Supporting Information for “Drastic Selectivity Reversal on Crown-Ether Based Ion-Sensing Membranes Made of Ordered Mesoporous Silica and Conventional Sol-Gel Derived One”
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Experimental Syntheses
The neutral carrier, 3-(chlorodimethylsilyl)propyloxymethyl-15-crown-5, was synthesized as follows.

**Allyloxymethyl-15-crown-5** 2-(Hydroxymethyl)-15-crown-5 was obtained with some modification of a published method. Sodium hydride (0.52 g, 22 mmol) was suspended in 50 mL dry tetrahydrofuran (THF), and 2-(hydroxymethyl)-15-crown-5 (1.5 g, 6.0 mmol) in dry THF (20 mL) was then added from a dropping funnel. After the mixture was stirred for 30 min at room temperature, allyl bromide (3.5 g, 29 mmol) was added dropwise. The mixture was refluxed under N$_2$ atmosphere for 25 h while stirring. The solvent was evaporated off, and 100 mL of deionized water was added to the residue. The aqueous solution was extracted with diethyl ether (50 mL X 3), and the combined organic solution was dried with magnesium sulfate, and the solvent was evaporated off. The crude product was purified by silica gel column chromatography (ethyl acetate / chloroform = 50/50 v/v) (pale yellow liquid, yield 77 %): $^1$H NMR (400 MHz, CDCl$_3$) δ3.46-3.86 (21H, m, CH$_2$OCH$_2$, OCH), 4.03 (2H, d, J = 5.5 Hz, CH$_2$CH=CH$_2$), 5.22 (1H, d, J = 10.6 Hz, =CH$_2$), 5.28 (1H, d, J = 17.0 Hz, =CH$_2$), 5.85-5.96 (m, 1H, CH=CH$_2$).

**3-(Chlorodimethylsilyl)propyloxymethyl-15-crown-5** Allyloxymethyl-15-crown-5 (1.5 g, 5.2 mmol) was dissolved in dry benzene (50 mL), and a dry 2-propanol solution (0.1 mL) of H$_2$PtCl$_6$・6H$_2$O (3.8 mg, 7.3 μmol) was then added. The mixture was stirred under N$_2$ atmosphere at 60 °C for 1 h. After addition of chlorodimethylsilane (760 mg, 80 mmol), the mixture was stirred under N$_2$ atmosphere at 60 °C for 3 h. After the reaction, the obtained solution was filtered through a membrane filter (JAWP02500, Millipore Corp., MA, USA). The solvent was evaporated off, and a brown liquid was obtained. This compound was subjected to the following reaction without purification due to the easy polymerization.

$^{13}$C magic angle spinning nuclear magnetic resonance (MAS NMR) measurements  
$^{13}$C MAS NMR measurements were made at room temperature with JNM-ECA400 spectrometers (JEOL, Tokyo, Japan). The $^{13}$C cross-polarization (CP)/MAS measurements were made with the contact time of 1 ms. The sample spinning rate was 10 kHz. Modification of 15-crown-5 to mesoporous silica was confirmed by the peaks of -0.9 - 2.9 ppm (-Si-CH$_3$) and 65 - 74 ppm.
(-O-CH$_2$-).

X-ray photoelectron spectroscopy (XPS) measurements
XPS measurements were made with JPS9010MC equipped with a Mg K$\alpha$ X-ray source (JEOL, Tokyo, Japan). The spectra of 15-crown-5-modified MPS as a function of membrane depth were measured after argon-sputtered etching 6 times for 15 sec.

References