Supplementary Material (ESI) For Chemical Communications

An effective nanostructured assembly for ion-selective electrodes. Ionophore covalently linked to carbon nanotubes for Pb^{2+} determination†

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Chemical and reagents

The multi-walled carbon nanotubes (MWCNT) were purchased from HeJi in bulk form with >99% purity, 150 μm average length and 10-20 nm diameter. The reagents thionyl chloride (SOCl$_2$), 1,3-diaminopropane, N,N′-Dicyclohexylcarbodiimide (DCC), 1-Hydroxybenzotriazole (HOBt), 4′-Carboxybenzo-18-crown-6, benzo-18-crown-6 (B18C6), Poly(ethylene-co-acrylic acid) (PEAA) and analytical grade lead, zinc, calcium, copper, cadmium and magnesium nitrate salts were purchased from Sigma–Aldrich. Poly(vinyl chloride) high molecular weight (PVC), 2-Nitrophenyl octyl ether (NPOE), Tetrahydrofuran (THF) and Sodium tetrakis[3,5-bis(trifluoro-methyl)phenyl]borate (NaTFPB) were of selectophore® grade from Fluka. Deionized and charcoal-treated water (18.2 MΩ•cm specific resistance) were obtained with Milli-Q PLUS reagent-grade water system (Millipore). Sandpapers and alumina were obtained from Buehler. Sigradur G glassy carbon rods were obtained from HTW. Teflon blocks were obtained from RS Amidata. Environmental scanning electron microscope (ESEM) images were taken on a Quanta 600 (FEI Company, Inc.) in the Technical and Scientific Services of our university.

Synthesis of MWCNT-B18C6 hybrids

As-purchased MWCNTs (100 mg) were oxidized in a silica furnace chamber in order to selectively remove any amorphous carbon impurity (T = 365 ^{o}C, air flow-rate = 100 cm^3 min^{-1}, t = 90 min). Subsequently, the MWCNTs were refluxed in H$_2$SO$_4$/HNO$_3$ (3:1) for 30 min. The MWCNTs were then filtered on a Millipore membrane (Polycarbonate PC, 0.10 μm) and the solid on the filter was washed with Milli-Q water and dried to afford MWCNT-COOH as a black solid (60 mg).

To MWCNT-COOH (20 mg) in DMF (1 mL) was added SOCl$_2$ (20 mL) and the mixture was stirred with refluxing overnight. The resulting material was decanted and the supernatant was removed. Dry THF (5 mL) was then added, the mixture was centrifuged and the supernatant was removed. This operation was repeated 5 times. The solid was then filtered on a Millipore membrane (PTFE, 0.22 μm) and washed several times with CH$_2$Cl$_2$ and diethyl ether affording **1** as a black solid (20 mg).

Compound **1** (20 mg) was subsequently refluxed in 1,3-diaminopropane (1 mL) for 5 days. The reaction mixture was then filtered on a Millipore membrane (PTFE, 0.22 μm) and the solid on the filter was washed several times with CH$_2$Cl$_2$ and diethyl ether obtaining **2** as a black solid (22 mg).

To a mixture of 4′-Carboxybenzo-18-crown-6 (0.2 mmol, 71.2 mg), DCC (0.2 mmol, 40.6 mg), HOBt (0.2 mmol, 27 mg) in dry CH$_2$Cl$_2$ (2 mL) was added compound **2** (10 mg) in DMF/CH$_2$Cl$_2$ (1:1, 2 mL). The reaction mixture was stirred during 48 h at room temperature and then filtered on a Millipore membrane (PTFE, 0.22 μm) and the solid on the filter was washed several times with DMF, CH$_2$Cl$_2$ and diethyl ether affording **3** as a black solid (20 mg).
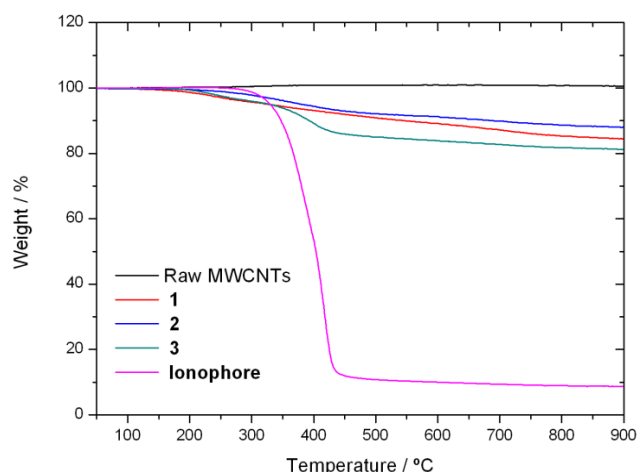
Fig. S1 TGA of raw MWCNTs, **1**, **2**, **3** and the ionophore 4′-Carboxybenzo-18-crown-6 (10 ºC min⁻¹ in N_2).

For a typical TGA experiment, 1-2 mg of MWCNTs were placed in the sample holder in the furnace of a Mettler Toledo TGA/SDTA851 instrument and the material was heated up at a rate of 10 ºC min⁻¹ in N_2, while the weight was recorded continuously. The degree of functionalization at 600ºC is 10%, 8% and 15% for **1**, **2** and **3** respectively.
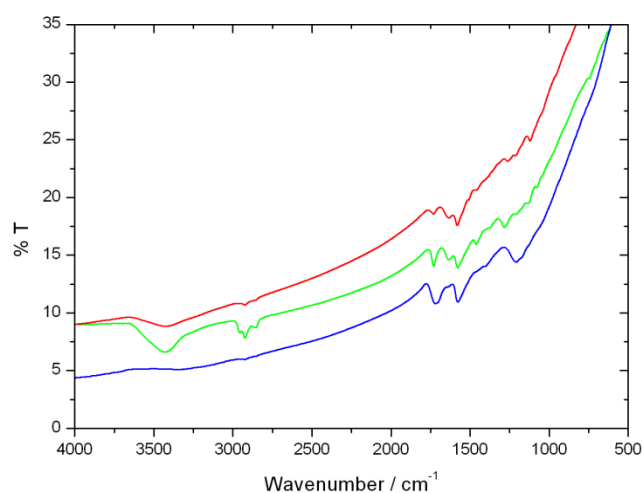

Fig. S2 FTIR spectra for **1** (blue), **2** (green) and **3** (red).

FTIR spectra were recorded with a Jasco FT/IR-600 PLUS spectrometer on KBr pellet. The FT-IR spectra of MWCNTs **1** display the characteristic bands at 1714 cm⁻¹ for the C=O stretching vibrations of acid groups as well as at 1576 cm⁻¹ for the C=C stretching of the carbon nanotube.[8] The FT-IR spectrum of **2** and **3** shows a similar trend with a new band at 1637 cm⁻¹ due to the C=O stretching of the CONH amide bond. It is worth noting that a new, sharp band is detected at 1120 cm⁻¹ due to the C-O stretching of the crown ether macrocycle in the spectrum of **3**. In addition to the characteristic bands, the C=O stretching vibrations of acid groups are shifted from 1714 cm⁻¹ for **1** up to 1727 and 1730 cm⁻¹ for **2** and **3** respectively. Noteworthy, the formation of a second amide in final compound **3** results as the loss of a peak at 1282 cm⁻¹ present in spectrum of **2**, which could be attributed to the C-N stretching of the free amine in **2**.
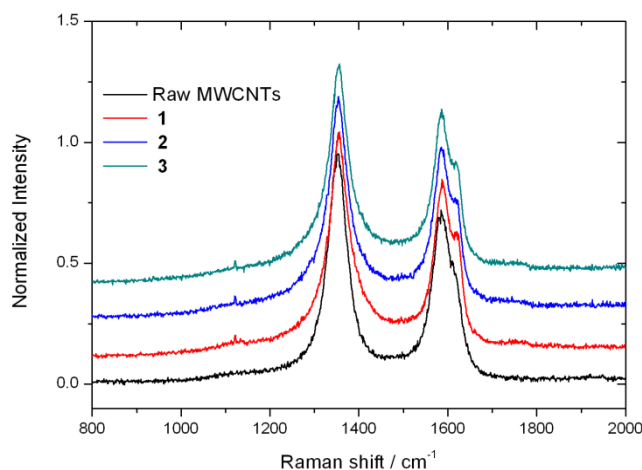
Fig. S3 Raman spectra of raw MWCNTs, **1**, **2**, **3** excited at 514 nm.

Raman spectra were recorded with an Invia Renishaw Raman microspectrometer (50 × objective) using a 514 nm laser line from an Ar laser. The Raman spectrum corresponding to the functionalized nanotubes is very similar to that of raw MWCNTs. There are no changes in the frequency of the tangential stretching mode (G band at 1585 cm^{-1}) and disorder one (D band at 1355 cm^{-1}). Slight difference is displayed by the ratio D/G from raw MWCNTs to **3** (1.30; 1.24; 1.26; 1.23 for raw MWCNTs, **1**, **2** and **3** respectively). Raman spectroscopy shows indeed that the ratio of the tangential stretching mode and the disorder mode peak was not affected by covalent synthesis.

Table T1. Elemental analysis for raw MWCNTs, **1**, **2** and **3**.

Sample	Carbon (%)	Hydrogen (%)	Nitrogen (%)
Raw MWCNT	98.81	0.20	-
1	82.44	1.11	-
2	83.96	1.45	4.70
3	72.12	1.78	4.61

The elemental analysis of the samples was performed with a Thermofinnigan Instrument (1110 CHNS-O).

Preparation of ISE membranes and electrodes

Since the ionophore content was 15 wt % of the MWCNT hybrids, a considerable amount of MWCNT-B18C6 was required to reach 1% ionophore in the ISM cocktail (6.67% of the total membrane weight). Due to the high dry matter content in the membrane, a higher ratio (3:1) of plasticizer/polymer was required.[7] Sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (NaTFPB) was used as a lipophilic cation exchanger to ensure the cation permselectivity of ISMs (30% mol ratio NaTFPB/B18C6).

The membrane cocktails were prepared in two steps: first, CNTs (MWCNT-B18C6 or MWCNT-COOH) with 5 mg of PEAA in 1 ml of THF were dispersed using a sonicator bath and, second, NaTFPB (30% per mole of ionophore) and PVC:NPOE in a 1:3 ratio were mixed to obtain a total of 100 mg of membrane. The sonicator bath was used until complete dissolution of components. Three different membranes were prepared: MWCNT-B18C6 membranes: the amount of MWCNT-B18C6 hybrid required to have an equivalent of 1% w/w of ionophore in 1 ml of THF (amount of CNT-B18C6 according to the TGA analysis). Free receptor membranes were prepared with the same composition as the MWCNT-B18C6 membranes, with the only difference of ionophore as free form (c.a. 1% w/w). Blank membranes were prepared following the same composition as the previously described membranes but without adding ionophore. All the membranes were prepared by drop

casting 50 µl of membrane cocktail onto the polished end of a glassy carbon rod (3 mm $\varnothing$) followed by solvent evaporation at room temperature.

EMF measurements

Potentiometric responses were recorded with a high-input impedance (10^{13} Ω) 16-channel EMF-16 interface (Lawson Labs) at room temperature (22 ± 2 ºC). A double-junction Ag/AgCl/3 M KCl reference electrode (type 6.0729.100, Methrom AG) containing a 1 M lithium acetate electrolyte bridge was employed. All measurements were corrected with the Henderson equation[1] and the Debye–Huckel approximation[2] and were done with three electrodes to evaluate the reproducibility of the sensors.

Potentiometric selectivity coefficients ($K_{Pb,J}^{pot}$) were calculated employing the separate solution method (SSM) using 10 mM nitrate solutions of the primary ion Pb^{2+} and interferences: Ca^{2+}, Mg^{2+}, Zn^{2+}, Cd^{2+}, Cu^{2+} as previously described.[3]

The calibration curves for lead were obtained by successive additions of different lead solutions (addition method, black in Fig. S4). The electrode was conditioned 24 h in a 10^{-3} M Pb^{2+} solution and then 48 h in a 10^{-9} M Pb^{2+} solution before measurements to avoid ion fluxes at low concentration due to the lack of membrane equilibrium. The limit of detection (LOD) calculated for this calibration curve using the addition method was $10^{-5.8}$ M. The limit of detection was also calculated using the continuous dilution procedure with Milli-Q water (dilution method, red in Fig. S4).[4] In this case the electrode was conditioned for 48 h in 10^{-2} M of Pb^{2+} obtaining a value of $10^{-6.4}$ M.
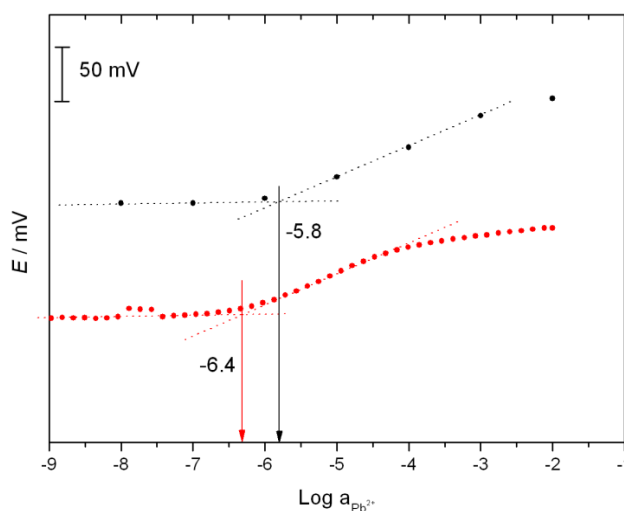

Fig. S4 Limit of detection. (black) LOD obtained by addition method. (red) LOD obtained by dilution method.

The intermediate-term potential stability (Fig. S5) was also assessed by measuring the EMF during 24 hours using a starting 10^{-5} M Pb^{2+} solution and adding after 45 min a Pb^{2+} solution to reach a final 10^{-3} M Pb^{2+} solution.
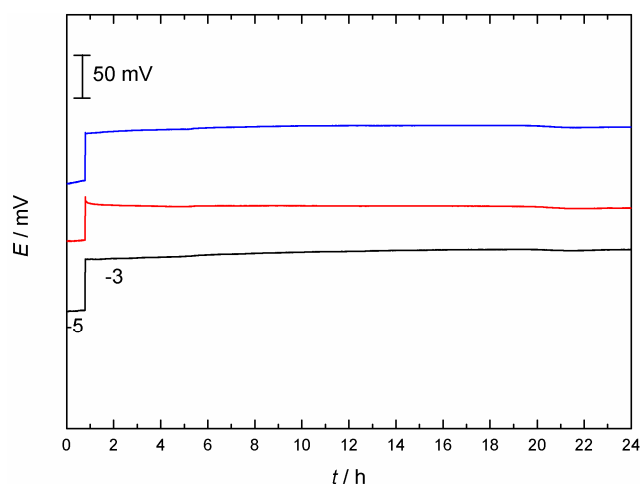
Fig. S5 Intermediate-term potential stability of the electrode over 24 hours for an activity change from 10^{-5} M Pb^{2+} to 10^{-3} M Pb^{2+}. *Black:* MWCNT-B18C6 membrane, *red:* Free receptor ion selective membrane and *blue:* blank membrane.

Optical characterization

The membranes were characterized using environmental scanning electron microscopy (ESEM, Quanta 600) and Transmission electron microscopy (TEM, JEOL model 1011). Fig. S6 shows a TEM image for MWCNT-B18C6 membrane where the low density network of dispersed carbon nanotubes is observed. A 60 µm membrane thickness was estimated by ESEM.
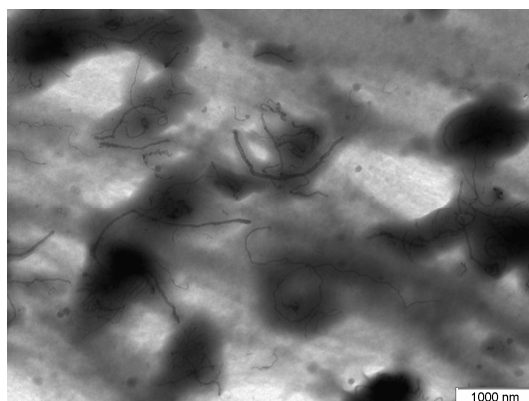

Fig. S6 Transmission electron microscopy image of ion-selective membrane with MWCNT-B18C6 hybrid.

Mass spectroscopy analysis

Mass spectroscopy analysis of the conditioning solution of MWCNT+B18C6 and MWCNT-B18C6 membrane ISEs were achieved to detect the presence of leaching components of the polymeric membrane. Experimentally, the aqueous solution (1 month conditioning) was concentrated under reduced pressure and the resulted material subjected to mass analysis (Fig. 7 and 8). Figures S7 and S8 present the Mass spectrum of MWCNT + B18C6 and MWCNT-B18C6 membranes respectively. In the conventional membrane, the mass of the ionophore was detected (Figure S7, M=330.19 gmol^{-1}) whereas in the hybrid membrane, such mass was not present. This experiment accounts for the leaching out of the ionophore when it is not covalently linked to the MWCNTs.
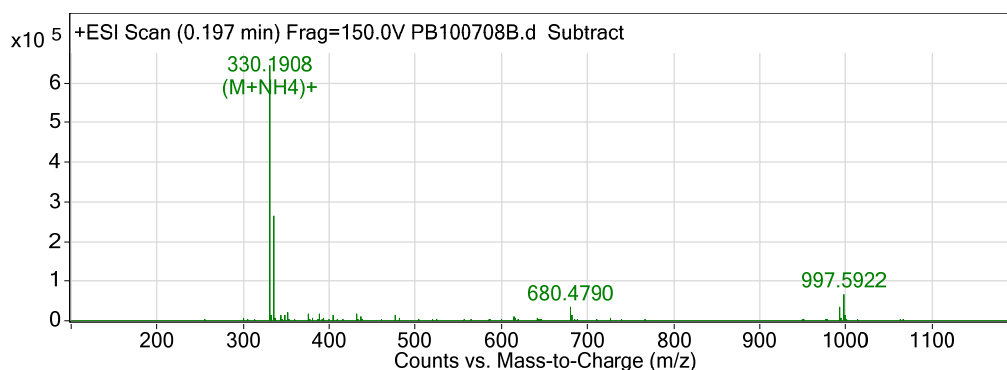
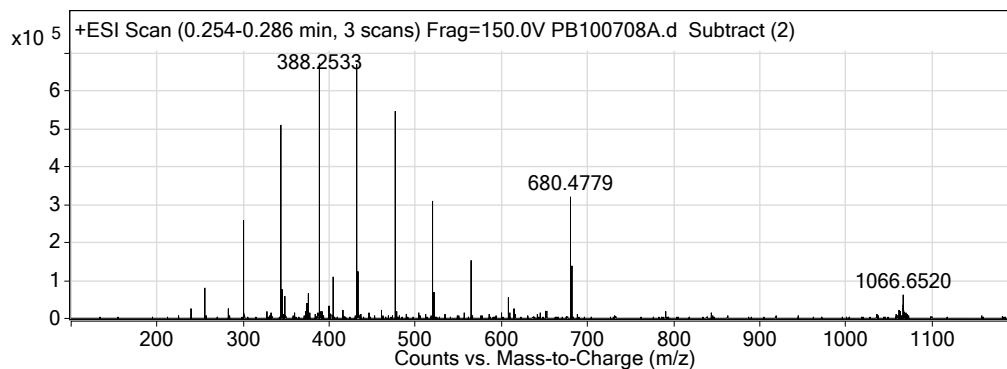**Fig. S7**. Mass spectrum of conditioning solution of MWCNT+B18C6 membrane.

Fig. S8. Mass spectrum of conditioning solution of MWCNT-B18C6 membrane.

Water layer test

In order to show the effect of the water layer between the ion-selective membrane and glassy carbon, the water layer test was performed. This water layer has harmful effects since it can favour the presence of the atmospheric gases like O_2 or CO_2, diffused through the ion-selective membrane. The presence of O_2 can favour redox side-reactions while CO_2 can change the pH of the interface, what may result in response drifts. This procedure follows three steps[5]: in the first and the third step (area A, Fig. S9) the potential was recorded in a 10^{-3} M Pb^{2+} solution, in the second step (area B, Fig. S9) the electrode was submerged into a 10^{-3} M Mg^{2+} solution. The water layer test was recorded for the three different membranes (Fig. S9): MWCNT-B18C6 membrane, MWCNT + B18C6 membrane and blank membrane. The same responses were observed for the three membranes, no water layers were detected due to the high hydrophobic character of the MWCNTs inside membrane.
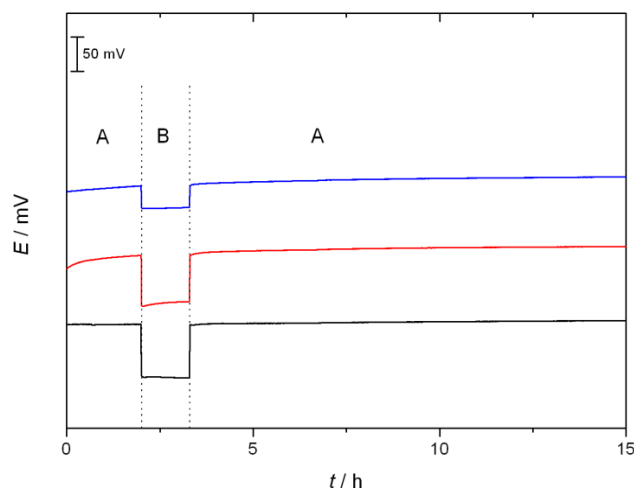
Fig. S9 Water layer test of Pb^{2+} selective electrodes. *Area A*: solution of 10^{-2} M Pb^{2+}. *Area B*: solution of 10^{-2} M Mg^{2+}. *Black:* MWCNT-B18C6 membrane, *red:* free receptor ion selective membrane and *blue:* blank membrane.

Electrochemical impedance spectroscopy (EIS)

All electrochemical impedance measurements were made using a potentiostat/galvanostat Autolab PGSTAT128N with frequency response analyser electrochemical impedance module (FRA2) (AUTOLAB, Eco Chemie). EIS was performed in a three-electrodes electrochemical cell. The working electrode was a glassy carbon rod with a drop casted on it (area 0.07 cm^2) [6], the counter electrode was a glassy carbon rod and the reference electrode was a single junction Metrohm Ag,AgCl/3M KCl (type 6.0733.100, Methrom AG). All measurements were performed at room temperature (22 ± 2 °C). The impedance spectra were recorded in a frequency range (100 kHz – 10 mHz). The impedances were recorded for four different composition of membranes: membrane with dispersed MWCNT-B18C6 (fig. S10), membrane containing only PVC (fig. S11), membrane containing dispersed MWCNT-COOH (Fig. S12), membrane with dispersed MWCNT-COOH and B18C6 (Fig. S13)
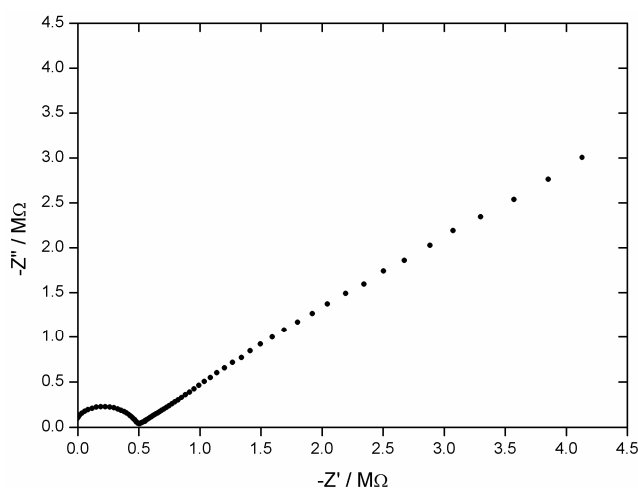

Fig. S10 Complex plane impedance plot of MWCNT-B18C6 electrode in 10^{-3} M Pb(NO$_3$)$_2$ solution. Experimental conditions: E_{dc}=0.2 V, Frequency range =100 kHz-10 mHz, Amplitude = 0.1V.
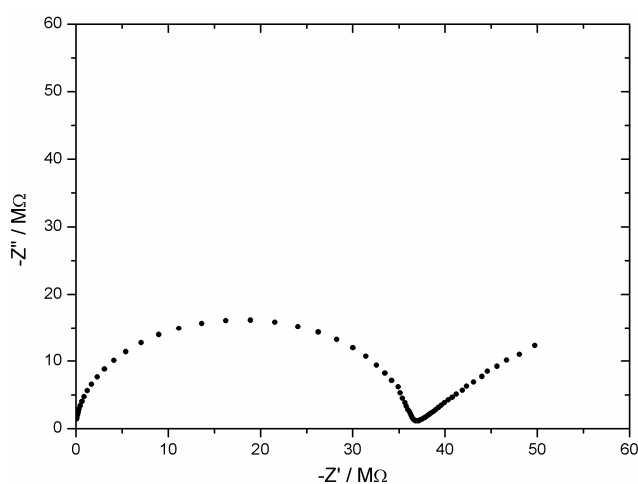

Fig. S11. Complex plane impedance plot of the membranes with PVC: NPOE electrode in 10^{-3} M Pb(NO$_3$)$_2$. Experimental conditions: E_{dc}=0.2 V, Frequency range =100 kHz -10 mHz, Amplitude = 100 mV. Parameters

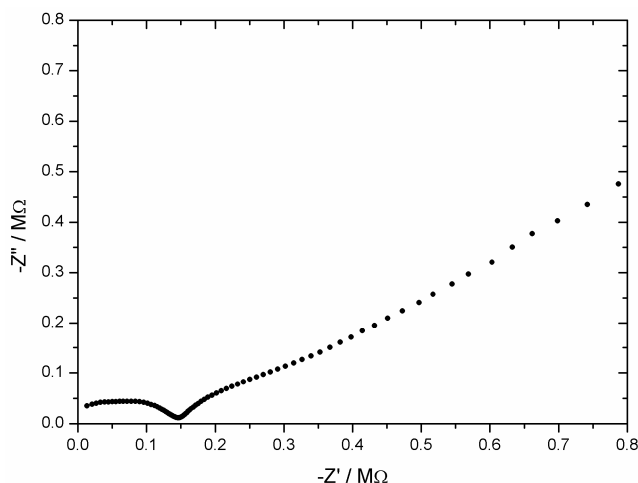from the RC circuit R_b=35.5 MΩ ; C_g=14 pF (Time constant: 1.7 ms)

Fig. S12. Complex plane impedance plot of MWCNT-COOH electrode in 10^{-3} M Pb(NO$_3$)$_2$ solution. Experimental conditions: E_{dc}=0.2 V, Frequency range =100 kHz-10 mHz, Amplitude = 100 mV. Parameters from the RC circuit R_b=184 kΩ ; C_g=54 pF; (Time constant: 0.06 ms). Second RC R_{ct}=287 kΩ ; C_{dl}= 1.2 μF; (Time constant: 0.9 s)
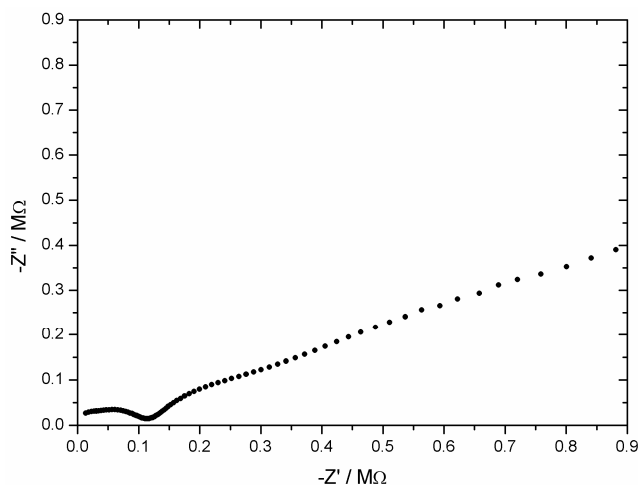

Fig. S13. Complex plane impedance plot of MWCNT-COOH with B18C6 free electrode in 10^{-3} M Pb(NO$_3$)$_2$ solution. Experimental conditions: E_{dc}=0.2 V, Frequency range =100 kHz-10 mHz, Amplitude = 100 mV. Parameters from the RC circuit R_b=150 kΩ ; C_g=30 pF (Time constant: 0.007 ms). Second RC R_{ct}=407 kΩ ; C_{dl}= 0.8 μF (Time constant: 0.5 s).

References

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