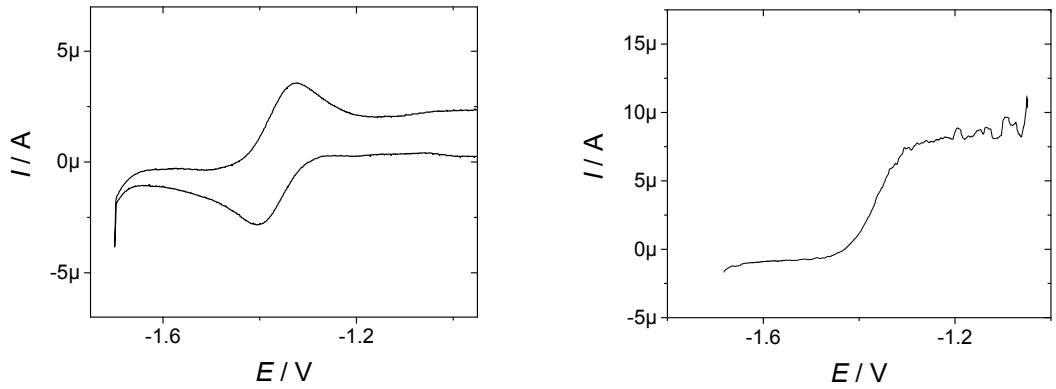

Fig. S12 Electrochemical behaviour of **GdL_3** after exhaustive electrolysis at -1.6 V (electrochemically generated **GdL_3^-**) at a carbon electrode. Left: CV curves (scan rate = 0.1 V/sec). Right: Voltammetry curve at the RDE (500 rpm, scan rate = 0.05 V/sec). The potentials are referenced vs. the Fc^+/Fc redox couple. 0.5 mM CH_2Cl_2 solution (containing 0.1 M TBAP as supporting electrolyte). *T* = 298 K.

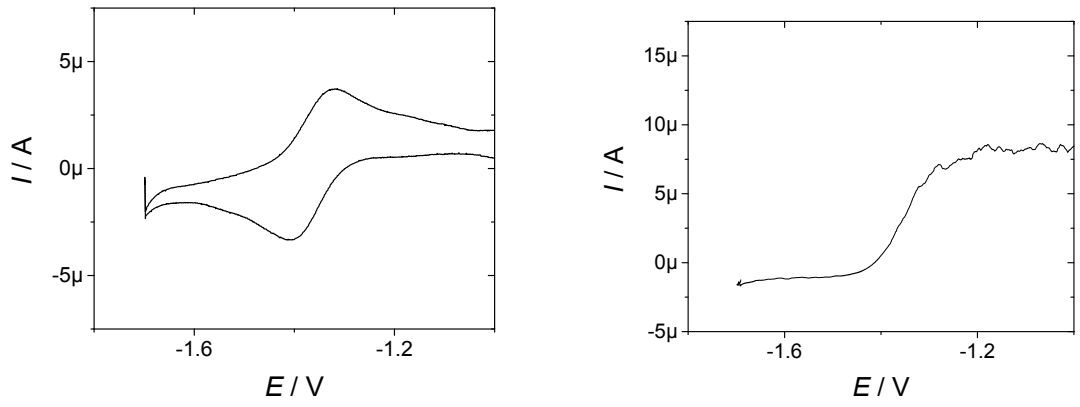

Fig. S13 Electrochemical behaviour of **EuL_3** after exhaustive electrolysis at -1.6 V (electrochemically generated **EuL_3^-**) at a carbon electrode. Left: CV curves (scan rate = 0.1 V/sec). Right: Voltammetry curve at the RDE (500 rpm, scan rate = 0.05 V/sec). The potentials are referenced vs. the Fc^+/Fc redox couple. 0.5 mM CH_2Cl_2 solution (containing 0.1 M TBAP as supporting electrolyte). *T* = 298 K.

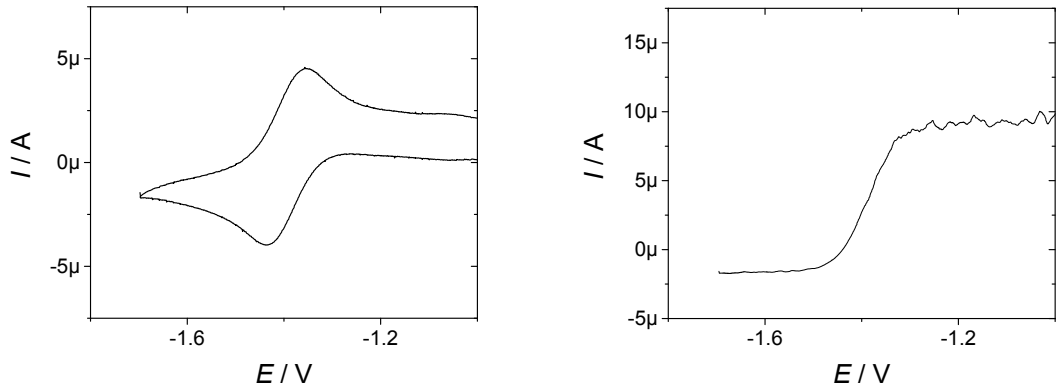

Fig. S14 Electrochemical behaviour of **YbL_3** after exhaustive electrolysis at -1.6 V (electrochemically generated **YbL_3^-**) at a carbon electrode. Left: CV curves (scan rate = 0.1 V/sec). Right: Voltammetry curve at the RDE (500 rpm, scan rate = 0.05 V/sec). The potentials are referenced vs. the Fc^+/Fc redox couple. 0.5 mM CH_2Cl_2 solution (containing 0.1 M TBAP as supporting electrolyte). *T* = 298 K.

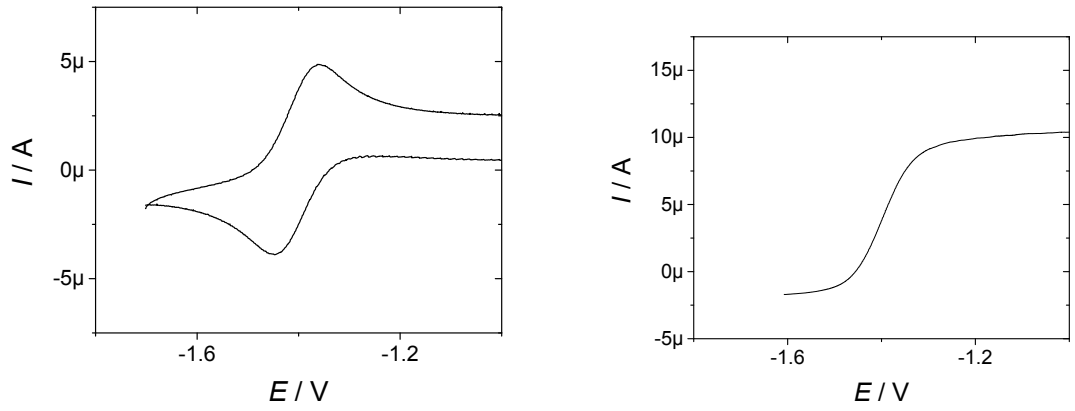

Fig. S15 Electrochemical behaviour of **LuL_3** after exhaustive electrolysis at -1.6 V (electrochemically generated **LuL_3^-**) at a carbon electrode. Left: CV curves (scan rate = 0.1 V/sec). Right: Voltammetry curve at the RDE (500 rpm, scan rate = 0.05 V/sec). The potentials are referenced vs. the Fc^+/Fc redox couple. 0.5 mM CH_2Cl_2 solution (containing 0.1 M TBAP as supporting electrolyte). *T* = 298 K.

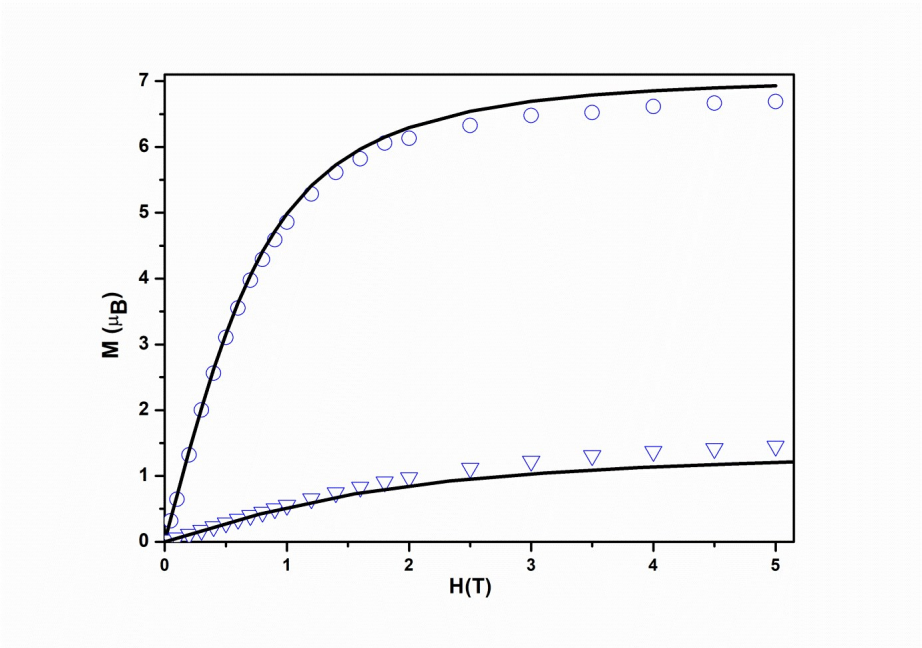

Fig. S16 Experimental M vs. H plots for **YbL_3** (bottom) and **GdL_3** (top) with simulations as solid lines from best fit parameters of magnetic susceptibility with PHI software (see text).[1]

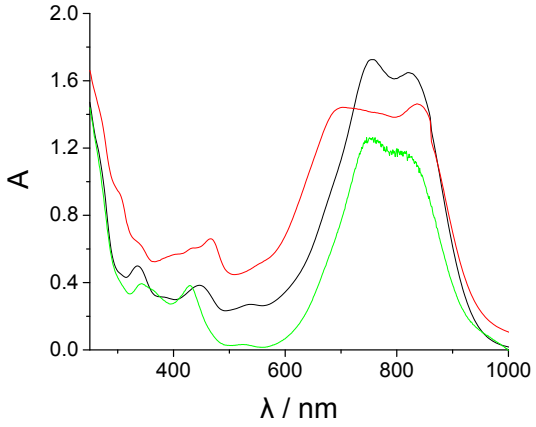

Fig. S17 UV-Vis-NIR spectra of 0.44 mM CH_2Cl_2 solutions (containing 0.1 M TBAP as supporting electrolyte) of **GdL_3**. Black line: neutral complex (0.44 mM); Red line: cation (0.33 mM); Green line: after exhaustive electrolysis at -1.6 V (0.33 mM) . *l* = 1.00 mm. *T* = 298 K.

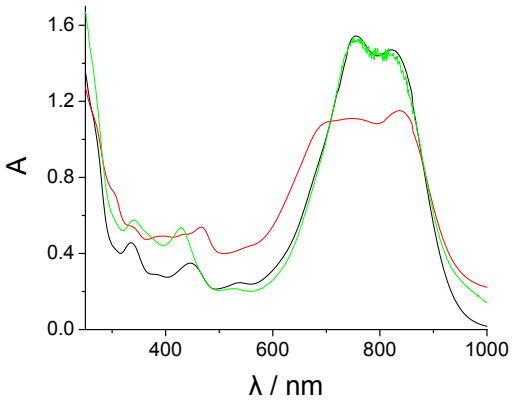

Fig. S18 UV-Vis-NIR spectra of CH_2Cl_2 solutions (containing 0.1 M TBAP as supporting electrolyte) of **EuL_3**. Black line: neutral complex (0.41 mM); Red line: cation (0.38 mM); Green line: after exhaustive electrolysis at -1.6 V (0.38 mM). *l* = 1.00 mm. *T* = 298 K.

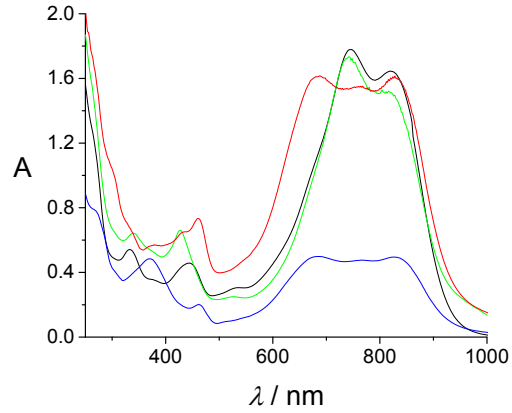

Fig. S19 UV-Vis-NIR spectra of CH_2Cl_2 solutions (containing 0.1 M TBAP as supporting electrolyte) of **YbL_3**. Black line: neutral complex (0.49 mM); Red line: cation (0.48 mM); Green line: after exhaustive electrolysis at -1.6 V (0.48 mM); Blue line: after exhaustive electrolysis at +0.6 V (0.48 mM). *l* = 1.00 mm. *T* = 298 K.

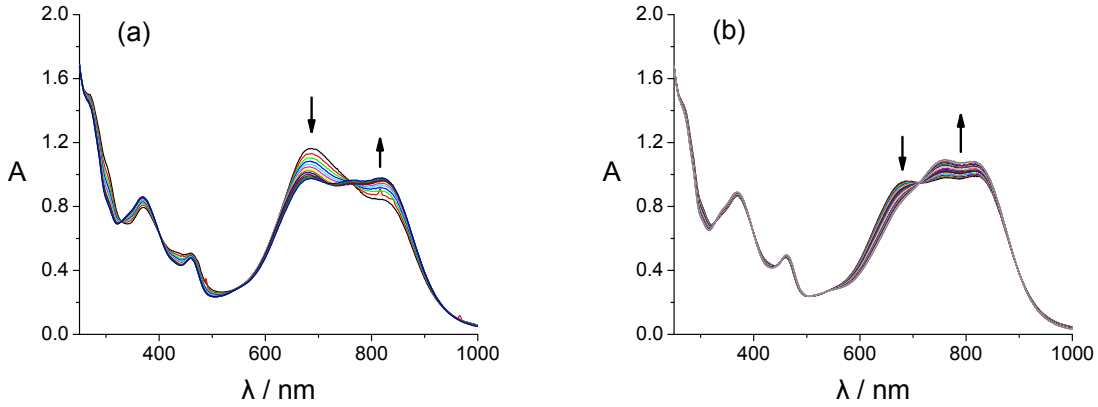

Fig. S20 UV-Vis-NIR monitoring of the decomposition of the electrochemically generated $\mathbf{LuL_3^{2+}}$ in 0.5 mM CH_2Cl_2 solution (containing 0.1 M TBAP as supporting electrolyte). (a) First 10 minutes; (b) Further 1 hour. *l* = 1.00 mm. *T* = 298 K.

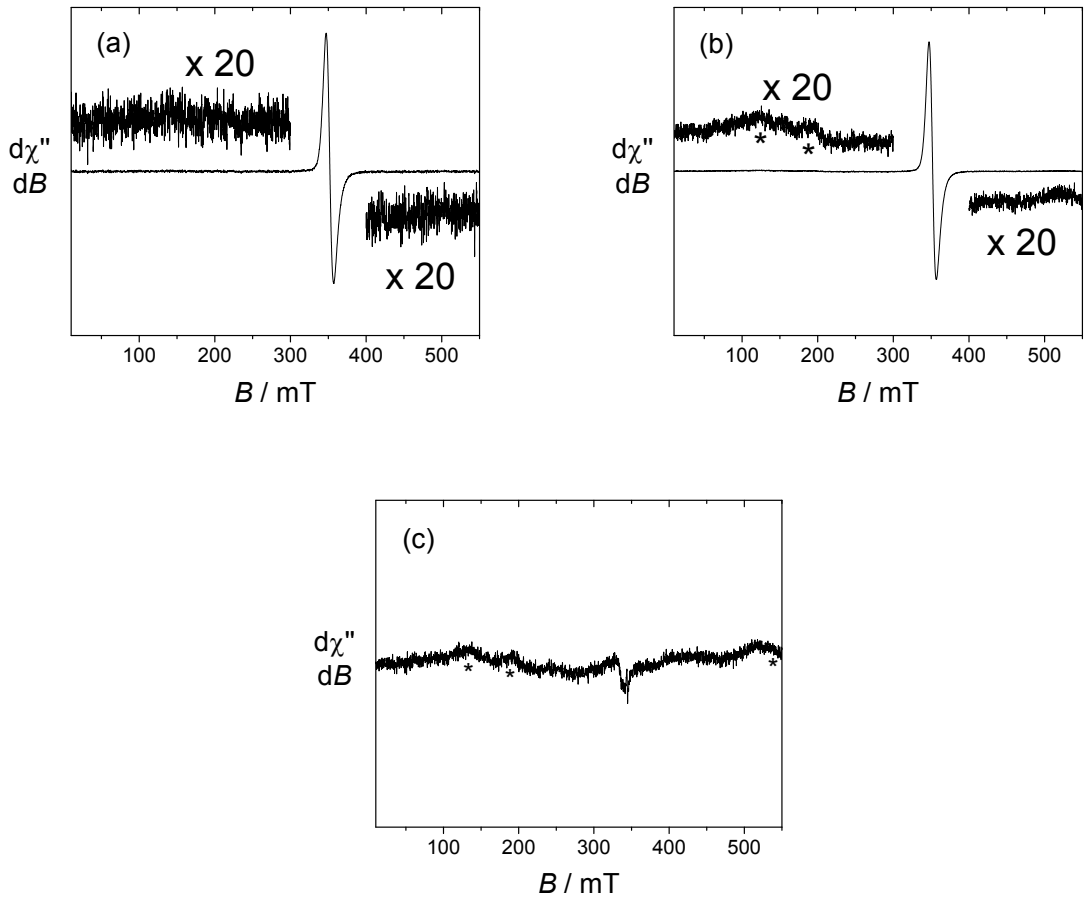

Fig. S21 X-Band EPR spectra of 0.5 mM CH_2Cl_2 solutions (containing 0.1 M TBAP as supporting electrolyte) of the cations (a) $\mathbf{GdL_3^+}$; (b) $\mathbf{EuL_3^+}$; (c) $\mathbf{YbL_3^+}$. The stars denote the triplet dioxygen resonances. Microwave Freq. 9.6362 GHz, power: (a and c) 0.4 (b) 2 mW. Mod. Freq. 100 KHz; Amp. 0.4 mT. *T* = 7 K.

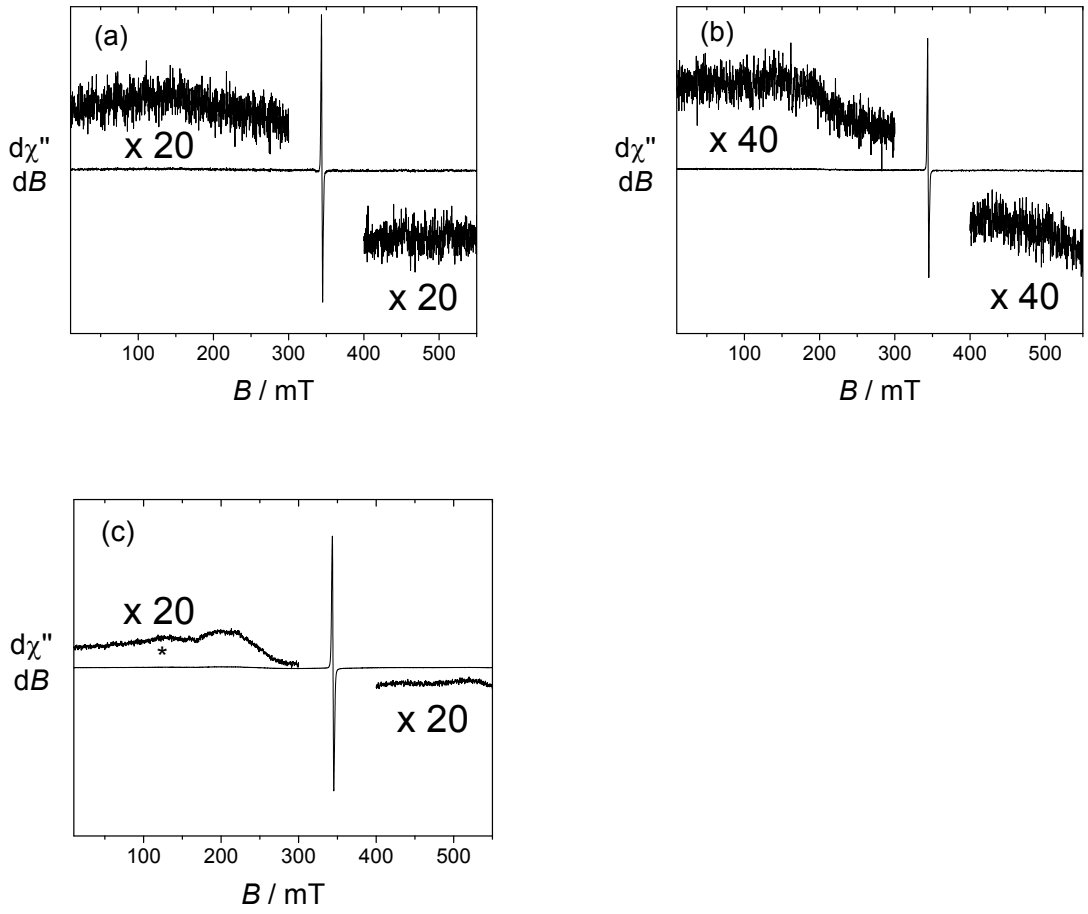

Fig. S22 X-Band EPR spectra of 0.5 mM CH_2Cl_2 solutions (containing 0.1 M TBAP as supporting electrolyte) of the anions: (a) $\mathbf{GdL_3^-}$; (b) $\mathbf{EuL_3^-}$; (c) $\mathbf{YbL_3^-}$. The stars denote the triplet dioxygen resonances. Microwave Freq. 9.64 GHz, power: 2 mW;. Mod. Freq. 100 KHz; Amp. 0.4 mT. T = 7 K.

2. Tables

Table S1. Calculated values for nine-coordinated geometries from SHAPE software. [2]

			Gd	**Lu**
EP	D9h	Enneagon	32.611	34.126
OPY	C8V	Octagonal pyramid	23.844	23.771
HBPY	D7h	Heptagonal bipyramid	17.936	21.065
JTC	C3v	Johnson triangular cupola J3	13.189	14.844
JCCU	C4v	Capped cube J8	9.580	10.872
CCU	C4v	Spherical-relaxed capped cube	8.794	10.183
JCSAPR	C4v	Capped square antiprism J10	2.173	1.817
CSAPR	C4v	Spherical capped square antiprism	1.560	1.231
JTCTPR	D3h	Tricapped trigonal prism J51	1.424	0.839
TCTPR	**D3h**	**Spherical tricapped trigonal prism**	**1.341**	**0.769**
JTDIC	C3v	Tridiminished icosahedron J6	11.173	14.131
HH	C2v	Hula-hoop	12.154	14.131
MFF	Cs	Muffin	2.240	1.965

Table S2. Crystal field parameters for **YbL_3** after fitting of magnetic data with PHI software.[1]

	YbL_3
B_2^0	318(7)
B_4^0	-280(2)
B_6^0	-97(1)
g_x	0.7(1)
g_y	1.537(3)
g_z	1.564(3)
Residual	0.003

3. References

[1] N. F. Chilton, R. P. Anderson, L. D. Turner, A. Soncini and K. S. Murray Phi: A powerful new program for the analysis of anisotropic monomeric and exchange-coupled polynuclear d- and f-block complexes. *J. Comput. Chem.* 2013, **34**, 1164-1175.

[2] M. Llunell, D. Casanova, J. Cirera, P. Alemany and S. Alvarez, *Shape, v2.1* University of Barcelona and The Hebrew University of Jerusalem, Barcelona and Jerusalem, 2013.