Electronic Supplementary Material (ESI) for Dalton Transactions.

ESI for

Divalent ytterbium complexes of crown and heterocrown ethers

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Experimental methods

All reactions were carried out using standard Schlenk and vacuum line techniques. Samples were handled and stored in a glove-box and under a dry dinitrogen atmosphere. Acetonitrile were distilled over CaH_2 and toluene and n-hexane from sodium benzophenone ketyl. Anhydrous YbI_2, $[18]aneO_4N_2$ and 18-crown-6 were obtained from Aldrich. 18-Crown-6 was dried by dissolution in anhydrous CH_2Cl_2 followed by addition of thionyl chloride and then stirred for 1 h. when the solvent and excess thionyl chloride were removed under vacuum. $[18]aneO_4S_2$ and $[18]aneO_4Se_2$ were prepared according to literature procedures.[S1,S2,S3]

IR spectra were obtained as Nujol mulls on a Perkin Elmer Spectrum 100 spectrometer. ^1H NMR spectra were recorded on a Bruker DPX400 spectrometer and referenced to residual solvent (^1H). $^{77}Se\{^1H\}$ NMR spectra were obtained on a Bruker AVII-400 spectrometer and referenced to neat external Me_2Se. Microanalyses were conducted by London Metropolitan University. Conductivity measurements were carried out in ~ 10^{-3} mol dm^{-3} solutions in MeCN under an inert atmosphere, using a platinum electrode conductivity cell on a PYE & Co conductance bridge.

Electrochemistry

Electrochemical experiments were performed using a three-electrode electrochemical system. A platinum mesh was used as the counter electrode, and a 0.5 mm diameter platinum disk was used as a pseudo-reference electrode. Platinum disks of 0.5 mm diameter or 25 μm diameter, polished to a mirror finish with alumina paste (1.0 and 0.3 μm) on microfiber cloth (Buehler), were used as the working electrodes. Electrolyte solutions were prepared in anhydrous MeCN with 0.5 to 1.0 x 10^{-3} mol dm^{-3} of the Yb complexes as the redox species, and 0.1 mol dm^{-3} of $[N^nBu_4][BF_4]$ as the supporting electrolyte. All solution preparation and electrochemical experiments were carried out inside in a glove-box and under a dry dinitrogen atmosphere. Cyclic voltammetry measurements were recorded at a potential sweep rate of 200 mV s^{-1}, using a Metrohm µ-Autolab Type III potentiostat with the GPES electrochemical software package.

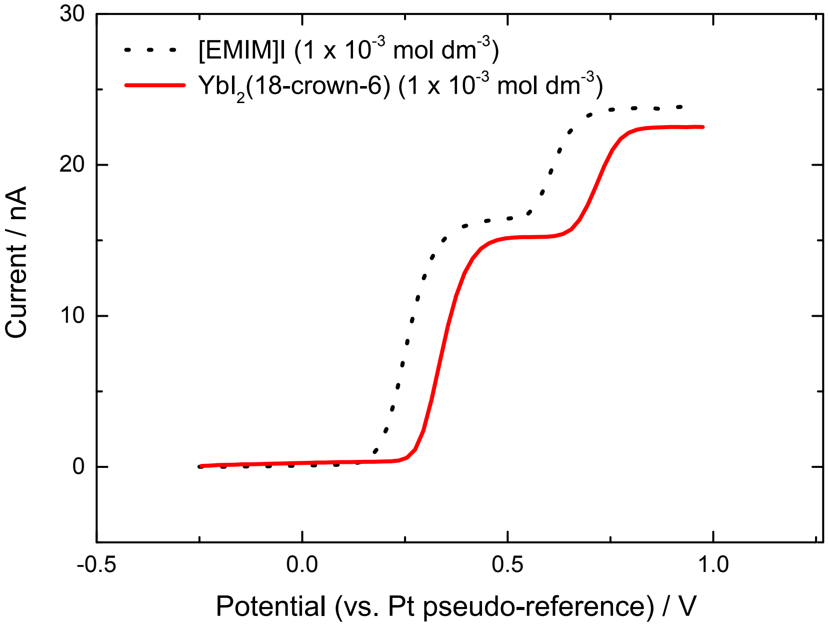

Figure S1 Cyclic voltammetry of 1 x 10^{-3} mol dm^{-3} of $[YbI_2(18\text{-crown-}6)]$ and [EMIM]I in anhydrous MeCN at a 25 µm platinum micro-disk electrode, with 0.1 mol dm^{-3} $[N^nBu_4][BF_4]$ as the supporting electrolyte. The scan rate was 200 mV s^{-1}.

Figure S1 shows cyclic voltammetry of 1 x 10^{-3} mol dm^{-3} of $[YbI_2(18\text{-crown-}6)]$ and [EMIM]I at a 25 µm diameter platinum micro-disk, in anhydrous MeCN. The voltammetry of the [EMIM]I gives rise to two well-defined oxidative waves with half-wave potentials at 0.25 V and 0.61 V *vs.* the Pt pseudo-reference. Very similar voltammetry has previously been observed for the electrochemical oxidation of iodide at platinum electrodes in MeCN.[S4,S5,S6] It is therefore likely that the first wave relates to the oxidation of iodide ion to the triiodide ion and the second wave to the oxidation of triiodide ion to iodine. The magnitude of the wave heights relative to each other (i.e. 2:1) is proportional to the number of electrons transferred in each process.

Wave 1 ($E_{1/2}$ = 0.25 V) $6I^- - 4e^- \rightarrow 2I_3^-$

Wave 2 ($E_{1/2}$ = 0.61 V) $2I_3^- - 2e^- \rightarrow 3I_2$

The **Error!**voltammetry of the $[YbI_2(18\text{-crown-6})]$ complex is very similar to that of the [EMIM]I, with two oxidative waves observed at 0.34 V and 0.72 V, suggesting the electro-oxidation of free iodide (the ~100 mV shift in the half-wave potentials relative to the [EMIM]I is due to shifts in the platinum pseudo-reference potential). The similar magnitude in the wave heights between the $[YbI_2(18\text{-crown-6})]$ complex and the [EMIM]I indicates that only one of the iodide ions is liberated per mole of Yb(II) complex. No other peaks attributed to electrochemical process were observed in the voltammetry of all four of the Yb(II) complexes.

X-Ray crystallography: Details of the crystallographic data collection and refinement parameters are given in Table S1. Data collections used a Rigaku AFC12 goniometer equipped with an enhanced sensitivity (HG) Saturn724+ detector mounted at the window of an FR-E+ SuperBright molybdenum (λ = 0.71073 Å) rotating anode generator with VHF Varimax optics (70 μm focus) with the crystal held at 100 K (N_2 cryostream). Structure solution and refinements were performed with either SHELX(S/L)97 or SHELX(S/L)2013.[S7]

Table S1 X-Ray Crystallographic Data [a]

Compound	$[YbI_2([18]aneSe_2O_4)]$
Formula	$C_{12}H_{24}I_2O_4Se_2Yb$
M	817.07
Crystal system	Monoclinic
Space group (no.)	C2/c (no. 5)
a /Å	10.835(2)
b /Å	11.819(2)
c /Å	15.214(3)

α /°	90
β /°	92.989(2)
γ /°	90
U /Å^3	1945.7(6)
Z	4
μ(Mo-K$_\alpha$) /mm^{-1}	11.731
F(000)	1488
Total number reflns	6782
R_{int}	0.044
Unique reflns	2736
No. of params, restraints	96, 0
R_1, wR_2 [$I > 2\sigma(I)$] [b]	0.034, 0.091
R_1, wR_2 (all data)	0.0341, 0.0914

[a] T = 100 K; wavelength (Mo-K$_\alpha$) = 0.71073 Å; θ(max) = 27.5°;

[b] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{1/2}$

References

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