Supplementary Material (ESI) for Chemical Communications

Supplementary information

Aromatic ionomers with superacid groups

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Polymerization

A typical procedure is as follows. A 100 mL three-necked round-bottom flask equipped with a nitrogen inlet and magnetic stirrer was charged with 2,7-diiodo-9,9-bis(4-hydroxyphenyl)fluorene (1.806 g, 3 mmol, see *Russ. J. Org. Chem.* 2006, **42**, 1873-1876 for preparation), decafluorobiphenyl (1.002 g, 3 mmol, TCI Co., Inc.), potassium carbonate (1.036 g, 7.5 mmol, Kanto Chemical Co., Inc.) and N,N-dimethylacetamide (DMAc, 9 mL, Kanto Chemical Co., Inc.). The mixture was stirred at 90 °C for 18 h under nitrogen. Then the mixture was cooled to room temperature and precipitated from 300 mL of deionized water. The crude product was filtered, washed with hot water and methanol several times, and dried under vacuum at 80 °C for 16 h to obtain **1a** (R = I) in 86% yield.

Perfluorosulfonation

A typical procedure is as follows. A 100 mL three-necked round-bottom flask equipped with a nitrogen inlet, a dropping funnel and magnetic stirrer was charged with **1a** (R = I) (0.896 g), copper nanopowder (0.636 g, Aldrich Chemical Co.), DMAc (10 mL). The mixture was stirred at 120 °C for 4 h. After the dropwise addition of potassium 5-iodooctafluoro-3-oxapentanesulfonate (1.38 g) solution in 10 mL of DMAc, the mixture was stirred at 160 °C for 40 h (potassium 5-iodooctafluoro-3-oxapentanesulfonate was prepared by the hydrolysis of 5-iodooctafluoro-3-oxapentanesulfonyl fluoride (Aldrich Chemical Co.)). The reaction mixture was cooled to room temperature and precipitated from hot 1 M HNO_3. The crude product was filtered, purified by reprecipitation from DMAc / 1 M HNO_3 several times, and wash with deionized water. The resulting product was dried under vacuum at 80 °C for 16 h to give a pale yellow powder of **2a**.

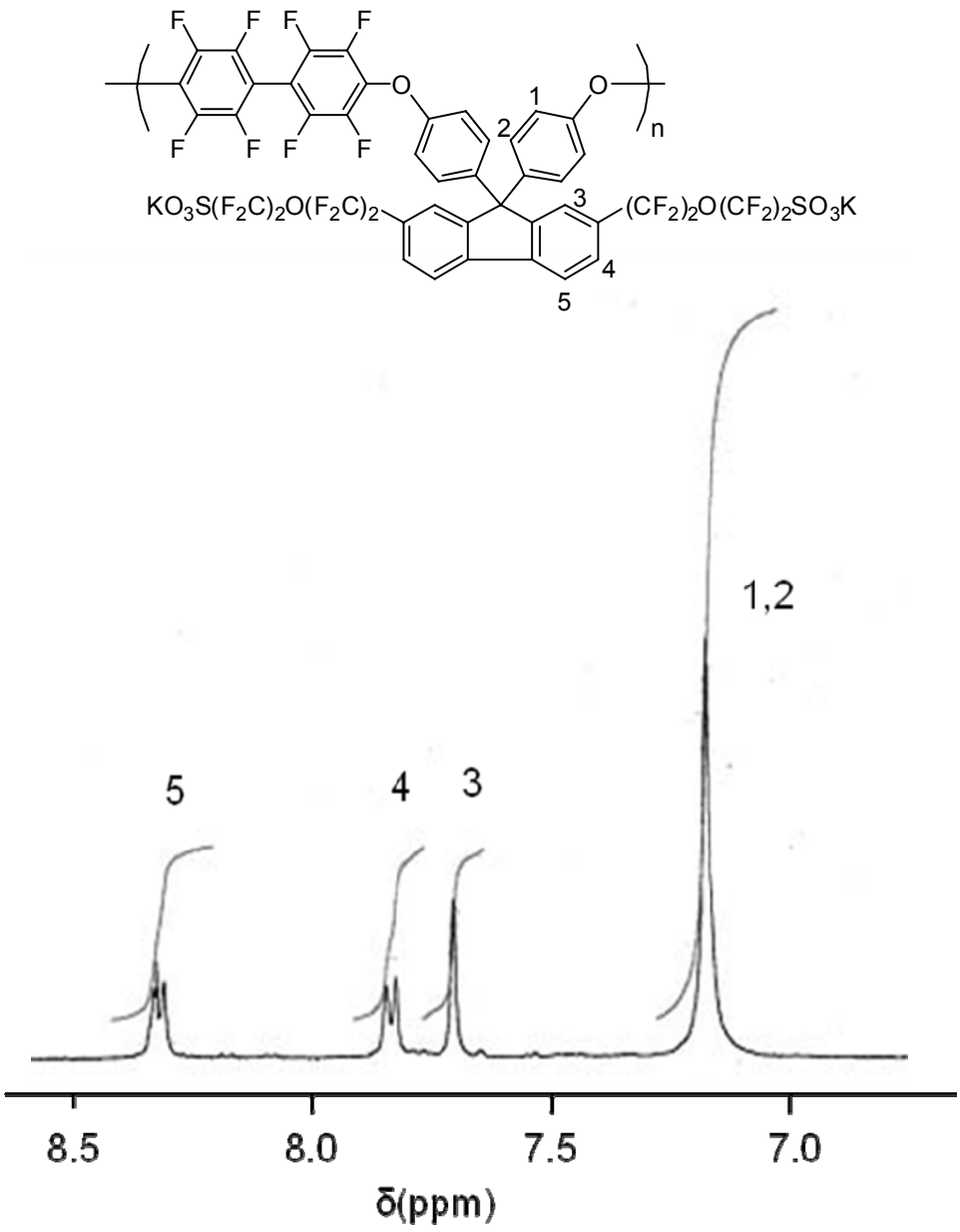

Fig. S1 ^{1}H NMR spectrum of **2a** (IEC = 1.52 meq/g) in DMSO-d_6.

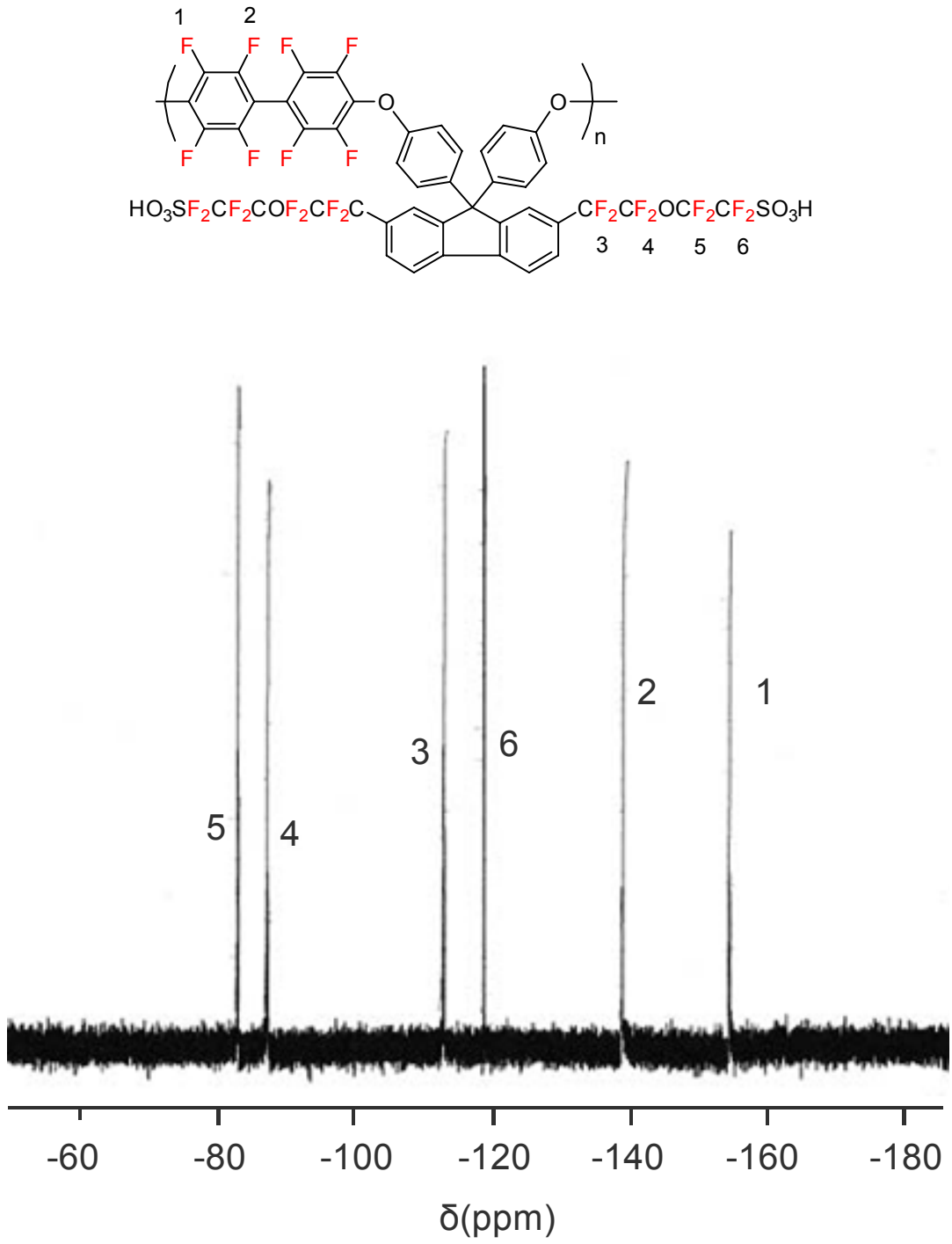

Fig. S2 ^{19}F NMR spectrum of **2a** (IEC = 1.52 meq/g) in DMSO-d_6.

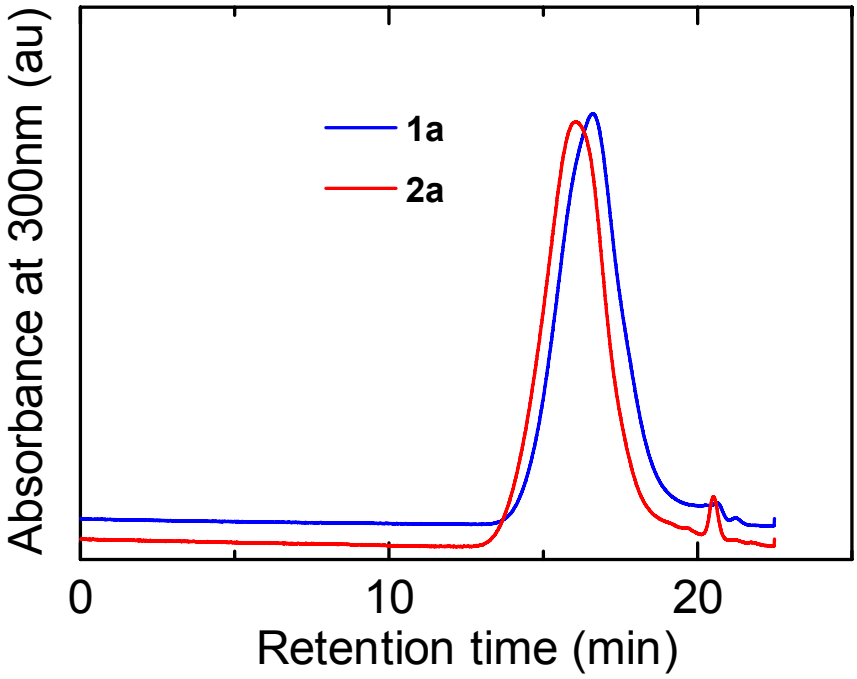

Fig. S3 GPC elution curves of **1a** and **2a** (IEC = 0.76 meq/g). The eluent was DMF containing 0.01M LiBr.

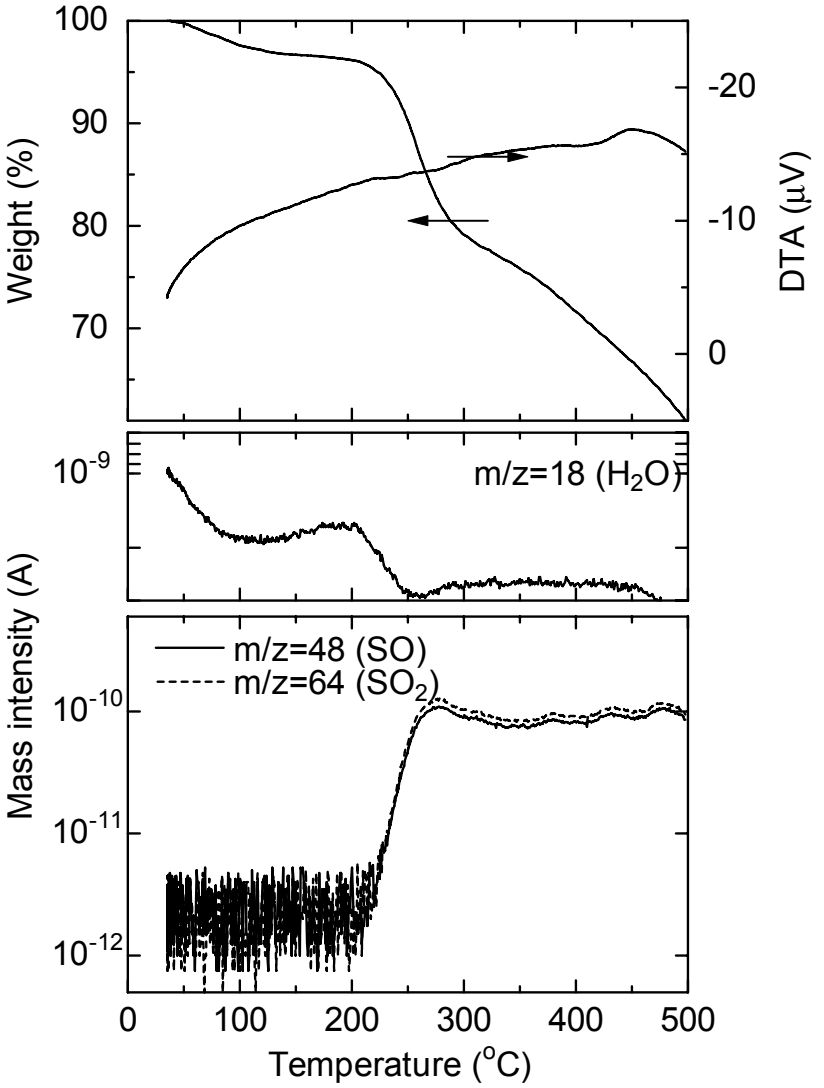

Fig. S4 TG/DTA-MS curves of **2a** (IEC = 0.76 meq/g) under Ar.