Electronic Supplementary Information (ESI)

Improving poly(arylene piperidinium) anion exchange membranes by monomer design

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1. Experimental description of monomer, polymer and membrane characterizations

Membrane preparation and ion exchange. AEMs in the I⁻ or Br⁻ form were prepared from 5% solutions of the respective polymer (0.15 g) in NMP (3 mL). The polymer solution was passed through a syringe filter (Millex LS, 5 μm) onto a clean Petri dish (ϕ = 50 mm), and the AEM was allowed to form in a ventilated casting oven at 80 °C during 48 h. Subsequently, the membranes were detached from the dishes by soaking in H_2O before stored in 1 M aq. NaBr solution for 72 h. Finally, the membranes were washed repeatedly with deionized water to remove the excess NaBr salt and kept in deionized water before further characterizations.

Structural characterization. The ^1H NMR spectra of monomer TFPip and polymers were acquired by a Bruker DRX 400 spectrometer using either DMSO-d_6 (δ = 2.50 ppm) or a mixture of DMSO-d_6 and TFA. The use of TFA (5 vol%) was to shift the water signal downfield and protonated any present secondary or tertiary amines, arose from either incomplete quaternization or degradations, resulting in signals above δ = 9 ppm.

An Ubbelohde viscometer was used to measure the intrinsic viscosity ([η]) of the polymers at 25 °C. Polymer stock solutions with a concentration of 0.1 g dL^{-1} were prepared with samples in the Br⁻ form, using 0.1 M LiBr in DMSO solution (blank solution). The stock solution was further diluted with the blank solution to prepare three samples with different concentrations (c_s). Each measurement was repeated four times and the average efflux time for the blank solution (t_b) and polymer solutions (t_s) was recorded. The inherent (η_{inh}) and reduced (η_{red}) viscosities were calculated as:

$$\eta_{inh} = \frac{\ln\left(\frac{t_s}{t_b}\right)}{c} \qquad (1),$$

$$\eta_{red} = \frac{\frac{t_s}{t_b} - 1}{c} \qquad (2).$$

From the plot of [η] as a function of c, the intrinsic viscosity was calculated by extrapolating η_{inh} and η_{red} to c = 0, and taking the intersection value with the y-axis.

Thermal characterization. Thermogravimetric analysis (TGA) of the AEMs and precursor polymers in the Br⁻ and triflate form, respectively, was performed using a TGA Q500 (TA Instruments). The analysis was carried out under a nitrogen atmosphere from 50 to 600 °C with a heating rate of 10 °C min^{-1}. To remove any residual solvents, the samples were preheated at 150 °C and equilibrated for 20 min prior to measurements. The thermal decomposition temperature ($T_{d,95}$) was determined at 5% weight loss.

Ion exchange capacity and water uptake evaluation. The ion exchange capacity (IEC) of the AEMs in the Br⁻ form (IEC$_{Br}$)was evaluated by Mohr titrations. The samples were dried at 50 °C under vacuum for 48 h and precisely weighed. Subsequently, the samples were soaked in 25 mL

0.2 M aq. NaNO$_3$ solutions for 72 h at 50 °C. Afterwards, the supernatant solutions (5 mL) were titrated with 0.01 M aq. AgNO$_3$ using 0.1 M aq. K$_2$CrO$_4$ as indicator. The titration was repeated three times for each sample, and IEC$_{Br}$ values were calculated by taking the average of the endpoints. The IECs of the AEMs in the OH$^-$ form (IEC$_{OH}$) were calculated from IEC$_{Br}$:

$$IEC_{OH} = \frac{IEC_{Br}}{1 - 0.0629 \times IEC_{Br}} \tag{3}.$$

Water uptake (WU) and swelling ratio (SW) values of the AEMs in the OH$^-$ form were measured after equilibration at different temperatures. As illustrated above, samples in Br$^-$ form were dried before measuring the weight ($m_{dry,Br}$), thickness ($t_{dry, Br}$), and length ($l_{dry, Br}$) before immersing in 1 M aq. NaOH for at least 48 h, and the basic solution was changed three times to ensure complete ion exchange. The samples were quickly rinsed with degassed deionized water until pH became neutral, and then equilibrated at 20 °C for 24 h, and 40−80 °C for 8 h, in degassed deionized water under nitrogen atmosphere. The surface water of samples was wiped quickly with tissue paper before measuring the weight ($W_{wet, OH}$), length ($l_{wet, OH}$), and thickness ($t_{wet, OH}$) in the hydrated state. Dry weight ($W_{dry, OH}$) of samples was calculated using the titrated IEC$_{Br}$ as:

$$W_{dry,OH} = W_{dry,Br} \times (1 - 0.0629 \times IEC_{Br}) \tag{4}.$$

The water uptake value was calculated as:

$$WU = \frac{W_{wet,OH} - W_{dry,OH}}{W_{dry,OH}} \times 100\% \tag{5}$$

, while the swelling ratio values were calculated as:

$$SW_{in-plane} = \frac{l_{wet,OH} - l_{dry,Br}}{l_{dry,Br}} \times 100\% \tag{6},$$

$$SW_{through-plane} = \frac{t_{wet,OH} - t_{dry,Br}}{t_{dry,Br}} \times 100\% \tag{7}.$$

Small angle X-ray scattering. The morphology and phase separation of dry AEMs in the Br$^-$ form was investigated by small angle X-ray scattering (SAXS) using SAXLAB ApS system (JJ-Xray, Denmark) equipped with a Pilatus detector. The scattering vector (q) was calculated according to equation (8), in which l represents the scattering wavelength of the Cu K(α) radiation (1.542 Å) and the 2θ represents the scattering angle:

$$q = \frac{4\pi}{l \ \sin 2\theta} \tag{8}.$$

The distance between the ionic clusters (d) was calculated according to Bragg's law:

$$d = \frac{2\pi}{q}$$ (9).

Hydroxide conductivity. The hydroxide ion conductivity of fully hydrated AEMs between 20 to 80 °C was measured using electrochemical impedance spectroscopy with a Novocontrol high-resolution dielectric analyzer V 1.01S. Data were recorded at a constant voltage of 50 mV and the frequency was varied between 10^0 to 10^7 Hz. Samples in the OH⁻ form were prepared as described above and stored in degassed deionized water under N₂ prior to the measurements. Two samples of each AEM were measured, and the average value of the two measurements was reported.

Alkaline stability. The chemical stability of the AEMs were evaluated by immersion in 2 M and 5 M aq. NaOH at 90 °C. Samples were taken out after different time intervals and ion-exchanged to the Br⁻ form and washed as described above. Subsequently, the samples were thoroughly dried under vacuum at 50 °C, before dissolution in DMSO-d_6 and TFA (5 vol%) and analysis by ¹H NMR spectroscopy. The degree of ionic loss was estimated by comparing the integral of the emerging signals of the degradation products with the intensity of the full aromatic region.
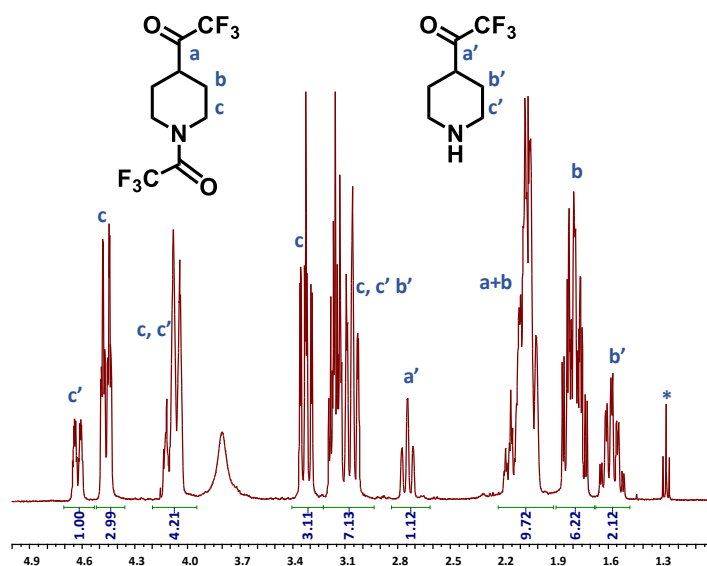
2. Figures and tables

Fig. S1 ¹H NMR spectrum of the isolated intermediate obtained by flash column chromatography, recorded in CDCl₃.

Table S1. HRMS[a] result of TFPip in the hydrochloric salt form.

Formula	Ion.	Found m/z	Predicted m/z	mDa*	ppm*
$C_7H_{11}NOF_3Cl$	-Cl$^-$	182.0793	182.0793	0.0	0.0

[a]HRMS was conducted on a Micromass QTOF mass spectrometer. The sample was dissolved in water and diluted with methanol. The identity was confirmed within 2 mDa and 3 ppm.
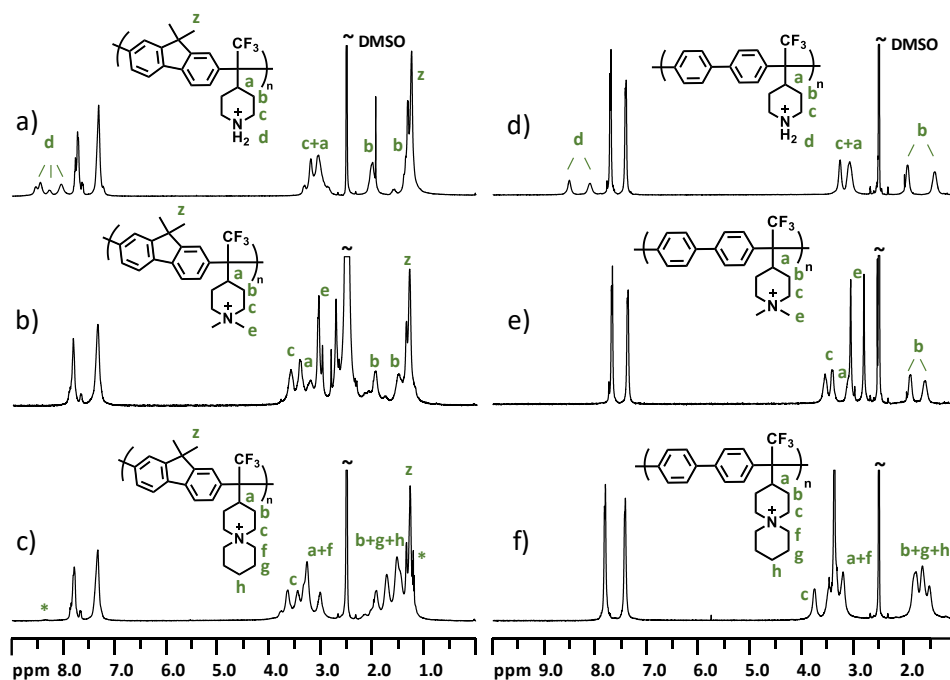

Fig. S2 ^{1}H NMR spectra of the precursors and cationic polymers based on (a-c) dimethylfluorene and (d-f) biphenyl, recorded in DMSO-d_6 with 5% TFA. Signals marked with an asterisk in figure c correspond to traces of DIPEA.
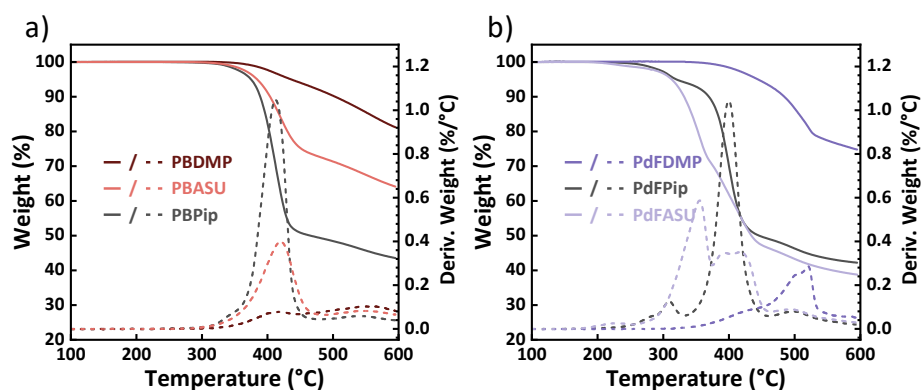
Fig. S3 TGA traces of the precursors based on (a) biphenyl and (b) dimethylfluorene in the triflate form (TFSA$^-$) and the corresponding cationic polymers in the Br$^-$ form recorded under N$_2$ atmosphere at a heating rate of 10 °C min^{-1}.

Table S2. Thermal decomposition temperatures of AEMs based on biphenyl (B) and dimethylfluorene (dF), as measured by TGA.

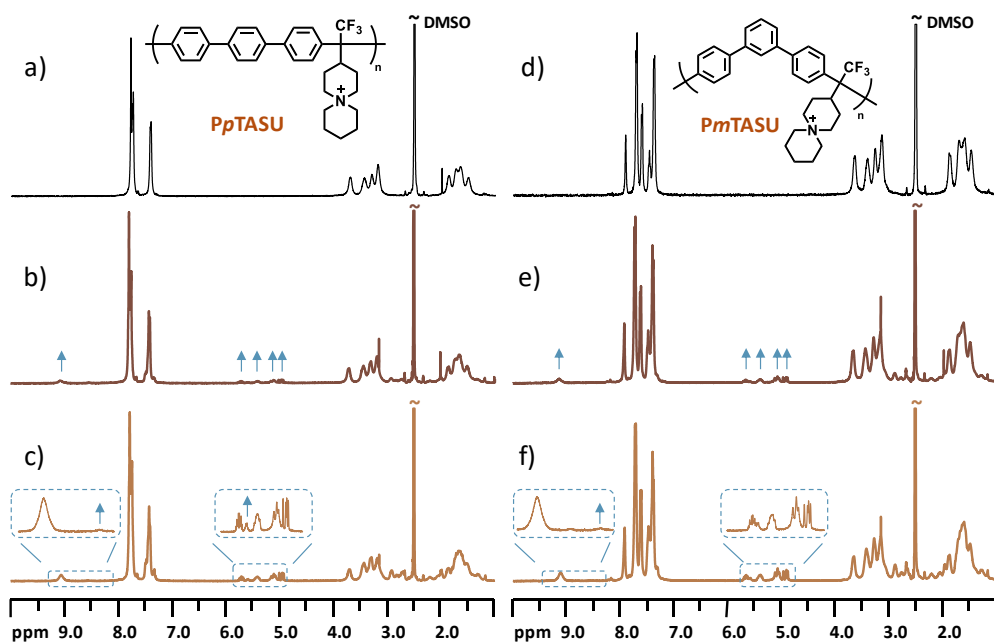| AEM	PBPip	PBDMP	PBASU	PdFPip	PdFDMP	PdFASU
$T_{d,95}$ (°C)	375	436	384	320	444	313

Fig. S4 ^{1}H NMR spectra of (a-c) P*p*TASU and (d-f) P*m*TASU AEMs before and after storage in 5 M aq. NaOH at 90 °C for 10 and 20 days. Spectra were recorded in DMSO-d_6 with 5% TFA.
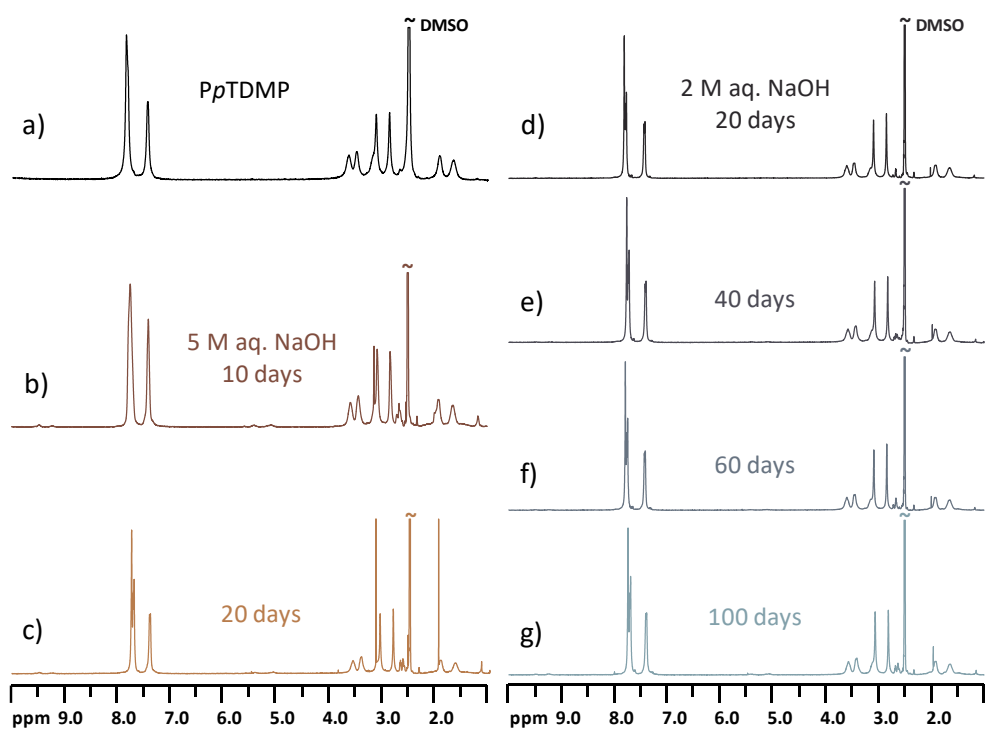
Fig. S5 Overview of the alkaline stability of P*p*TDMP characterized by ¹H NMR spectroscopy under various conditions: (a) pristine; (b-c) 5 M aq. NaOH at 90 °C for 10 and 20 days; (d-g) 2 M aq. NaOH at 90 °C for 20−100 days.
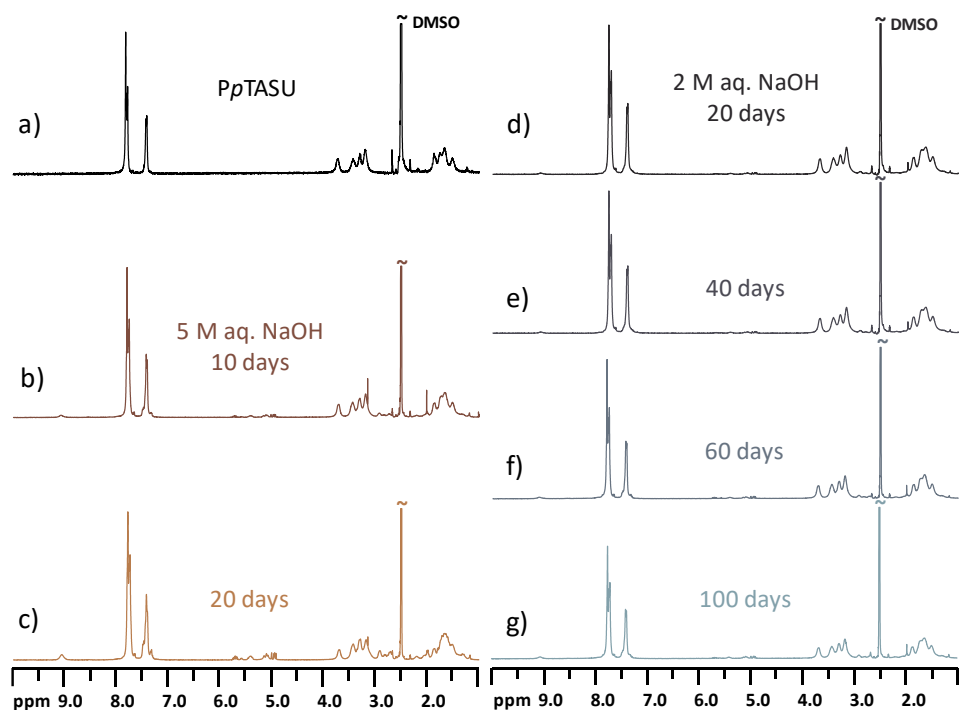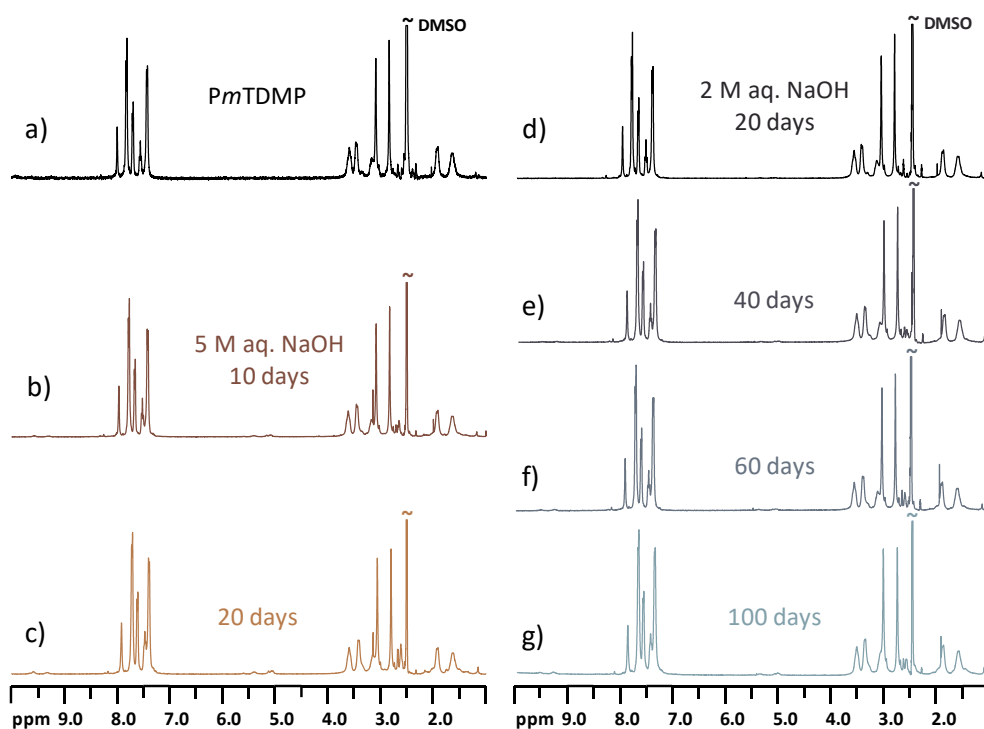

Fig. S6 Overview of alkaline stability of P*p*TASU characterized by ¹H NMR spectroscopy under various conditions: (a) pristine; (b-c) 5 M aq. NaOH at 90 °C for 10 and 20 days; (d-g) 2 M aq. NaOH at 90 °C for 20−100 days.
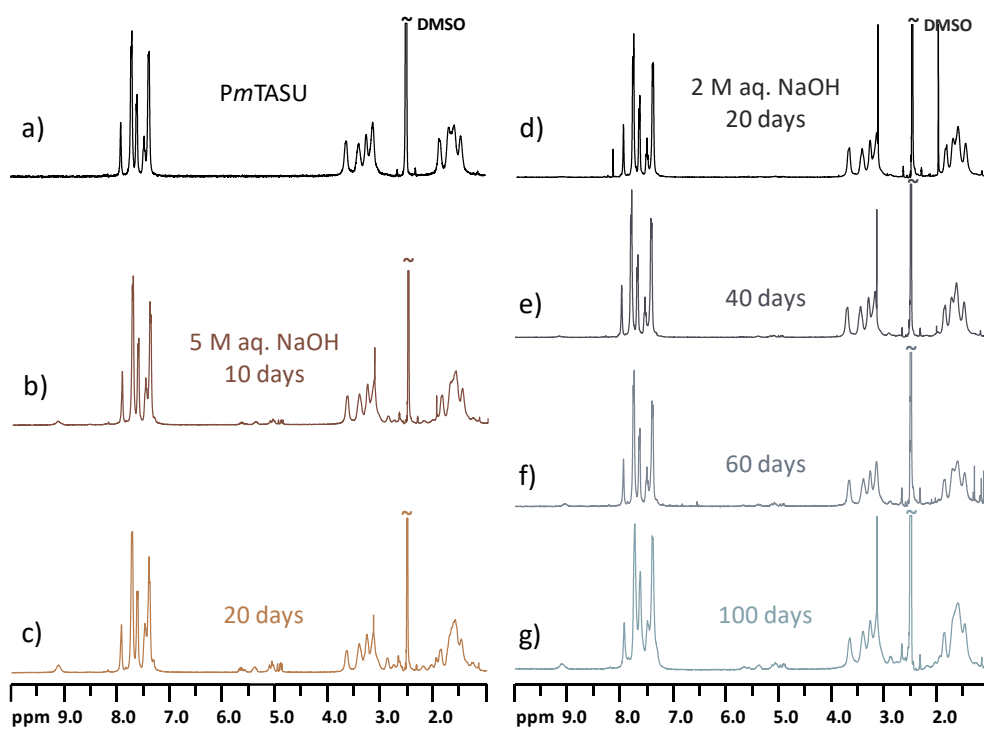
Fig. S7 Overview of alkaline stability of P*m*TDMP characterized by ^{1}H NMR spectroscopy under various conditions: (a) pristine; (b-c) 5 M aq. NaOH at 90 °C for 10 and 20 days; (d-g) 2 M aq. NaOH at 90 °C for 20−100 days.

Fig. S8 Overview of alkaline stability of P*m*TASU characterized by ^{1}H NMR spectroscopy under various conditions: (a) pristine; (b-c) 5 M aq. NaOH at 90 °C for 10 and 20 days; (d-g) 2 M aq. NaOH at 90 °C for 20−100 days.
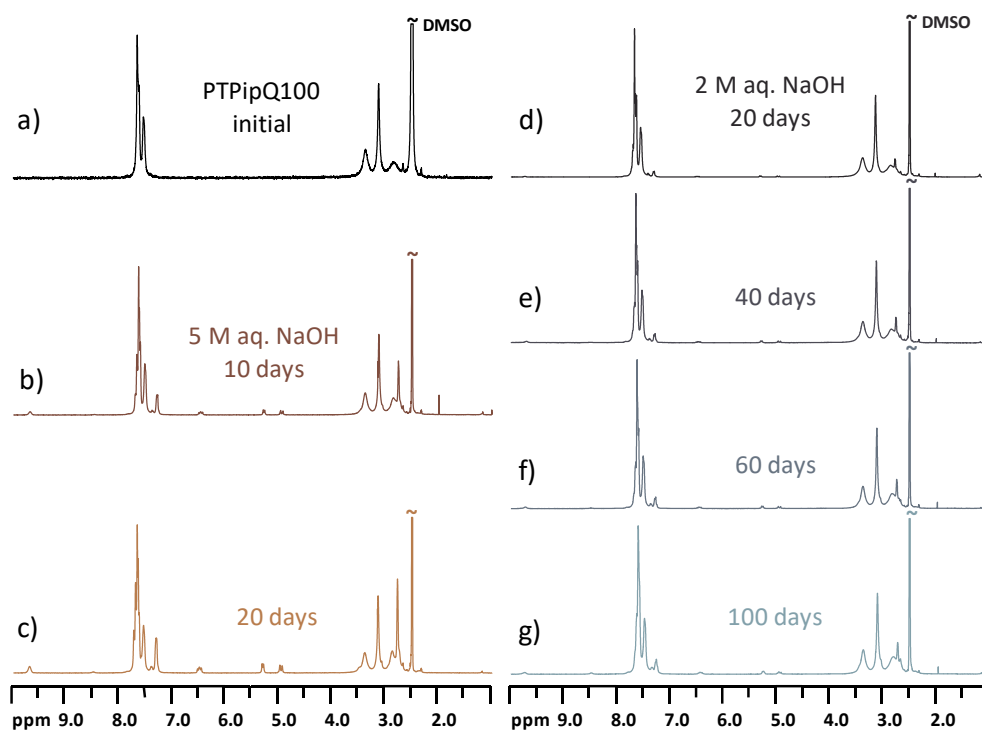
Fig. S9 Overview of alkaline stability of the reference PTPipQ100 characterized by ^{1}H NMR spectroscopy under various conditions: (a) pristine; (b-c) 5 M aq. NaOH at 90 °C for 10 and 20 days; (d-g) 2 M aq. NaOH at 90 °C for 20−100 days.
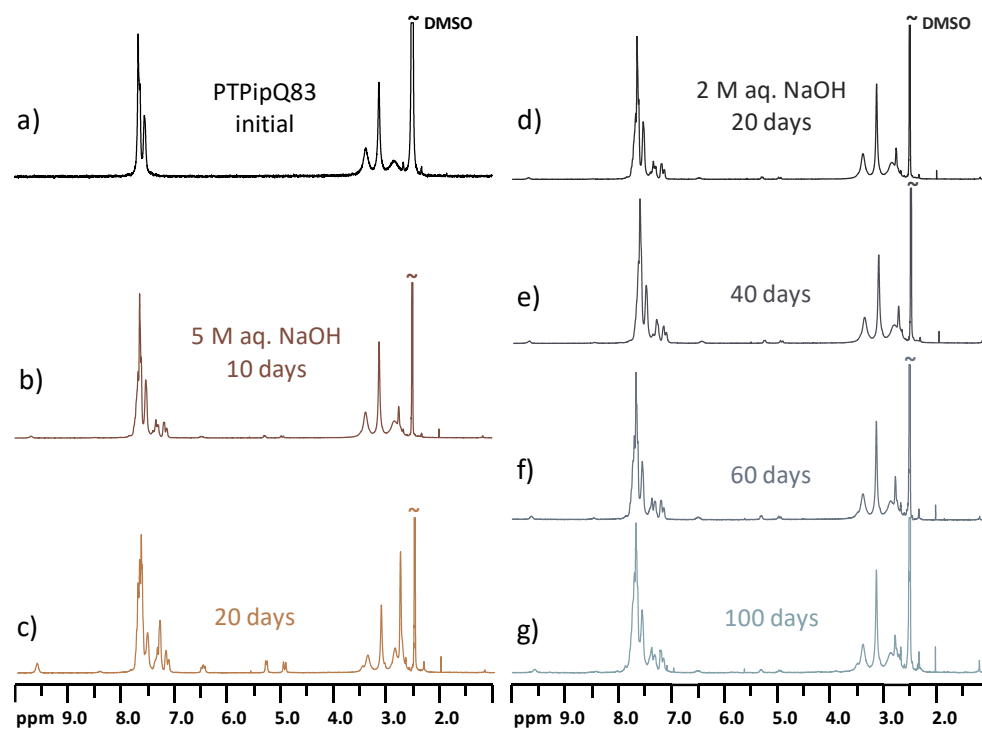

Fig. S10 Overview of alkaline stability of the reference PTPipQ83 characterized by ^{1}H NMR spectroscopy under various conditions: (a) pristine; (b-c) 5 M aq. NaOH at 90 °C for 10 and 20 days; (d-g) 2 M aq. NaOH at 90 °C for 20−100 days.