Nanostructured assemblies for ion-sensors: functionalization of multi-wall carbon nanotubes with benzo-18-crown-6 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 thionyle 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.

Characterization techniques

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. FTIR spectra were recorded with a Jasco FT/IR-600 PLUS spectrometer on KBr pellet. The elemental analysis of the samples was performed with a Thermofinnigan Instrument (1110 CHNS-O). Raman spectra were recorded with an Invia Renishaw Raman microspectrometer (50 × objective) using a 514 nm laser line from an Ar laser.

Chemical synthesis

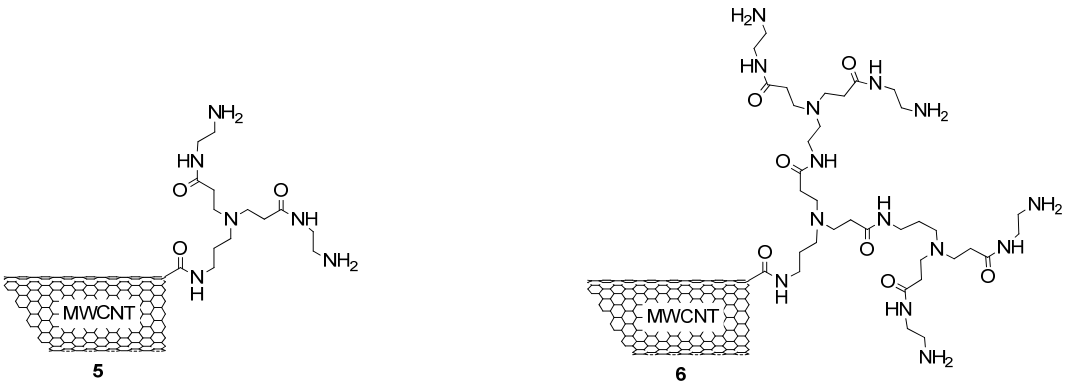

Fig. S1 Chemical structures of MWCNTs **5** and **6**

To a suspension of MWNTs **4** (20 mg) in dry methanol (10 mL) were added N-ethyldiisopropylamine (2 mL) and methyl acrylate (10 mL). The reaction mixture was stirred at 80 °C for 3 days and then filtered on a Millipore membrane (PTFE, 0.22 µm), and the resulting solid was washed with CH_2Cl_2 and diethyl ether (20 mg). To a suspension of the resulting solid in dry methanol (10 mL) was added ethylenediamine (10 mL). The reaction mixture was stirred at 80 °C for 3 days and then filtered on a Millipore membrane (PTFE, 0.22 µm), and the solid was washed with CH_2Cl_2 and diethyl ether to afford MWCNT **5** (20 mg). The same procedure was followed from MWCNT **5** to give MWCNT **6** (See Fig. S1).

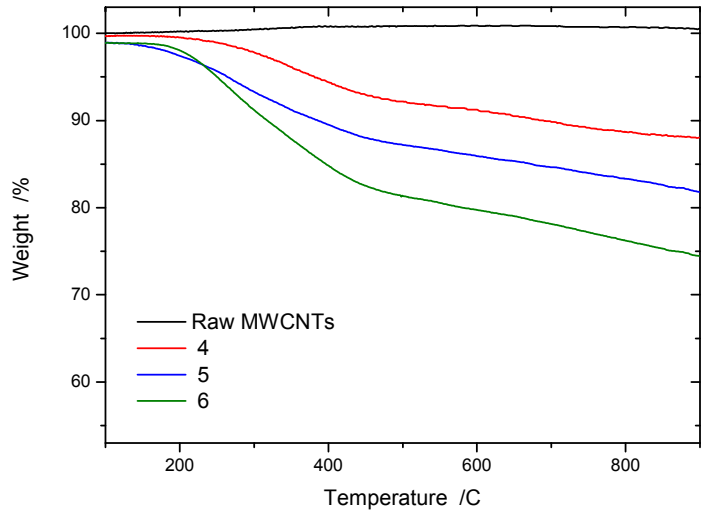

Fig. S2 TGA curves for: raw MWCNTs, **4**, **5** and **6** (10 ºC min^{-1} in N_2)

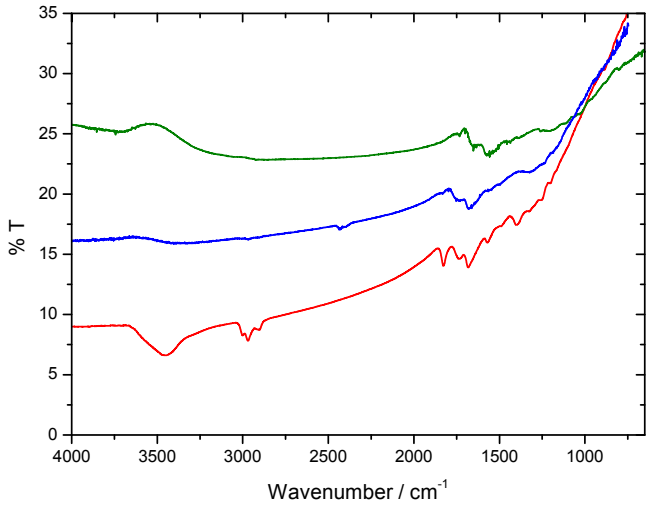

Fig. S3 FT-IR spectrum of **4** (red), **5** (blue) and **6** (green).

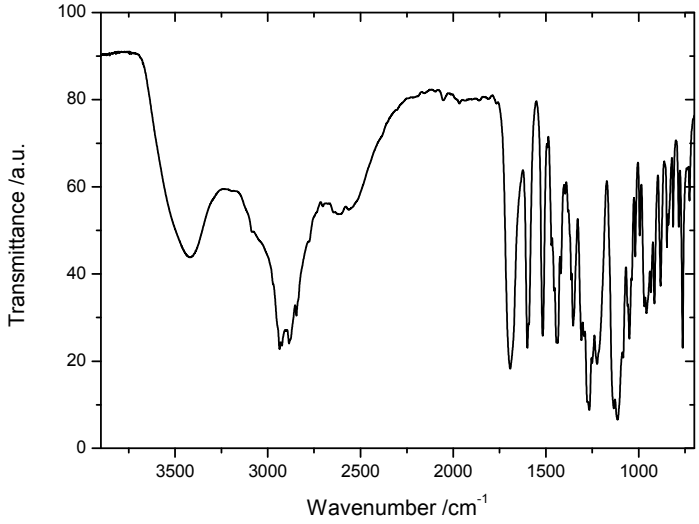

Fig. S4 FT-IR spectrum of 4′-Carboxybenzo-18-crown-6

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

Sample	Carbon (%)	Hydrogen (%)	Nitrogen (%)
Raw MWCNT	98.81	0.20	-
MWCNT-COOH	82.44	1.11	-
4	83.96	1.45	4.70
1	72.12	1.78	4.61
2	77.08	2.39	4.72
3	74.75	3.17	6.60

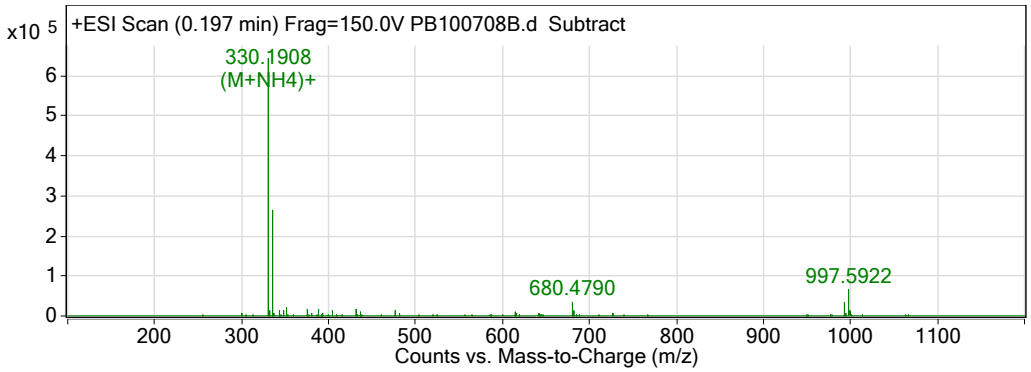

Fig. S5. Mass spectrum of conditioning solution of MWCNT+B18C6 membrane.

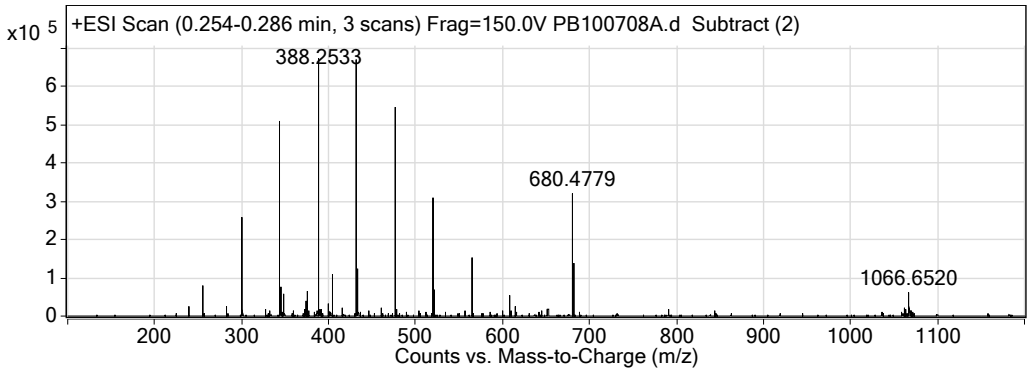

Fig. S6. Mass spectrum of conditioning solution of MWCNT-B18C6 membrane.

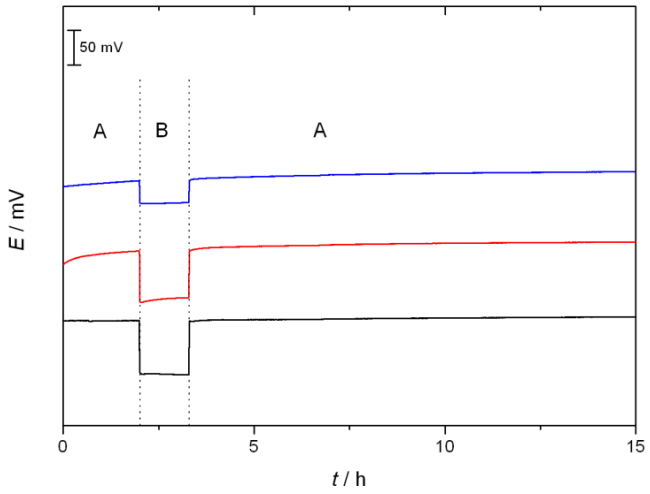

Fig. S7 Water layer test of Pb^{2+} selective electrodes. *Area A*: solution of 10^{-2} M Pb^{2+}. *Area B*: solution of 10^{-2} M Mg^{2+}. *Black:* **1**, *red:* MWCNT+B18C6 and *blue:* blank membrane.

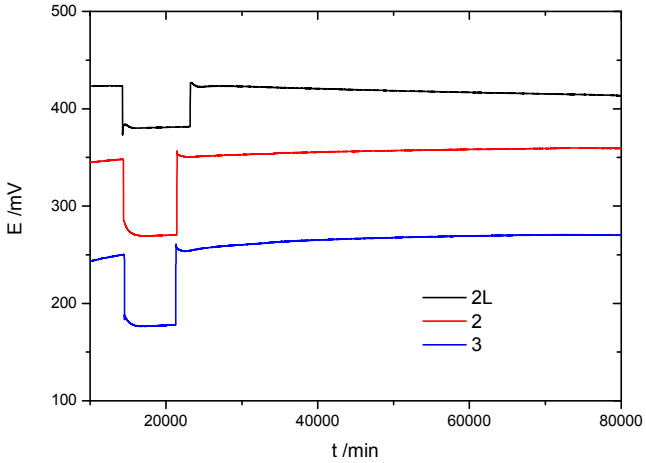

Fig. S8 Water layer test of Pb^{2+} selective electrodes. *Black:* Two-steps, *red:* **2** and *blue:* **3** *Area A*: solution of 10^{-2} M Pb^{2+}. *Area B*: solution of 10^{-2} M Mg^{2+}.