

Supporting Information for

Tertiary Sulfonium as Cationic Functional Group for Hydroxide Exchange Membranes

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1. Experimental methods

Synthesis of diphenyl(3-methyl-4-methoxyphenyl) sulfonium triflate: 16.2 g (80 mmol) diphenyl sulfoxide and 9.77 g (80 mmol) methylanisole were dissolved in 800 mL dichloromethane. The solution was cooled to -78 °C in a dry ice-acetone bath and 22.6 g (80 mmol) trifluoromethanesulfonic anhydride was added dropwise. The mixture was stirred at room temperature for 1 h. After the reaction, the mixture was washed three times with saturated sodium bicarbonate solution and then with double deionized water (DDI) water and dried under anhydrous magnesium sulfate for 24 h. The treated solution was concentrated to 100 mL by a rotary evaporator and added dropwisely into 500 mL ethyl ether to precipitate (3-methyl-4-methoxyphenyl) sulfonium triflate. The white precipitate was filtered and dried under vacuum at room temperature for 24 hrs.

Synthesis of diphenyl(3-bromomethyl-4-methoxyphenyl) sulfonium chloride: 4.56 g (10 mmol) diphenyl(3-methyl-4-methoxyphenyl) sulfonium triflate and 1.78 g (10 mmol) N-bromosuccinimide (NBS) was dissolved in 100 mL dichloroethane. The solution was heated to 85 °C, followed by addition of 0.12 g (0.5 mmol) benzoyl peroxide (BPO). The mixture was stirred at room temperature for 24 h. After the reaction, the mixture was added dropwise into 300 mL ethyl ether to precipitate diphenyl(3-bromomethyl-4-methoxyphenyl) sulfonium triflate. The precipitate was washed three times with ethyl ether and dried under vacuum at room temperature for 24 h. Then, diphenyl(3-bromomethyl-4-methoxyphenyl) sulfonium triflate was dissolved in 1000 mL DDI water, followed by addition of 120 g IRA-900 anion exchange resin to convert triflate ions to chloride ions. After 48 h, the resin was filtered and the water was evaporated to give diphenyl(3-bromomethyl-4-methoxyphenyl) sulfonium chloride.

Synthesis of chloromethylated polysulfone (CMPSf): 15 g (33.9 mmol) polysulfone (PSf) was dissolved in 750 mL chloroform. 10.18 g (339 mmol) paraformaldehyde and 36.9 g (339 mmol) trimethylchlorosilane were added into PSf solution, followed by dropwise addition of 1.767 g (6.78 mmol) stannic chloride. The mixture was stirred at 55 °C for 72 h. After the reaction, the mixture was poured into ethanol to precipitate CMPSf. The precipitate was separated by filtration, washed three times with ethanol and dried under vacuum at room temperature for 24 h. The degree of chloromethylation is 128% (¹H NMR in Figure S3).

Synthesis of butylaminated polysulfone (PSf-BA): 2.02 g (4 mmol) chloromethylated polysulfone was dissolved in 40 mL 1-methyl-2-pyrrolidinone, followed by addition of 4.69 mL (40 mmol) butyl amine and 3.16 g (8 mmol) cesium carbonate. The mixture was stirred at room temperature for 48 h. After the reaction, the mixture was added dropwise into 400 mL DDI water to precipitate butylaminated polysulfone. The precipitate was washed three times with DDI water, filtered and dried in vacuum at 60

°C for 48 h. The conversion of chloromethyl group to secondary amine is close to 100% (^1H NMR in Figure S4).

Synthesis of diphenyl(3-methyl-4-methoxyphenyl) tertiary sulfonium (MeOTAS) chloride functionalized polysulfone (PSf-MeOTASCl): 0.110 g (0.2 mmol) PSf-BA and 0.227g (0.4 mmol) MeOTAS chloride were dissolved in 1 mL NMP. The solution was stirred at 60 °C for 24 hrs. After the reaction, the solution was added dropwise into ethanol to precipitate PSf-MeOTASCl. The precipitate was washed with ethanol three times, filtered and dried in vacuum at room temperature for 24 h. The degree of functionalization of MeOTAS cation was 46% (^1H NMR in Figure S5).

Preparation of MeOTAS hydroxide functionalized polysulfone (PSf-MeOTASOH) based HEM: The PSf-MeOTASCl/N-methylpyrrolidone (NMP) solution (10 wt %) was poured onto a flat glass sheet, followed by evaporating the solvent at 30 °C for 24 h to obtain a PSf-MeOTASCl membrane. The PSf-MeOTASOH membrane was obtained by treating PSf-MeOTASCl in 1 M KOH at room temperature for 48 h to exchange chloride ions for hydroxide ions. Then the membrane was washed thoroughly and immersed in DDI water for 48 h to remove residual KOH.

Measurement: ^1H NMR spectra were measured at 400 MHz on an AV400 spectrometer. Thermogravimetric analysis (TGA) was performed in nitrogen (flow rate: 20 mL/min) with a Mettler Toledo TGA/DSC1 thermogravimetric analyzer at a heating rate of 10 °C/min. Small-angle X-ray scattering (SAXS) pattern was obtained on Anton Paar SAXSess with a PANalytical PW3830 X-ray generator. The conductivity measurements were carried out by using an ex-situ four-electrode AC impedance method at room temperature¹. The alkaline stability test of TAS based HEMs was carried out by immersing the membranes in a 1 M KOH solution at 60 °C or room temperature for a certain time period. Then the membranes were washed thoroughly by and immersed in DDI water for 48 h to remove residual KOH, followed by the ^1H NMR analysis. The alkaline stability test of the model compounds was carried out by dissolving and keeping the compounds in 1 M KOD/D₂O solution at 60 °C for 10 days, followed by ^1H NMR analysis.

2. ^1H NMR spectra

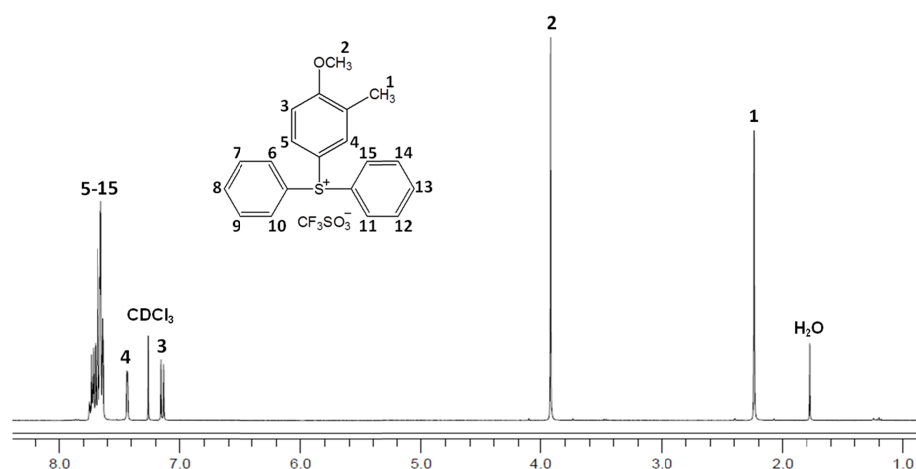


Figure S1. ^1H NMR spectrum of *diphenyl(3-methyl-4-methoxyphenyl) sulfonium triflate*. Deuterated chloroform (CDCl_3) as solvent and tetramethylsilane (TMS) as internal standard.

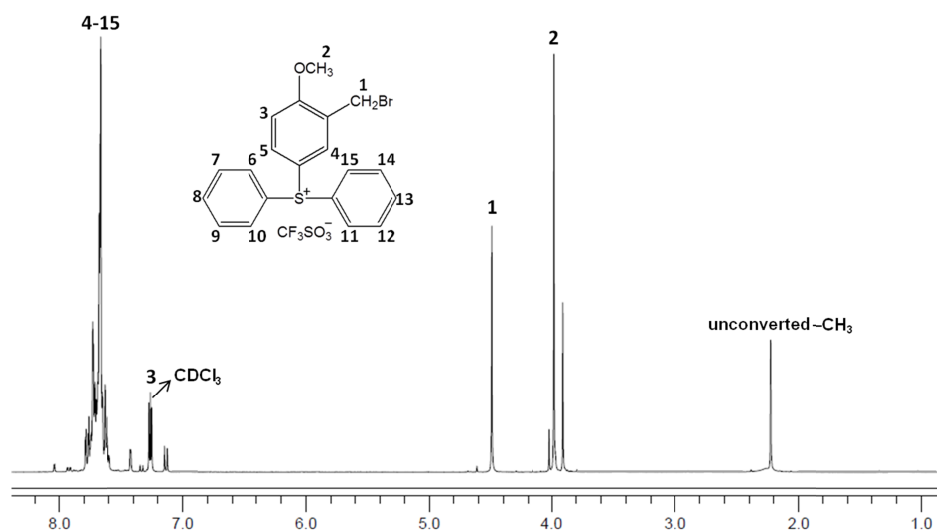


Figure S2. ^1H NMR spectrum of *diphenyl(3-bromomethyl-4-methoxyphenyl) sulfonium triflate*. Deuterated chloroform (CDCl_3) as solvent and tetramethylsilane (TMS) as internal standard.

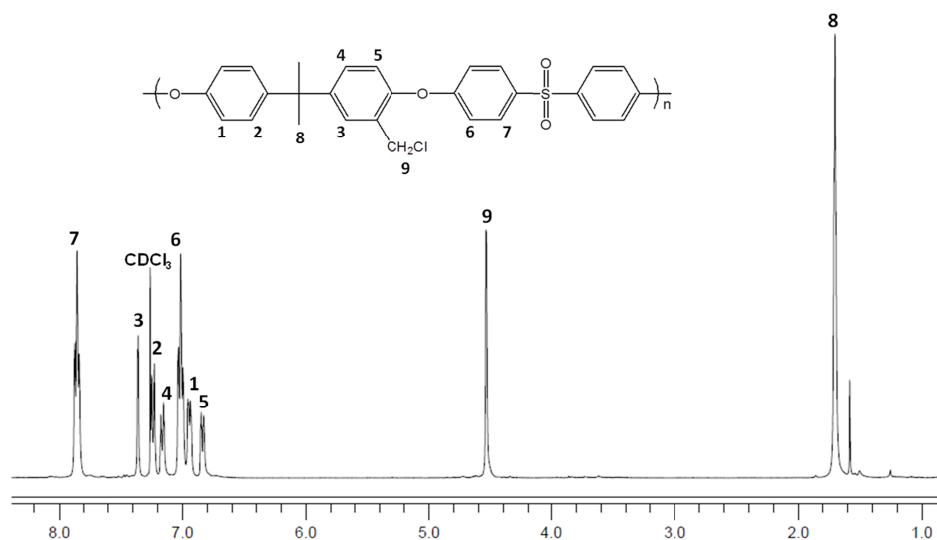


Figure S3. ^1H NMR spectrum of *chloromethylated polysulfone (CMPSf)*. Deuterated chloroform (CDCl_3) as solvent and tetramethylsilane (TMS) as internal standard. The degree of chloromethylation (DC) of CMPSf was calculated from the following equation:

$$DC = \frac{2A_9}{A_7} \times 100\%$$

Where, A_9 and A_7 are integral area of 9 (proton in $-\text{CH}_2\text{Cl}$) and 7 (proton adjacent to $-\text{SO}_2-$ group in the aromatic ring) in the spectrum of CMPSf.

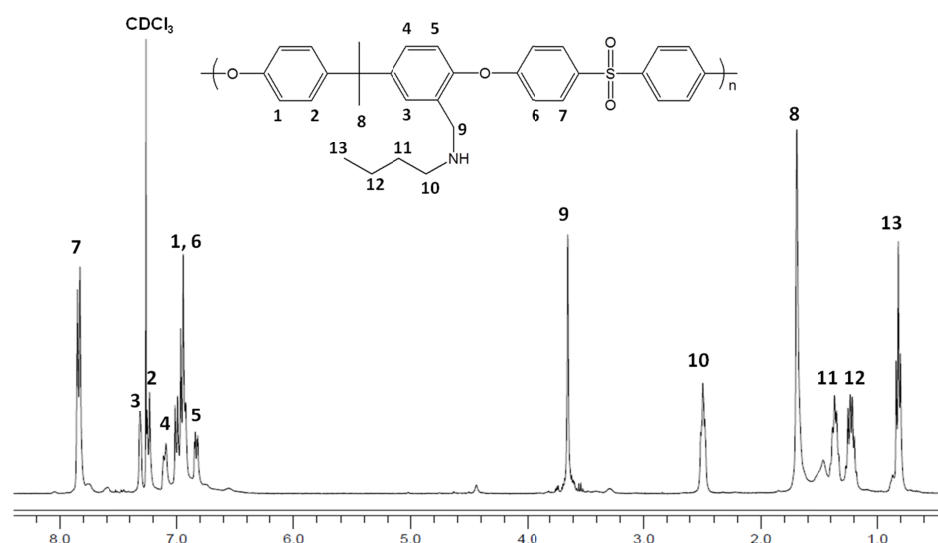


Figure S4. ^1H NMR spectrum of butylaminated polysulfone (PSf-BA). Deuterated chloroform (CDCl_3) as solvent and tetramethylsilane (TMS) as internal standard. The disappearance of the chemical shift 4.44 ppm indicates that the conversion of chloromethyl group to butyl amine is close to 100%.

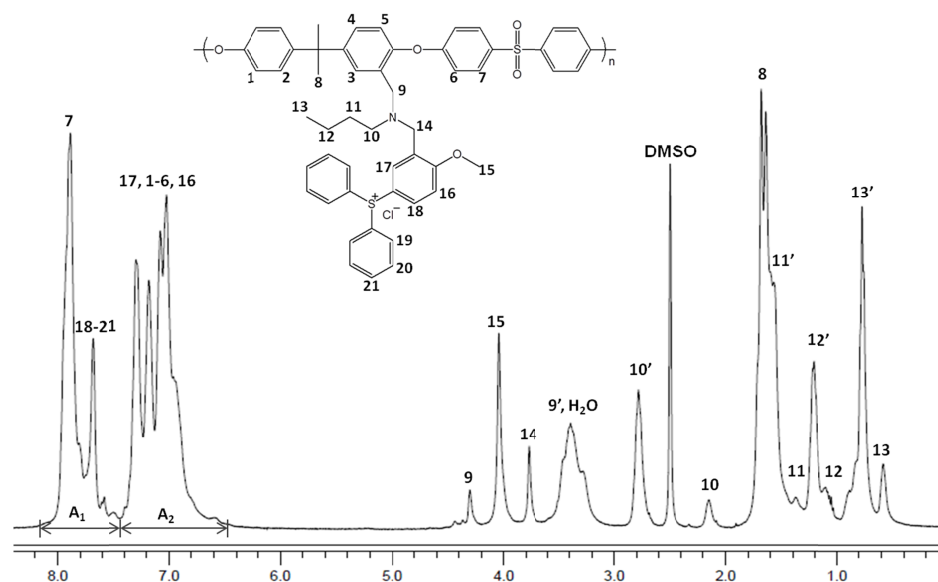


Figure S5. ^1H NMR spectrum of MeOTAS chloride functionalized polysulfone (PSf-MeOTASCl). Deuterated dimethyl sulfoxide (DMSO) as solvent and tetramethylsilane (TMS) as internal standard. $\text{H}_{9-13'}$ are assigned to the unconverted butylamine group (as shown in Figure S4). The degree of functionalization of MeOTAS cation (DS) was calculated from the following equation:

$$DS = \frac{4 - (12 - DC) \times \frac{A_1}{A_2}}{2 \times DC - 11} \times 100\%$$

3. SAXS diffraction pattern

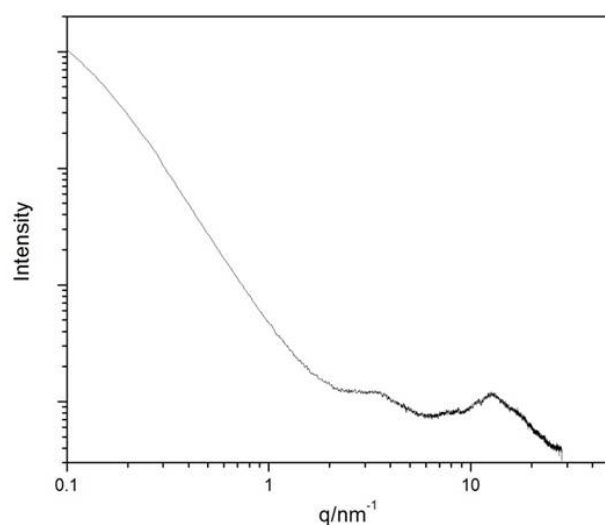


Figure S6. SAXS pattern of PSf-MeOTASCl with an IEC of 0.69 mmol g⁻¹.

4. Stability tests

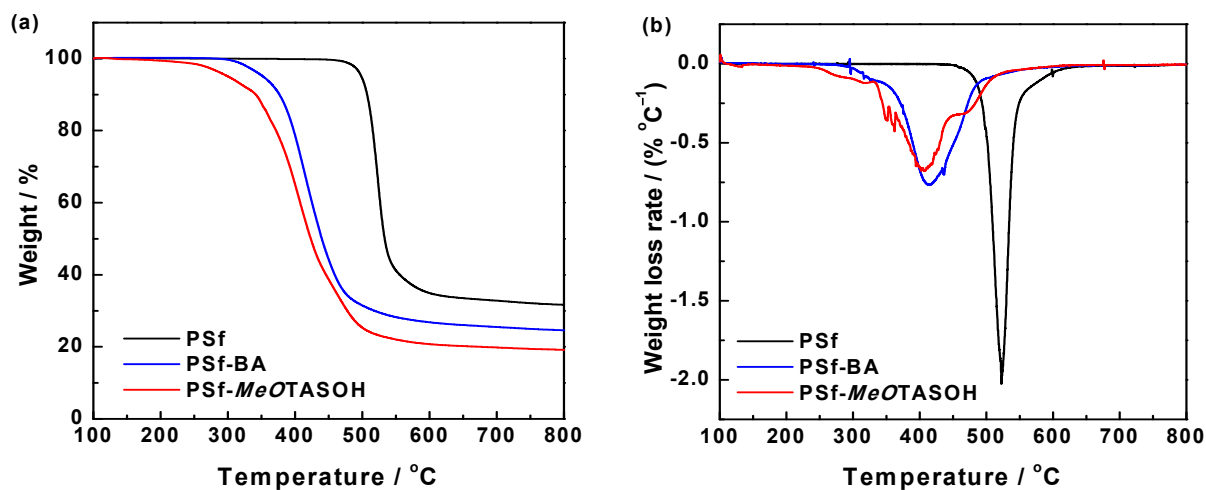


Figure S7. Thermal gravimetric analysis (TGA) curves (a) and derivative thermal gravimetric (DTG) curves (b) of the pristine PSf (black line), butylaminated PSf (PSf-BA) (blue line) and PSf-MeOTASOH (red line). Test conditions: nitrogen atmosphere with 20 mL min⁻¹ of flow rate, and 10 °C min⁻¹ of heating rate.

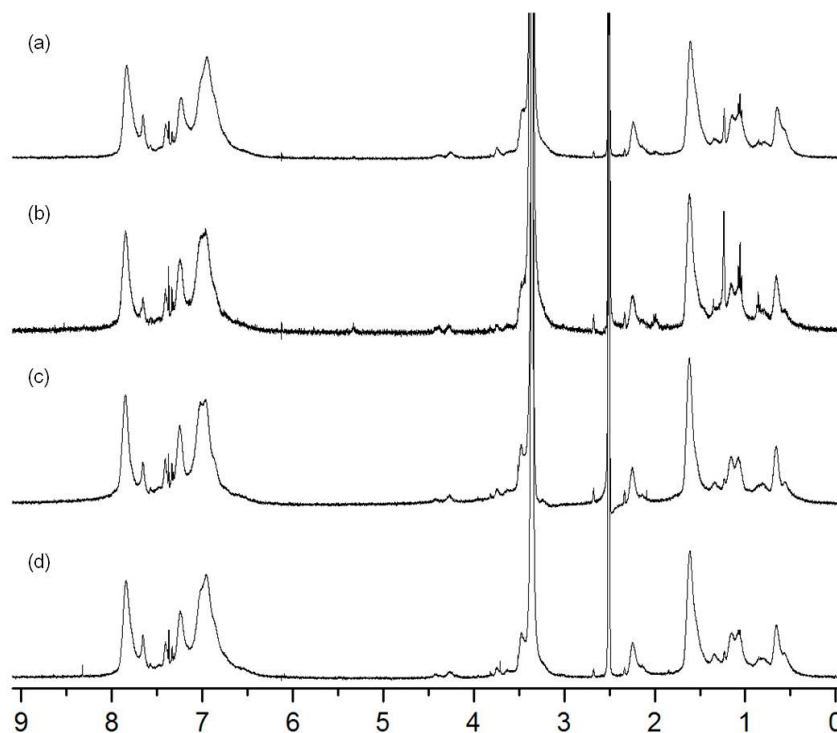


Figure S8. ^1H NMR spectra of PSf-MeOTAS polymer subjected to alkaline degradation test for different time. (a) 0 day or before test, (b) 1 day, (c) 5 days, and (d) 10 days. Deuterated dimethyl sulfoxide ($\text{DMSO-}d_6$) as solvent and tetramethylsilane (TMS) as internal standard. Test conditions: 1 M KOD/ D_2O for test solution and 60 °C for test temperature.

(a) (b)

Scheme S1. Chemical structures of two model compounds: MeOTAS (a) and MeO-free TAS (b).

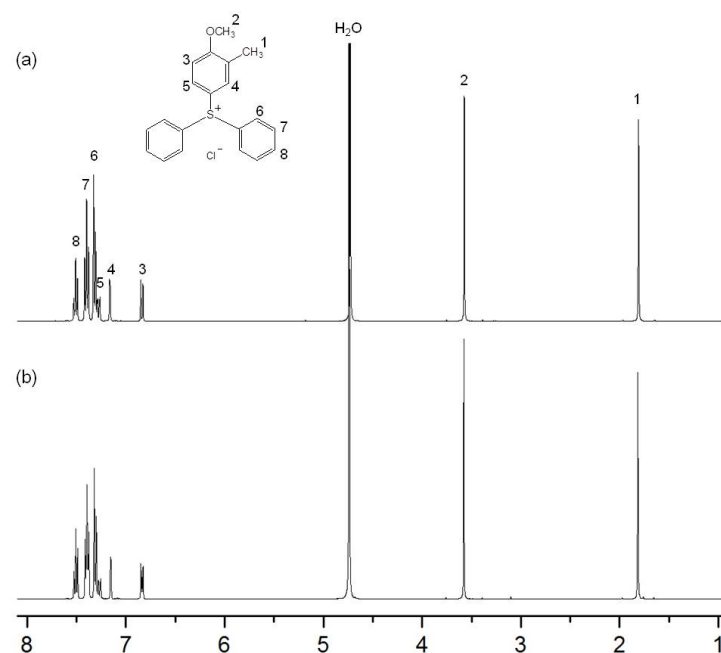


Figure S9. ^1H NMR spectra of MeOTAS cation compound. (a) before alkaline degradation test, and (b) after degradation test. Deuterated water (D_2O) as solvent and tetramethylsilane (TMS) as internal standard. Test conditions: 1 M KOD/ D_2O for test solution, 60 °C for test temperature, and 10 days for test time period.

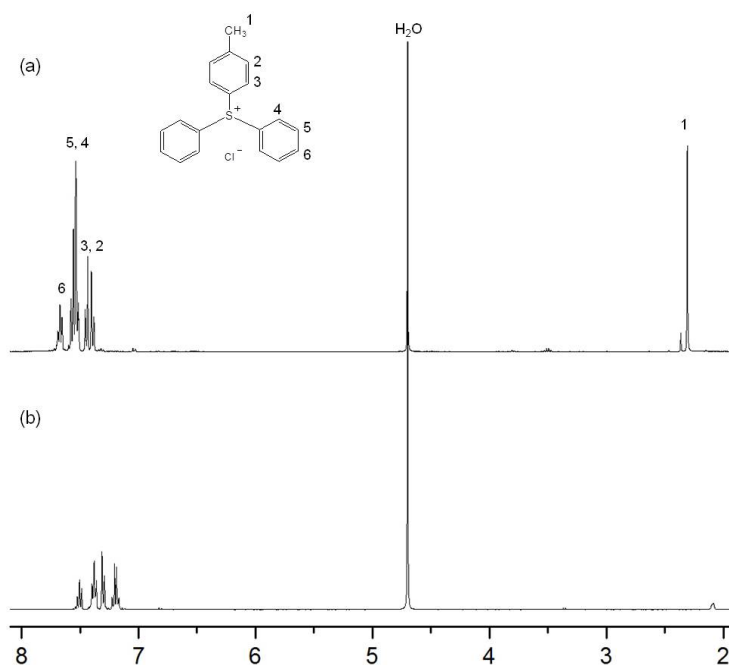


Figure S10. ^1H NMR spectra of MeO-free TAS cation compound. (a) before alkaline degradation test, and (b) after alkaline degradation test. Deuterated water (D_2O) as solvent and tetramethylsilane (TMS) as internal standard. Test conditions: 1 M KOD/ D_2O for test solution, 60 °C for test temperature, and 10 days for test time period.

1. S. Gu, R. Cai, T. Luo, Z. W. Chen, M. W. Sun, Y. Liu, G. H. He and Y. S. Yan, *Angew. Chem., Int. Ed.*, 2009, **48**, 6499-6502.