

Electronic Supplementary information for:

**Electrochemical ion transfer mediated by a lipophilic  
Os(II)/Os(III) dinonyl bipyridyl probe incorporated in thin film  
membranes**

Sutida Jansod, Lu Wang, Maria Cuartero and Eric Bakker\*

*Department of Inorganic and Analytical Chemistry, University of Geneva, 1211 Geneva, Switzerland.*

*\*corresponding Author: [eric.bakker@unige.ch](mailto:eric.bakker@unige.ch)*

## Table of Content

	<b>Page</b>
<b>1. Experimental Details</b>	
Materials, reagents and instruments	SI-3
Electrode preparation	SI-3
Synthesis of $(\text{Os}(\text{II})(\text{dnbpy})_3)(\text{PF}_6)_2$	SI-3
a) NMR of $(\text{Os}(\text{II})(\text{dnbpy})_3)(\text{PF}_6)_2$	SI-4
b) Mass Spectrum of $(\text{Os}(\text{II})(\text{dnbpy})_3)(\text{PF}_6)_2$	SI-4
<b>2. Tables</b>	<b>SI-5</b>
<b>3. Supporting Figures</b>	<b>SI-6</b>
Fig. S1-CVs of $(\text{Os}(\text{II})(\text{dnbpy})_3)(\text{PF}_6)_2$ in acetonitrile	SI-6
Fig. S2-Impedance plots	SI-6
Fig. S3-CVs for increasing concentrations of NaCl using membrane M1	SI-7
Fig. S4-CVs for increasing concentrations of NaCl using membrane M1	SI-7
Fig. S5-Reproducibility of membrane M2 in $\text{NaNO}_3$ and NaCl	SI-8
Fig. S6-Thin layer behaviour for cation transfer using membrane M3	SI-9
Fig. S7-CVs for decreasing amount of NaTFPB using membrane M3, M8 and M9	SI-10
Fig. S8-Calibration graph for $\text{PF}_6^-$ using membrane M2 and M14	SI-11
Fig. S9-CVs of different amounts of $(\text{Os}(\text{II})(\text{dnbpy})_3)(\text{PF}_6)_2$ in $\text{NaPF}_6$ and NaCl	SI-12
Fig. S10-Impedance plots	SI-13
Fig. S11-Reproducibility of membrane M14 in $\text{NaPF}_6$ and NaCl	SI-13
Fig. S12-Thin layer behaviour for anion transfer using membrane M14	SI-14

## 1. Experimental Details

### Material, reagents and instruments

Sodium chloride (NaCl), sodium hexafluorophosphate (NaPF<sub>6</sub>), sodium perchlorate (NaClO<sub>4</sub>), sodium nitrate (NaNO<sub>3</sub>), potassium chloride (KCl), lithium chloride (LiCl), magnesium chloride (MgCl<sub>2</sub>), calcium chloride (CaCl<sub>2</sub>), tridodecylmethylammonium nitrate (TDMANO<sub>3</sub>), tetrabutylammonium chloride (TBACl, >97.0%), tetrahydrofuran (THF), sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (NaTFPB), high molecular weight poly(vinyl chloride) (PVC) and bis(2-ethylhexyl)sebacate (DOS) were purchased from Sigma-Aldrich.

Glassy carbon (GC) electrode tip (6.1204.300) with an electrode diameter of 3.00 ± 0.05 mm were sourced from Metrohm (Switzerland). Cyclic voltammograms were recorded with a PGSTAT 101 (Metrohm Autolab B.V.) controlled by NOVA 1.8 software. A double-junction Ag/AgCl/3 M KCl/1 M LiOAc reference electrode (6.0726.100 model, Metrohm, Switzerland) and a platinum electrode (6.0331.010 model, Metrohm, Switzerland) were used in a three-electrode cell. A rotating disk electrode (Autolab, RDE, Metrohm Autolab B.V., Utrecht, The Netherlands) was used to spin coat the membranes on the electrode at 1500 rpm.

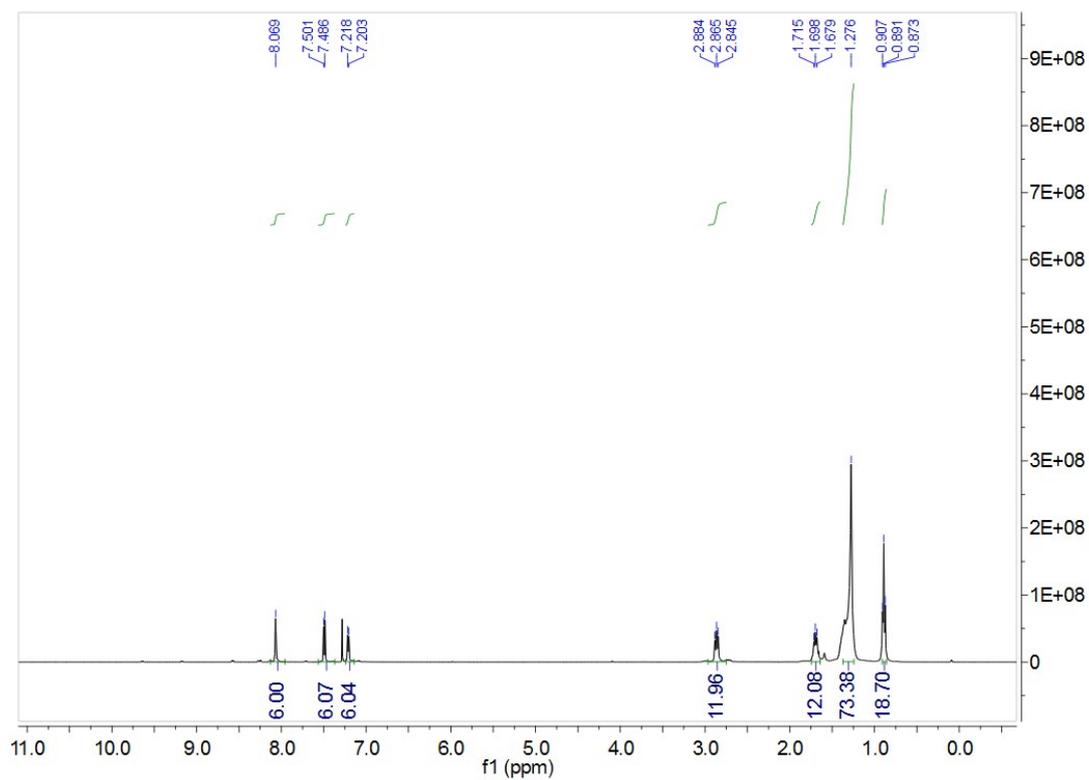
### Electrode preparation

Different membrane cocktails were prepared by dissolving appropriate amounts of the components in 1 mL of THF (see **Table S1** for the membrane compositions). A dilution of each cocktail (50 µL + 250 µL of THF) was prepared to be deposited on the electrode surface. Thin layer membrane was spin coated at 1500 rpm onto the GC electrode by dropping a volume of 25 µL of the diluted cocktail for 1 min.

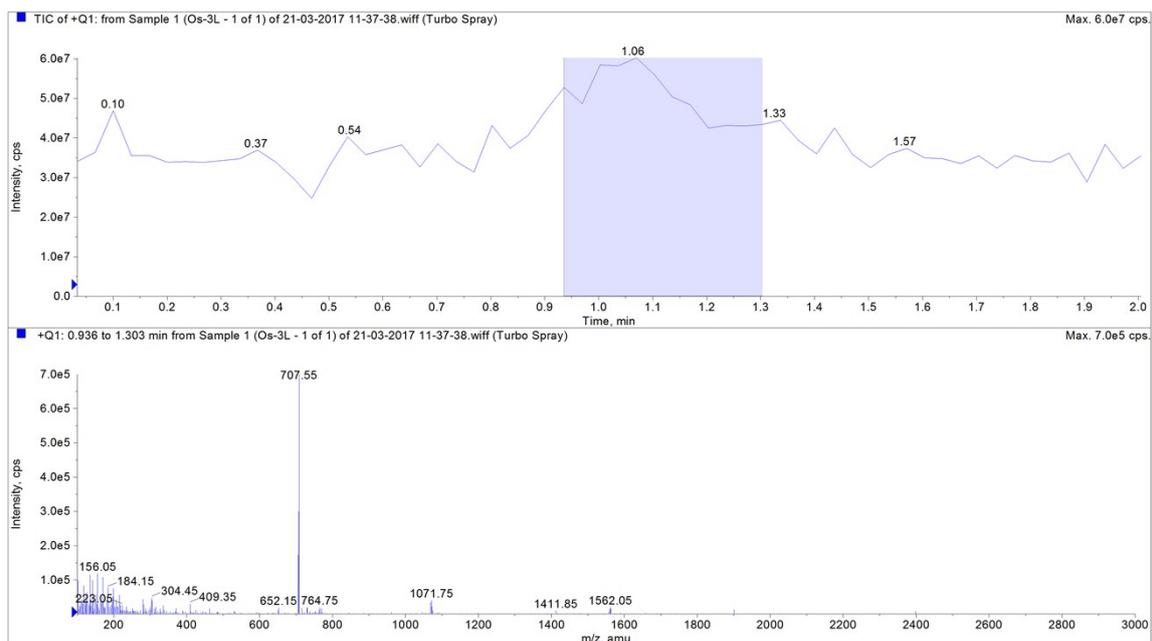
### Synthesis of (Os(II)(dnbpy)<sub>3</sub>)(PF<sub>6</sub>)<sub>2</sub>

Potassium hexachloroosmate (K<sub>2</sub>OsCl<sub>6</sub>, 120 mg, 0.25 mmol), and 4,4'-dinonyl-2,2'-Bipyridine (dnbpy, 318 mg, 0.78 mmol) were dissolved in DMF (10 mL), purged with nitrogen for 10 min, and refluxed under nitrogen atmosphere overnight. Then the solution was cooled to room temperature, and was added drop-wise to a sodium dithionite solution (185 mg of sodium dithionite in 20 mL of cooled deionized ice water). The resulting dark green solution was concentrated by vacuum distillation. Thereafter, an aqueous solution of NH<sub>4</sub>PF<sub>6</sub> (20 mL, 200 mg) was added. The mixture was extracted with chloroform (200 mL). The crude product was eluted by silica gel column chromatography (1/25 (v/v) methanol/chloroform as eluent). After removal of solvent, dark green solid of (Os(II)(dnbpy)<sub>3</sub>)(PF<sub>6</sub>)<sub>2</sub> was obtained. Yield: 67%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ= 8.06 (s, 6H), 7.50 (d, 6H), 7.21 (d, 6H), 2.87 (t, 12H), 1.69 (t, 12H), 1.28 (m, 72H), 0.89 (t, 18H). m/z [M]<sup>2+</sup>/2=707.55. Following NMR and MASS of the obtained product are shown:

a)  $^1\text{H-NMR}$  of  $(\text{Os(II)}(\text{dnpby})_3)(\text{PF}_6)_2$ :



b) Electro spray–Mass Spectrum of  $(\text{Os(II)}(\text{dnpby})_3)(\text{PF}_6)_2$ :



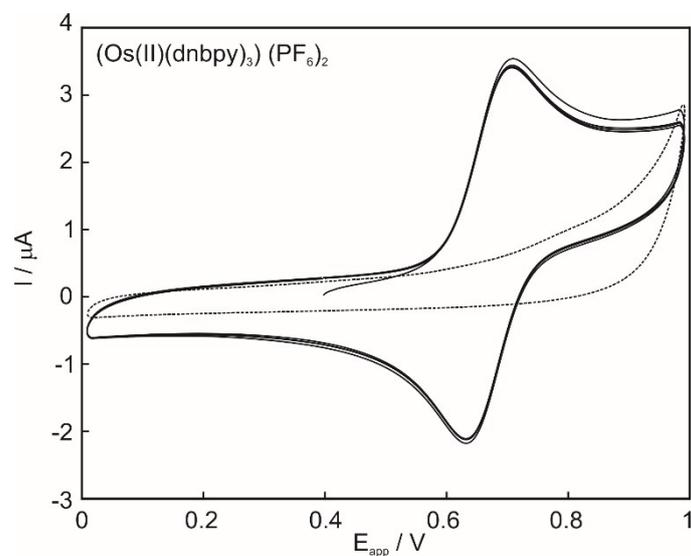
## 2. Tables

**Table S1.** Compositions of the membranes used in the present work. The amounts are relative to a total mass of 100 mg dissolved in 1 mL of THF.

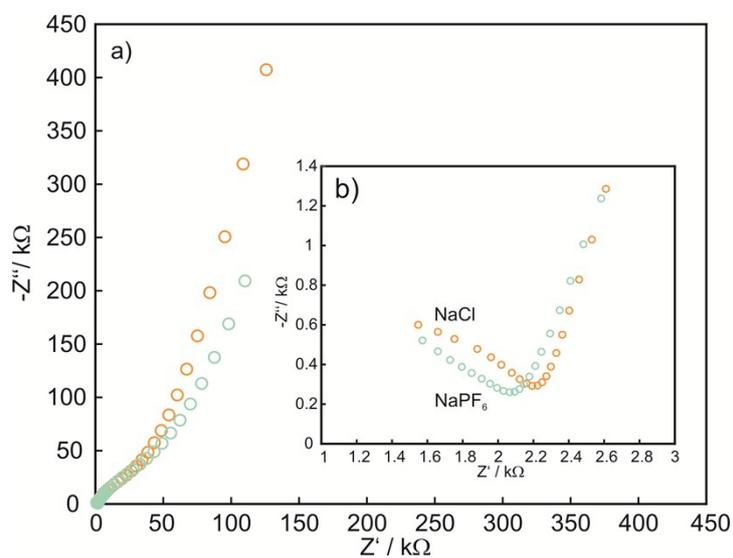
Membrane	component				
	NaTFPB <sup>a</sup>	TDMANO <sub>3</sub>	Os(II)(dnbpy) <sub>3</sub> :(PF <sub>6</sub> ) <sub>2</sub> <sup>a</sup>	PVC <sup>b</sup>	DOS <sup>b</sup>
M1	10	-	100	27	55
M2	-	-	100	28	55
M3	200	-	75	23	46
M4	150	-	75	25	49
M5	50	-	75	28	55
M6	-	-	75	29	58
M7	40	-	-	33	63
M8	100	-	37.5	28	57
M9	150	-	56.2	26	51
M10	-	-	75	29	58
M11	-	-	50	30	61
M12	-	-	25	32	64
M13	-	-	10	33	66
M14	-	25	50	30	60

<sup>a</sup>mmol kg<sup>-1</sup>, <sup>b</sup>mass percentage

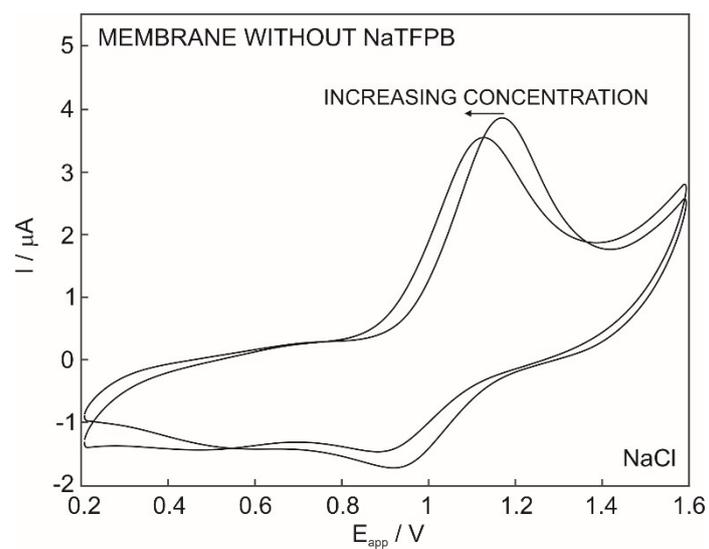
### 3. Figures



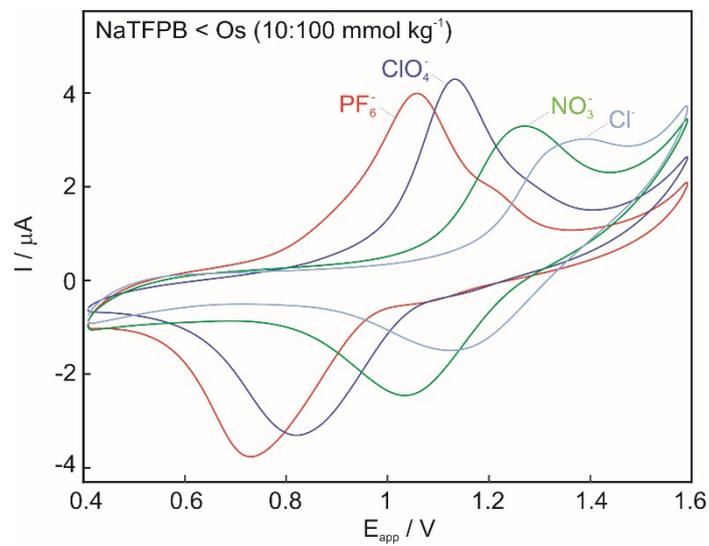
**Figure S1.** Consecutive cyclic voltammograms in 0.2 mM  $\text{Os(II)(dnbpy)}_3\text{.(PF}_6)_2$  and 0.1 M tetrabutylammonium perchlorate ( $\text{TBAClO}_4$ ) in acetonitrile. WE: Glassy carbon electrode, RE: Ag wire and CE: Pt electrode. Scan rate:  $100 \text{ mV s}^{-1}$ .



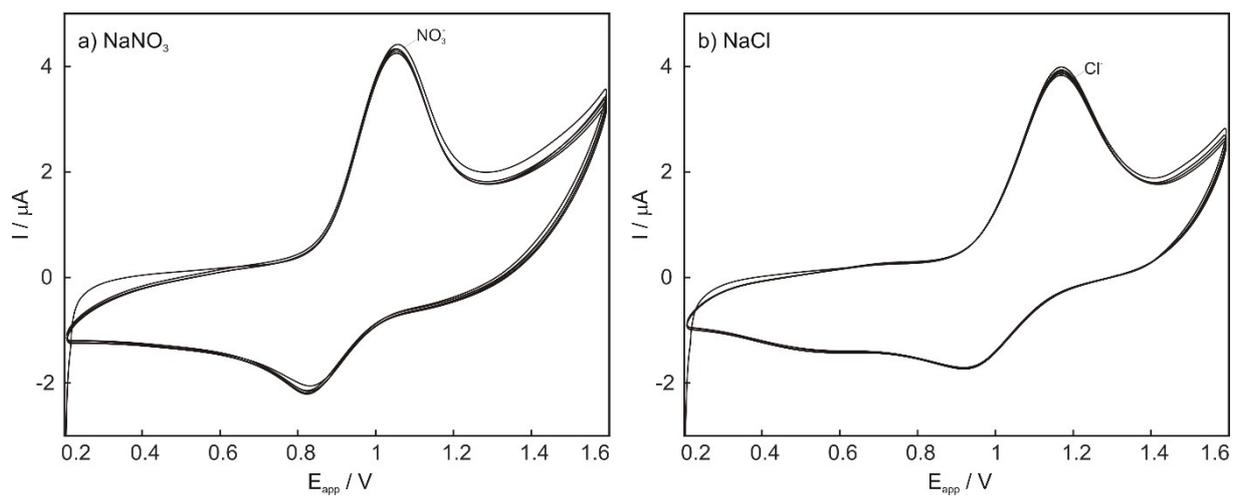
**Figure S2.** (a) Complex impedance plots observed for membrane M1 in 10 mM  $\text{NaCl}$  and  $\text{NaPF}_6$  solutions. (b) Zoom of the semicircles. Parameters: first frequency= $100000 \text{ Hz}$ , last frequency= $0.1 \text{ Hz}$ , number of frequencies= $50$ , amplitude= $0.01 \text{ V}$ , integration time= $0.125 \text{ s}$ ,  $E_{dc}=100 \text{ mV} + \text{OCP}$  ( $0.4$  and  $0.2 \text{ V}$  respectively).



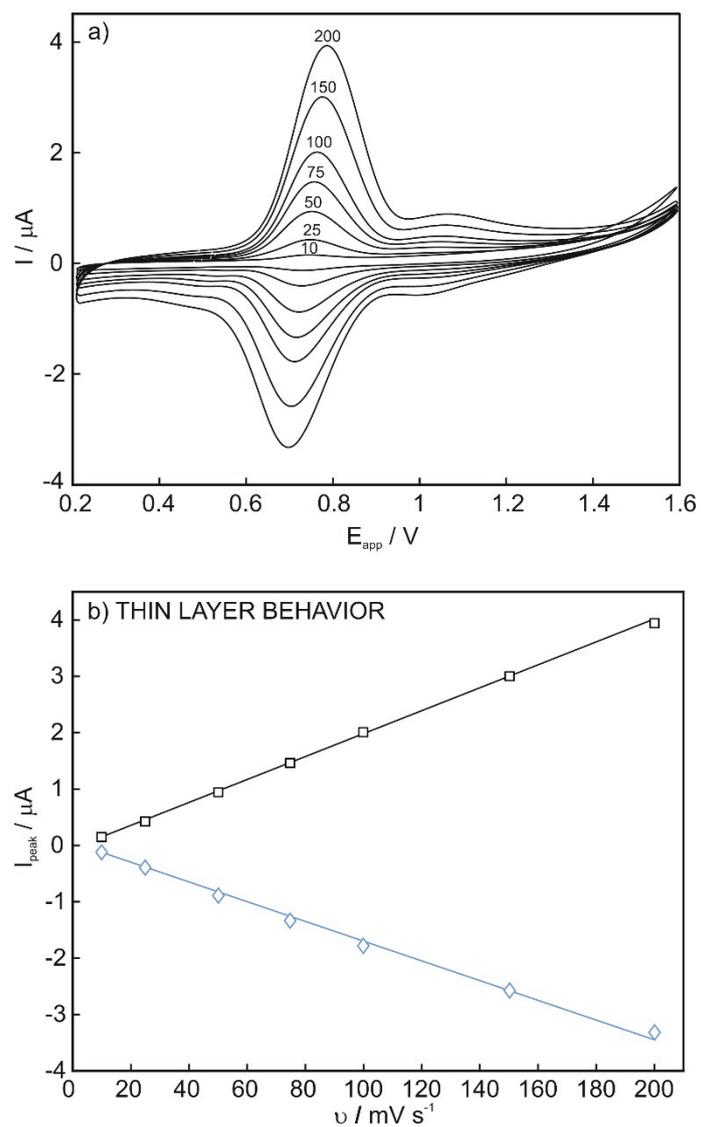
**Figure S3.** Cyclic voltammograms obtained for 10 and 100 mM NaCl using membrane M1 (10 mmol  $\text{kg}^{-1}$  of NaTFPB and 100 mmol  $\text{kg}^{-1}$  of  $(\text{Os}(\text{II})(\text{dnbpy})_3) \cdot (\text{PF}_6)_2$ ). Scan rate: 100  $\text{mV s}^{-1}$ .



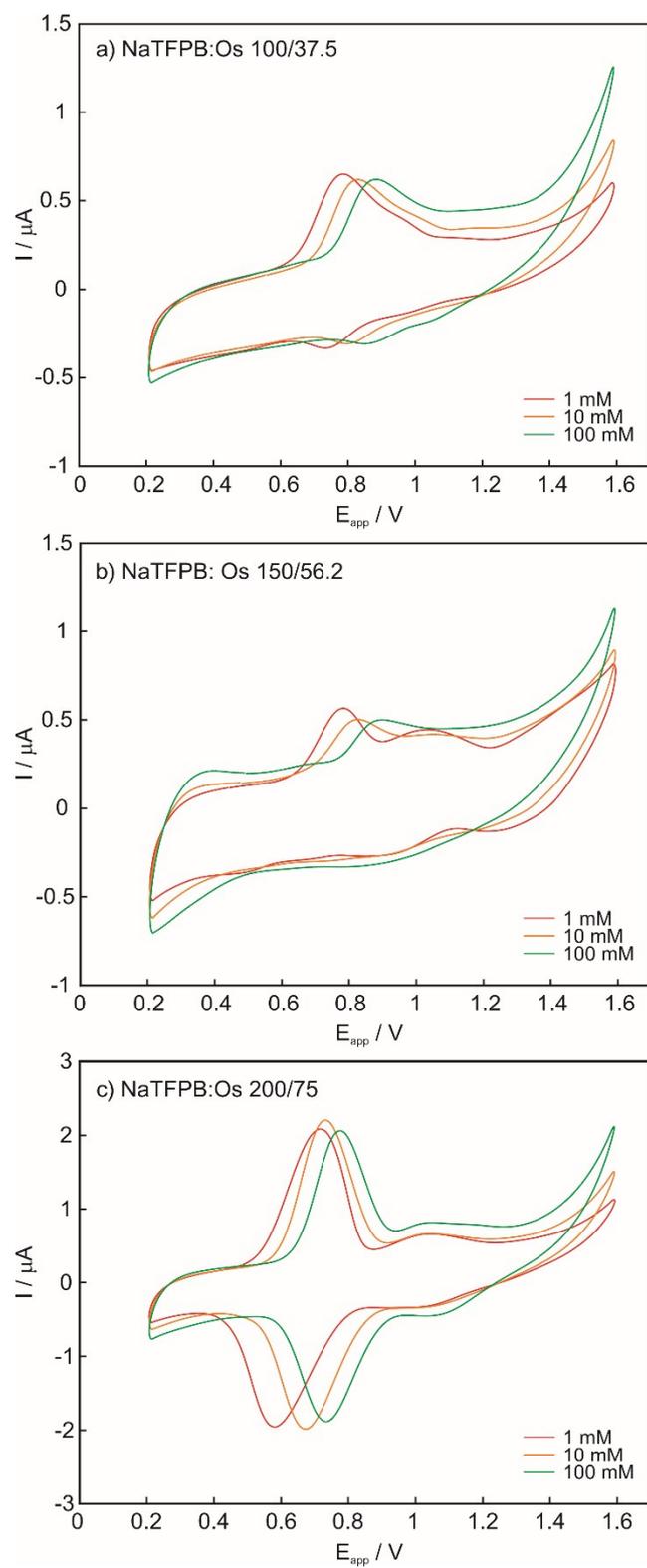
**Figure S4.** Cyclic voltammograms in 10 mM of sodium salts of different anions using membrane M1. Scan rate: 100  $\text{mV s}^{-1}$ .



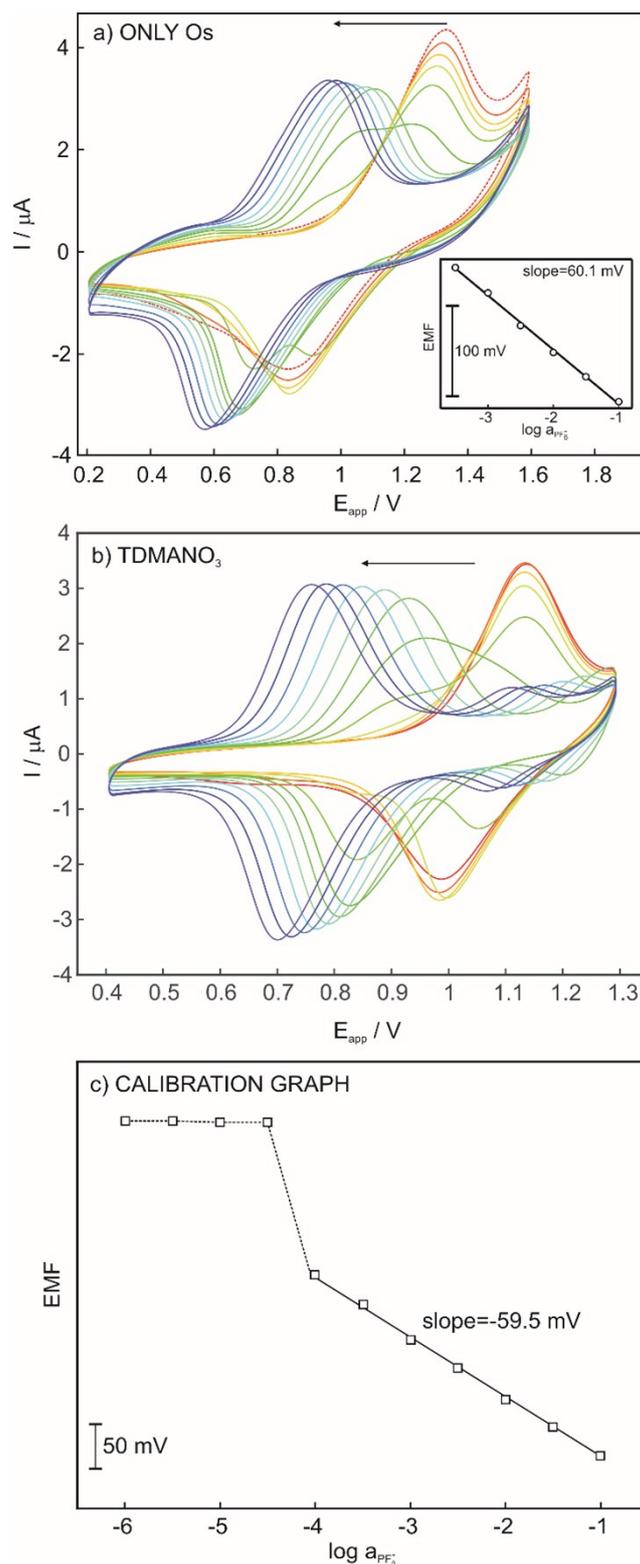
**Figure S5.** 10 consecutive voltammograms using membrane M2 containing 100 mmol kg<sup>-1</sup> of (Os(II)(dnpbpy)<sub>3</sub>)·(PF<sub>6</sub>) observed for (a) 10 mM NaNO<sub>3</sub> and (b) 10 mM NaCl. Scan rate: 100 mV s<sup>-1</sup>.



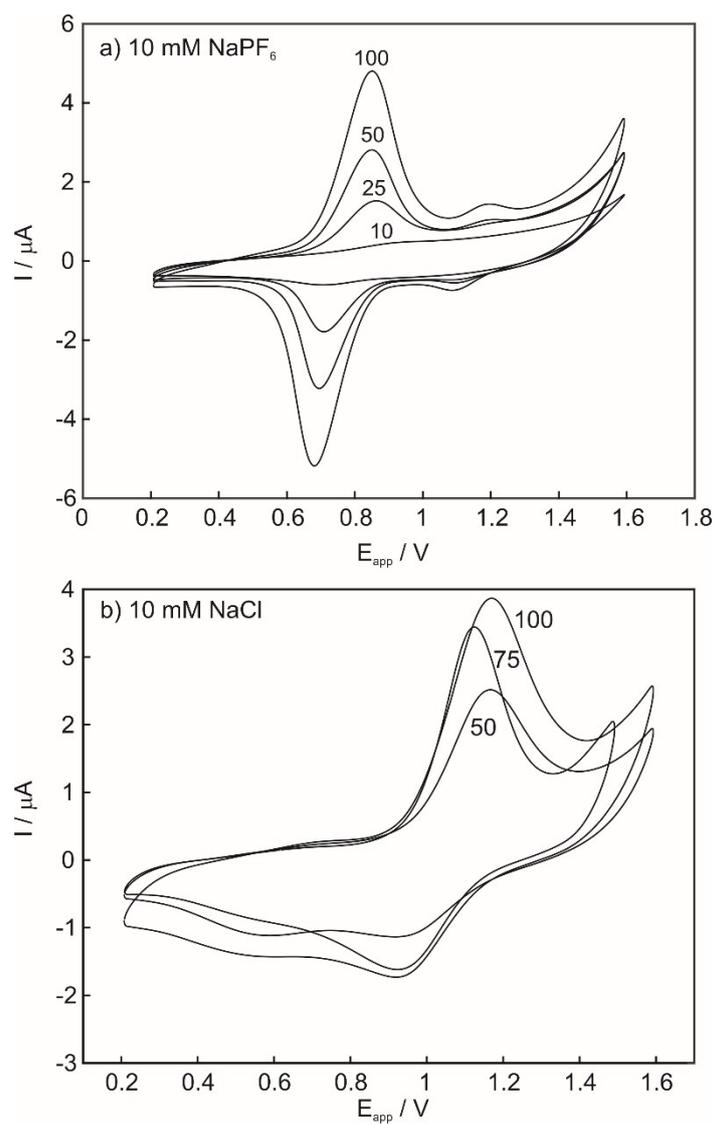
**Figure S6.** (a) Cyclic voltammograms in 10 mM NaCl using membrane M3 (200 mmol kg<sup>-1</sup> of NaTFPB and 75 mmol kg<sup>-1</sup> of (Os(II)(dnbpy)<sub>3</sub>)-(PF<sub>6</sub>)<sub>2</sub>) at different scan rates. b) Thin layer behavior for cathodic and anodic waves as confirmed by linear dependence of peak current on scan rate.



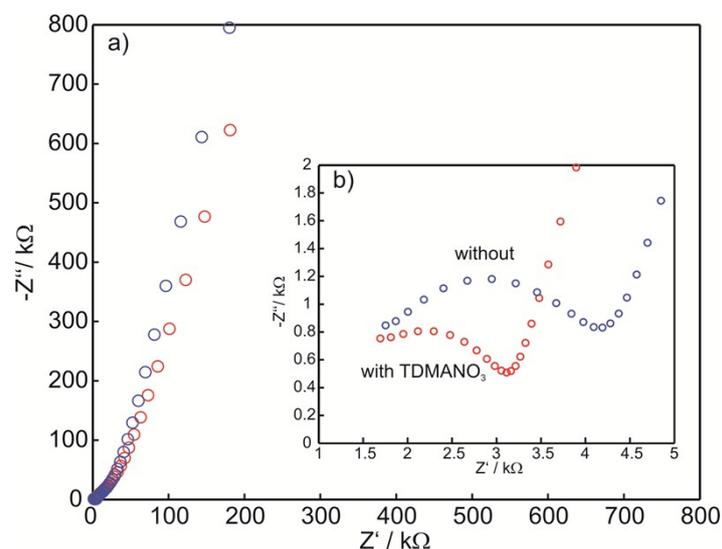
**Figure S7.** Cyclic voltammograms obtained using membranes containing a fixed NaTFPB:Os ratio of 2.7 and reducing their loading in the membrane: a) 100/37.5 (M8), b) 150/56.2 (M9) and c) 200/75 (M3). Scan rate:  $100 \text{ mV s}^{-1}$ .



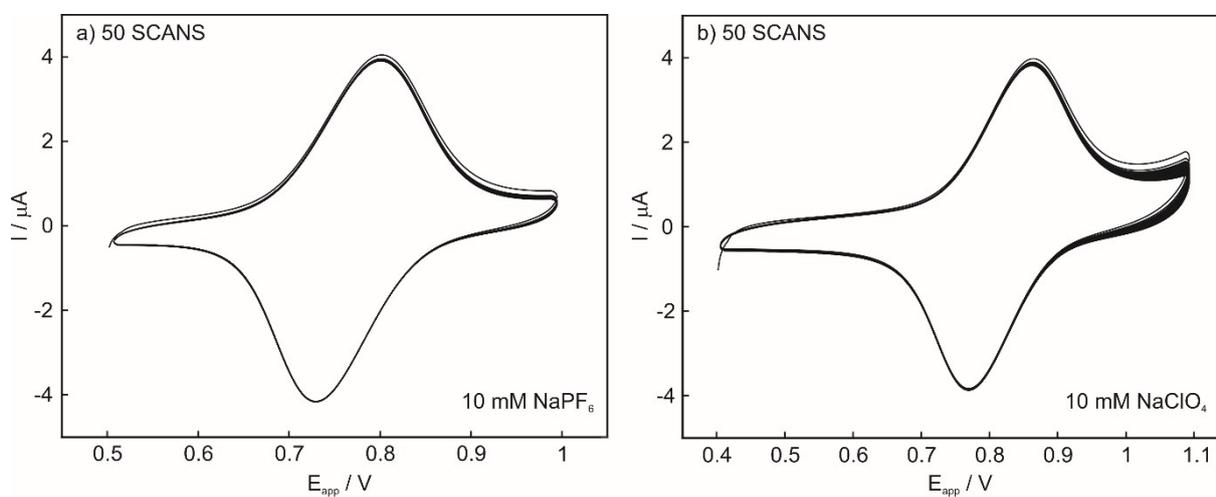
**Figure S8.** Cyclic voltammograms for increasing concentrations of  $\text{NaPF}_6$  (from  $10^{-6}$  to  $10^{-1}$  M in 1 mM  $\text{MgCl}_2$  background electrolyte): a) with membrane M2 containing 100 mmol  $\text{kg}^{-1}$  of  $(\text{Os}(\text{II})(\text{dnbpy})_3) \cdot (\text{PF}_6)_2$ . Inset: peak current vs. potential; b) with membrane M14 containing 25 mmol  $\text{kg}^{-1}$  of TDMANO<sub>3</sub> and 50 mmol  $\text{kg}^{-1}$  of  $(\text{Os}(\text{II})(\text{dnbpy})_3) \cdot (\text{PF}_6)$ . c) Observed calibration graph for  $\text{PF}_6^-$  using membrane M14. Scan rate: 100  $\text{mV s}^{-1}$ .



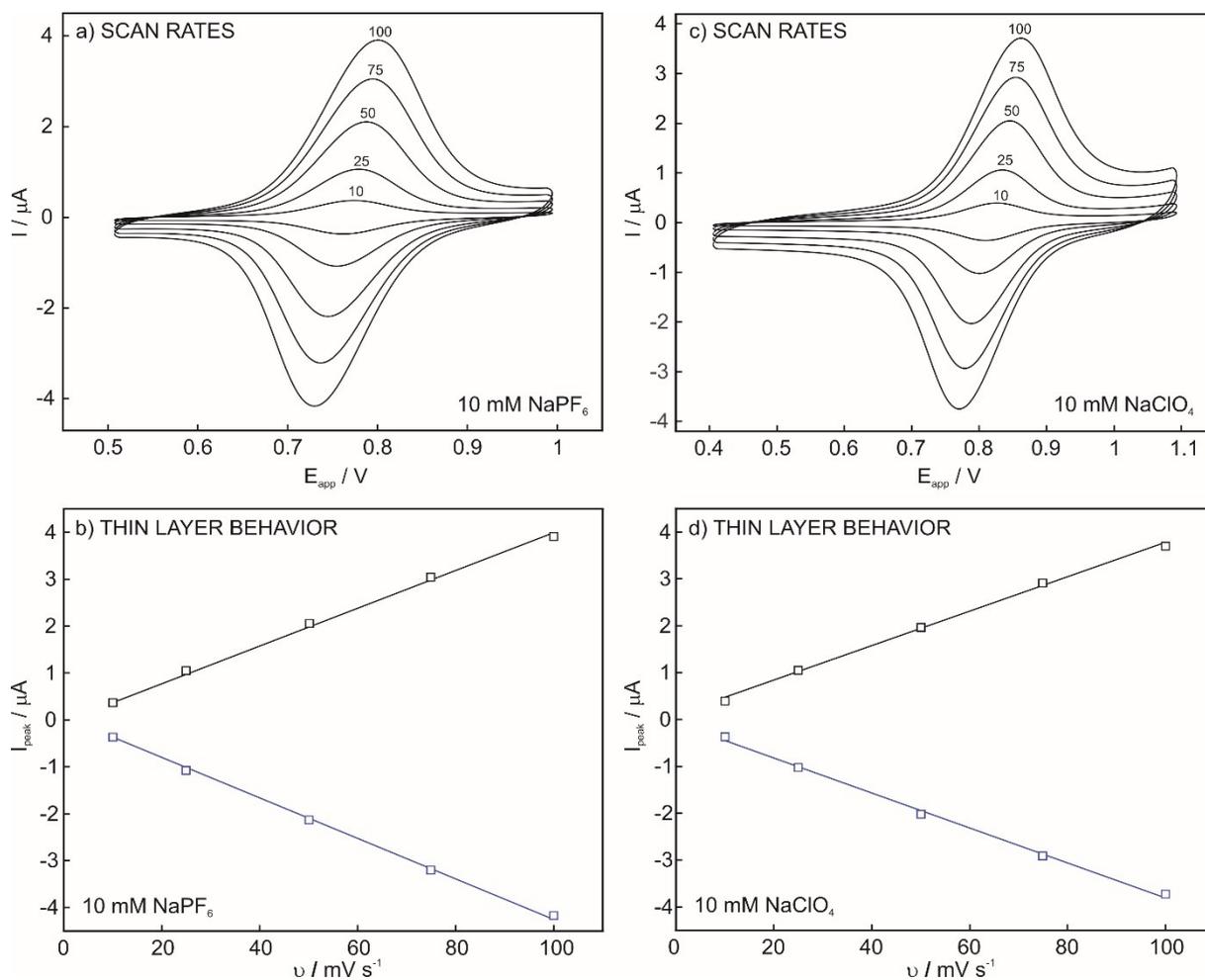
**Figure S9.** Cyclic voltammograms observed using membranes with increasing amount of  $(\text{Os}(\text{II})(\text{dnbpy})_3) \cdot (\text{PF}_6)_2$  and without any ion exchanger. a) Membranes M2, M11-13 containing 100, 50, 25 or 10 mmol kg<sup>-1</sup> of  $(\text{Os}(\text{II})(\text{dnbpy})_3) \cdot (\text{PF}_6)_2$  in 10 mM NaPF<sub>6</sub>. b) Membranes M2, M10-11 containing 100, 75 or 50 mmol kg<sup>-1</sup> of  $(\text{Os}(\text{II})(\text{dnbpy})_3) \cdot (\text{PF}_6)_2$  in 10 mM NaCl. Scan rate: 100 mV s<sup>-1</sup>.



**Figure S10.** (a) Complex impedance plots observed for membranes M14 and M11 with and without TDMANO<sub>3</sub> in 10 mM NaCl solution. (b) Zoom of the semicircles. Parameters: first frequency=100000 Hz, last frequency=0.1 Hz, number of frequencies=50, amplitude=0.01 V, integration time=0.125s, E<sub>dc</sub>=100 mV+OCP (0.4 and 0.3 V respectively).



**Figure S11.** Consecutive voltammograms using membrane M14 containing 25 mmol kg<sup>-1</sup> of TDMANO<sub>3</sub> and 50 mmol kg<sup>-1</sup> of (Os(II)(dnbpy)<sub>3</sub>):(PF<sub>6</sub>)<sub>2</sub>, demonstrating electrochemical stability. a) 10 mM NaPF<sub>6</sub>. b) 10 mM NaClO<sub>4</sub>. Scan rate: 100 mV s<sup>-1</sup>.



**Figure S12.** Cyclic voltammograms observed using membrane M14 (25 mmol kg<sup>-1</sup> of TDMANO<sub>3</sub> and 50 mmol kg<sup>-1</sup> of (Os(II)(dnpbpy)<sub>3</sub>)·(PF<sub>6</sub>)<sub>2</sub>) at different scan rates in: a) 10 mM NaPF<sub>6</sub> and b) 10 mM NaClO<sub>4</sub>. Graphs c) and d) confirm the corresponding thin layer behaviour, as evidenced by the linear dependence of peak current on scan rate.