Electronic Supplementary Information (ESI)

All reagents were commercially available and used as such unless otherwise specified. Tetrahydrofuran (THF) was dried over sodium and distilled. The composition of a potentiometric liquid membranes was 4.4 mg (2.5 wt%) of 5,10,15,20-tetraphenyl porphyrin (**TPP**), 48.8 mg (27.9 wt%) of poly(vinyl chloride) as an ionophore, 120.9 mg (69.0 wt%) of a membrane solvent, and 1.1 mg (0.6 wt%) of potassium tetrakis(4-chlorophenyl)borate (KTpClPB) as an anion excluder for potentiometric cation-sensing membranes. 2-Nitrophenyl octyl ether (*o*-NPOE), 2-nitrophenyl phenyl ether (*o*-NPPE), 4-nitrophenyl phenyl ether (*p*-NPPE), dibenzyl ether (DBE), and phosphoric acid tris(2-ethylhexyl) ester (TEHP) were employed as membrane solvents, respectively. The components were put into a 5 mL of sample glass tube and dissolved in ca. 3 mL of THF. The PVC plasticized membrane was obtained by spontaneous evaporation of THF for a few days.

The digital images of five kinds of potentiometric liquid membranes are shown in Figure S1. Since **TPP** is a very dark purple solid, the digital images of potentiometric liquid membranes incorporating an ionophore **TPP** were not distinct. So, the digital images of potentiometric liquid membranes without an ionophore **TPP** were also taken.

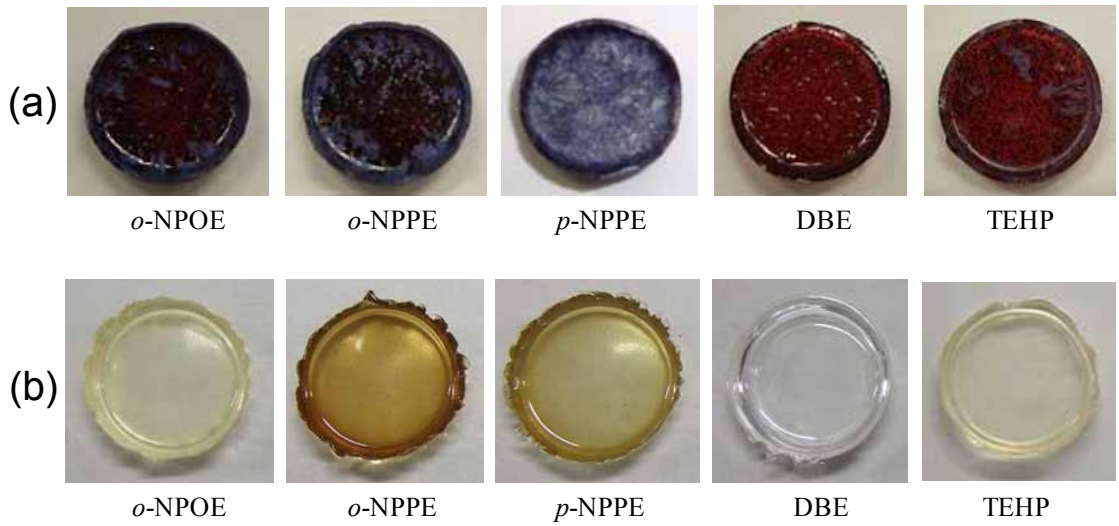

Fig. S1 Digital images of five kinds of potentiometric liquid membranes with (a) or without (b) an ionophore **TPP**.

Pulsed NMR measurements were carried out on JEOL JNM-MU-25 spectrometer operating at a frequency of 25 MHz. In all cases, one sheet of the above mentioned potentiometric liquid membrane was arranged in a 10 mmϕ NMR tube so that it took the pulse irradiation at the center. The free induction decay (FID) signals were recorded at probe temperature 35°C. The spin-spin relaxation time T_2 values were estimated from a Hahn-Echo method (the 90°–τ–180° pulse sequence) with a pulse width (Pw1) of 2.2 μs and a repetition time (Rep) of 4.0 s. The 90°–τ–180° pulse sequence using Hahn-Echo method rather than Solid-Echo method was suitable for the T_2 measurements of various types of the viscoelastic electrode membranes. The proton spin-spin relaxation times T_2 and the fraction of each component were calculated by fitting the FID signal to the Weibull function.

Figure S2 shows the FID signal analysis of the potentiometric liquid membranes incorporating *o*-NPPE, *p*-NPPE, DBE and TEHP.

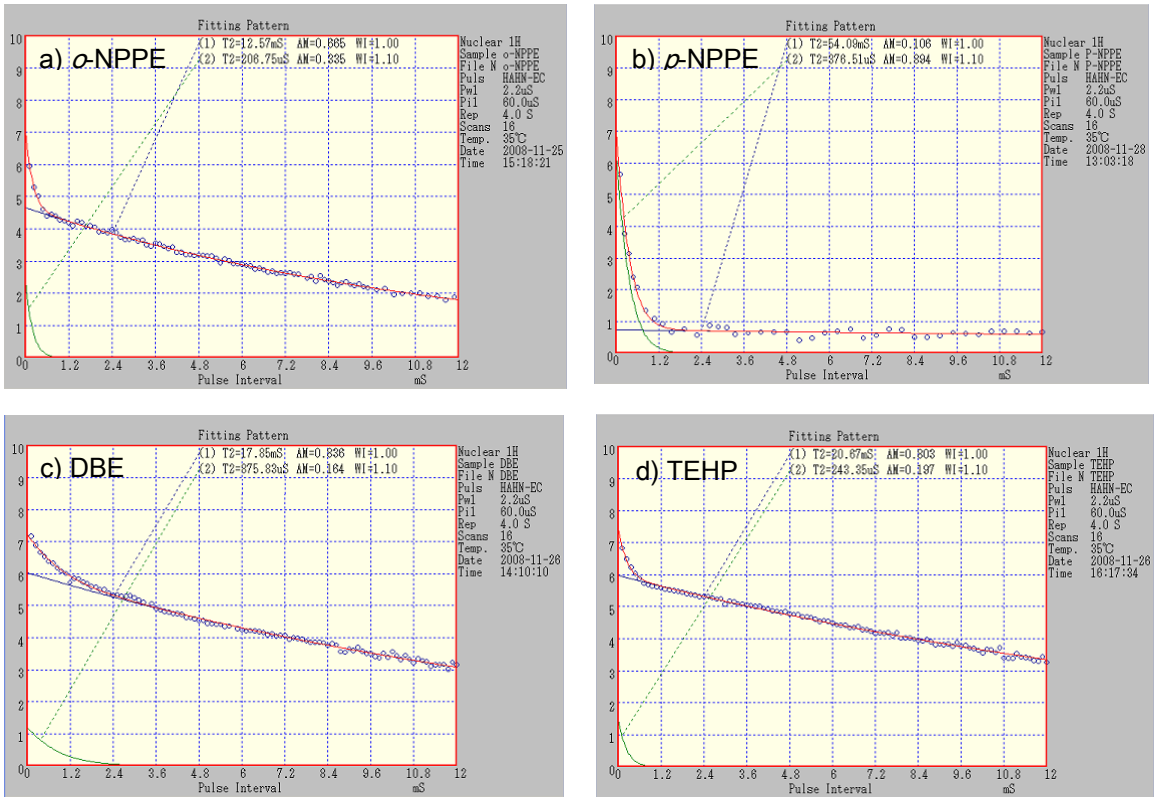

Fig. S2 The FID signal analyses of the potentiometric liquid membranes incorporating *o*-NPPE, *p*-NPPE, DBE and TEHP as solvent membranes.