Supporting Information

Incorporating chrysene units to improve the performance of poly(arylene piperidinium) and poly(arylene quinuclidinium) anion exchange membranes for water electrolysis

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1. Materials and experimental methods

1.1. Materials

Trifluoromethanesulfonic acid (TFSA, 99 %), trifluoroacetic acid (TFA, 99 %), *p*-terphenyl (99 %), iodomethane (98% with stabilizer), *N*-methyl-4-piperidone (98 %), *N*-methyl-2-pyrrolidone (NMP, reagent grade), dimethyl sulfoxide-*d*$_6$ (DMSO-*d*$_6$, 99.96% D), chloroform-*d* ($CDCl_3$, 99.8% D), sodium hydroxide (NaOH, ACS reagent, 97%, pellets), potassium carbonate (K_2CO_3, ≥99%), methyl iodide, dimethyl sulfoxide (DMSO, reagent grade) were purchased from Sigma Aldrich. Chrysene (98%) was purchased from Aaron chemicals, and 3-quinuclidone hydrochloride (98%) was purchased from Thermo Scientific Chemicals. Diethyl ether (ACS reagent grade), anhydrous sodium sulfate (Na_2SO_4, 99.5%), and anhydrous sodium bromide (NaBr, 99%) were purchased from VWR. All chemicals were used as received. Dichloromethane (DCM) for polymerization was collected from an MBraun MB-SPS 800 dry solvent dispensing system.

1.2. Synthesis of *pre*-PCP-*x*

The precursor polymers *pre*-PCP-*x*, where *x* denotes the molar fraction of chrysene units in the polymers, were synthesized via superacid-mediated polyhydroxyalkylation reactions. In the *pre*-PCP-*x* series, the chrysene content was varied by adjusting the *p*-terphenyl:chrysene feed ratio. As a representative example, the synthesis of *pre*-PCP-0.50 is described below. In a 25 mL one-necked round-bottom flask, chrysene (0.285 g, 0.00125 mol), *p*-terphenyl (0.288 g, 0.00125 mol), and *N*-methyl-4-piperidone (0.37 mL, 0.00325 mol) were dissolved in DCM (2.6 mL). The mixture was cooled to 0 °C in an ice bath, followed by dropwise addition of TFA (0.19 mL, 0.0025 mol) and TFSA (2.65 mL, 0.03 mol), respectively. The reaction was then stirred at 0 °C. As the reaction progressed, the viscosity of the solution increased, eventually rising sharply and preventing efficient stirring. After 3 h, the reaction was quenched by precipitating the product in deionized water. The resulting precipitate was collected, thoroughly washed with water, and dried under vacuum at 50 °C for 24 h. For the synthesis of the other polymers in the *pre*-PCP-*x* series, the reaction time varied depending on the feed ratio.

1.3. Synthesis of *pre*-PCQ-*x*

The synthesis of the *pre*-PCQ-*x* precursor polymers was carried out using chrysene, *p*-terphenyl, and 3-quinuclidone. The different compositions in the *pre*-PCQ-*x* series were obtained by adjusting the arene monomer ratio. As a representative example, the synthesis of *pre*-PCQ-0.50 is described below. In a 25 mL one-necked round-bottom flask, chrysene (0.285 g, 0.00125 mol), *p*-terphenyl (0.288 g, 0.00125 mol), 3-quinuclidone hydrochloride (0.525 g, 0.00325 mol) were dissolved in DCM (1 mL). The mixture was cooled to 0 °C in an ice bath, followed by dropwise addition of TFA (0.19 mL, 0.0025 mol) and TFSA (2.65 mL, 0.03 mol), respectively. The reaction was then stirred at room temperature. As the reaction progressed, the viscosity of the solution increased, eventually rising sharply to prevent efficient stirring. After 40 h, the reaction was quenched by precipitating the product in deionized water. The resulting precipitate was collected, thoroughly washed with water, and dried under vacuum at 50 °C for 24 h. For the synthesis of the other polymers in the *pre*-PCQ-*x* series, the reaction time varied depending on the feed ratio.

1.4. Quaternization

The *pre*-PCP-*x*, and *pre*-PCQ-*x* precursor polymers were quaternized by Menshutkin reactions with methyl iodide using K_2CO_3 as a base to produce the final AEM polymers. The quaternizations of the piperidine- and quinuclidine-functional precursor polymers were similar. Here, the quaternization of *pre*-PCP-0.50 is described as an example. Sample *pre*-PCP-0.50 (1 g, 0.0020 mol of methyl piperidine group) and K_2CO_3 (1 g, 0.0072 mol) were added to a 25 ml round-bottom flask, followed by 10 ml NMP. Next, methyl iodide (1 ml, 0.0160 mol) was added to the solution, and the flask was covered with aluminum foil to protect the methyl iodide. The reaction solution was first stirred at room temperature for 48 h and then poured into diethyl ether to precipitate the polymer. After filtration and washing with DI water, the dried solid was redissolved in NMP and reprecipitated into chloroform. The product was collected by filtration and dried under vacuum at 50 °C for an additional 24 h. The final PCP-0.50 polymer product was obtained as a yellow powder.

The membrane preparation and ex-situ characterization followed the procedures reported in Luong, et al., J. Membr. Sci. 2025, 719, 123724.

1.5. Membrane preparation

AEMs in the iodide form were prepared by dissolving 0.15 g polymer in 3 ml NMP to achieve 5 wt% solutions. The solutions were filtered through syringe filters (0.45 μm, VWR) onto Petri dishes (∅ = 50 mm). The Petri dishes were then placed in a ventilated casting oven at 80 °C for 48 h. After casting, the membranes were peeled off from the dishes, repeatedly washed with water, and ion-exchanged by immersion in 1 M aq. NaBr for 78 h. Finally, the membranes were extensively washed with deionized water before being stored in deionized water until further characterization.

1.6. NMR spectroscopy

The structure of the polymers was characterized using ^1H NMR spectroscopy. Data were collected with a Bruker DRX 400 spectrometer. Polymer samples were dissolved in DMSO-d_6 (δ = 2.50 ppm), before adding TFA (approximately 5 vol%) to shift the water signal and protonate any tertiary amine formed by degradation of quaternary ammonium cations in the alkaline stability test.

1.7. Thermal characterization

Thermogravimetric analysis (TGA) was used to study the thermal stability of the precursor polymers and AEMs. The analyses were conducted on a TA Instruments TGA Q500 under N_2 atmosphere. Samples of the precursor polymers and AEMs in the bromide form were preheated to 110 °C for 20 min. The samples were then cooled to 50 °C and heated to 600 °C at a rate of

10 °C min^{-1}. Data were recorded during the heating process from 50 to 600 °C, and the decomposition temperature ($T_{d,95}$) was noted at the point of 5% weight loss.

1.8. Intrinsic viscosity

The intrinsic viscosity ([η]) of the polymers was measured at 25 °C by using an Ubbelohde viscometer. Polymer samples were dried at 50 °C for 2 days and weighed before dissolution of approximately 0.1 g polymer in 10 ml of 0.1 M LiBr solution in DMSO. The polymer concentration (c) of the solution was then successively reduced by adding 1, 2, and 2 ml, respectively, of 0.1 M LiBr in DMSO to obtain three additional concentrations. The efflux time of the blank solution (0.1 M LiBr in DMSO) and the different sample solutions through the capillary were recorded four times for each solution. The reduced (η_{red}) and inherent (η_{inh}) viscosities were calculated as:

$$\eta_{red} = \frac{\frac{t_{sample}}{t_{blank}} - 1}{c}$$

$$\eta_{inh} = \frac{ln(\frac{t_{sample}}{t_{blank}})}{c}$$

, where t_{sample} and t_{blank} are efflux times of the polymer solution and the blank, respectively, and c is the concentration of the polymer solution. The [η] values were then determined by the intercept at the y-axis after extrapolating η_{inh} and η_{red} to $c = 0$.

1.9. Ion exchange capacity

The ion exchange capacity (IEC) of the AEMs was determined by Mohr titrations. Approx. 30 mg of each AEM sample in the bromide form was dried under vacuum for 48 h at 50 °C. The samples were weighed before immersion in 25 ml of 0.2 M aq. $NaNO_3$ at 40 °C for 72 h to accomplish complete ion exchange. Each sample was titrated four times with 0.01 M aq. $AgNO_3$ by extracting 5 ml portions of the solutions, using 0.1 M aq. K_2CrO_4 as a color indicator. The reported IEC_{Br^-} values were obtained as the average of the four titrations. The IEC in the hydroxide form was calculated as:

$$IEC_{OH^-} = \frac{IEC_{Br^-}}{1 - 0.0629 \times IEC_{Br^-}}$$

1.10. Water and alkaline uptake

AEM samples in the bromide form were dried under vacuum and weighed to obtain m_{dry,Br^-}. The samples were then immersed in 1 M aq. NaOH for 48 h to ion-exchange to the hydroxide form.

For the water uptake measurements, the samples were quickly washed and stored in DI water at 20 °C. After 24 h, the samples were taken out and weighed to obtain $m_{\mathrm{wet,OH^-}}$. For measurements at 40, 60, and 80 °C, the samples were stored in DI water for 8 h after exchange to OH^- form before measuring the weight. The water uptake was calculated as:

$$WU = \frac{m_{wet,\,OH^-} - m_{dry,OH^-}}{m_{dry,OH^-}}$$

Where $m_{\mathrm{dry,OH^-}}$ was calculated from $\mathrm{IEC_{Br^-}}$ values as:

$$m_{\mathrm{dry,OH^-}} = m_{\mathrm{dry,Br^-}} \times (1 - 0.0629 \times \mathrm{IEC_{Br^-}})$$

For the alkaline solution uptake, the samples were stored in 2 M aq. KOH solution instead of DI water.

1.11. Swelling ratio.

The dimensional changes in length (l) and thickness (t) were measured alongside the water and alkaline uptake to determine the in-plane ($\mathrm{SW_i}$) and through-plane ($\mathrm{SW_{th}}$) swelling at 20, 40, 60, and 80 °C. The swelling ratios were then calculated as follows:

$$SW_i = \frac{l_{wet,OH^-} - l_{dry,Br^-}}{l_{dry,Br^-}}$$

$$SW_{th} = \frac{t_{wet,OH^-} - t_{dry,Br^-}}{t_{dry,Br^-}}$$

1.12. Ion conductivity

The hydroxide conductivity of the AEMs was measured at 20, 40, 60, and 80 °C by electrochemical impedance spectroscopy (EIS). AEM samples (1.4 × 1.4 cm) in the bromide form were prepared and immersed in 1 M aq. NaOH during 2 days at room temperature. The NaOH solution was replaced three times during the immersion. The samples were then washed thoroughly with degassed DI water and stored in degassed DI water overnight in a desiccator with nitrogen purge. The measurements were conducted after placing the samples in a sealed 2-probe cell in a Novocontrol high-resolution dielectric analyzer V 1.01S operating at 10 mV and a frequency between 10^0 and 10^7 Hz. The original thickness of the samples before the measurements was used to calculate the conductivity values. Moreover, measurements were carried out on three samples per reported conductivity value, and the average values were reported together with the population standard deviation.

1.13. Small angle X-ray scattering

To study the bulk morphology of the AEMs, small angle X-ray scattering of the dry AEMs in the bromide form was measured with a SAXSLAB SAXS instrument (JJ X-ray Systems Aps, Denmark) equipped with a Pilatus detector. The radiation was Cu Kα with wavelength (l) of 1.542 Å. The wave vector (q) was determined as:

$$q = \frac{4\pi sin\theta}{l}$$

, where 2θ is the scattering angle.

1.14. Atomic force microscopy

A Bruker Icon Atomic Force Microscope instrument with AC240TS-R3 tips was used to record the phase images of dry AEM samples in bromide form under the tapping mode.

1.15. Mechanical properties

Mechanical properties of the AEMs were evaluated by measuringthe stress-strain data of dry AEM samples in the bromide form using a TA Instruments Q800dynamic mechanical analysis (DMA) instrument. Rectangular samples (approx. 0.5 cm × 3 cm, 50–60 μm in thickness) were prepared and mounted between the tension clamps before applying a 0.01 N preload force. The measurements were then conducted with a ramping force of 0.5 N min^{-1} at 30 °C in a controlled force mode. Three samples per reported value were measured, and the stress-strain curve with the lowest strain at break was displayed for each AEM. For the wet-state measurements, the AEM samples in bromide form were immersed in DI water and taken out to be instantly measured.

1.16. Alkaline stability

AEM samples were placed in sealed pressure-resistant tubes filled with 2 and 5 M aq. NaOH solutions, respectively. The tubes were then stored at 90 °C for specified periods (20 or 40 days for different samples). After this period, the samples were taken out and converted to the bromide form by immersion in 1 M aq. NaBr solution at room temperature for 24 h. Next, the samples were washed with DI water and dried under vacuum. Any changes in the polymer structure were monitored by ^{1}H NMR spectroscopy of AEMs dissolved in DMSO-d_6 containing 5–10 vol% TFA. Spectra of samples before and after immersion in alkaline solution were compared to determine degradation mechanisms and the extent of ionic loss.

1.17. AEMWE performance and durability test

A 2.5 × 2.5 cm active area test cell was used to evaluate the AEMWE performance. The nickel foam electrode material was purchased from Redox Flow, Denmark. The 65 μm-thick PCQ-0.25 AEM and a 60 μm-thick commercial benchmark AEM (PiperION® 60) were evaluated in the cell. A 2 M aq. KOH electrolyte solution was circulated and fed into both the anode and the cathode with a flow rate of 2 mL min^{-1}. The cell was assembled at a torque of 6 Nm. Polarization curves were obtained by conducting Staircase Galvanostatic Electrochemical Impedance Spectroscopy (SGEIS) measurements using 100 mA stepwise increases in the current. EIS measurements were conducted in galvanocontrol (GEIS) modes at frequencies of 0.1 Hz to 100 kHz at a current density of 16 mA/cm^2. The long-term stability test was conducted at a constant current density of 500 mA cm^{-2} with electrolyte changes every 25 h. All electrochemical measurements were conducted using a VSP potentiostat, Bio-Logic, France.

2. Supplementary data

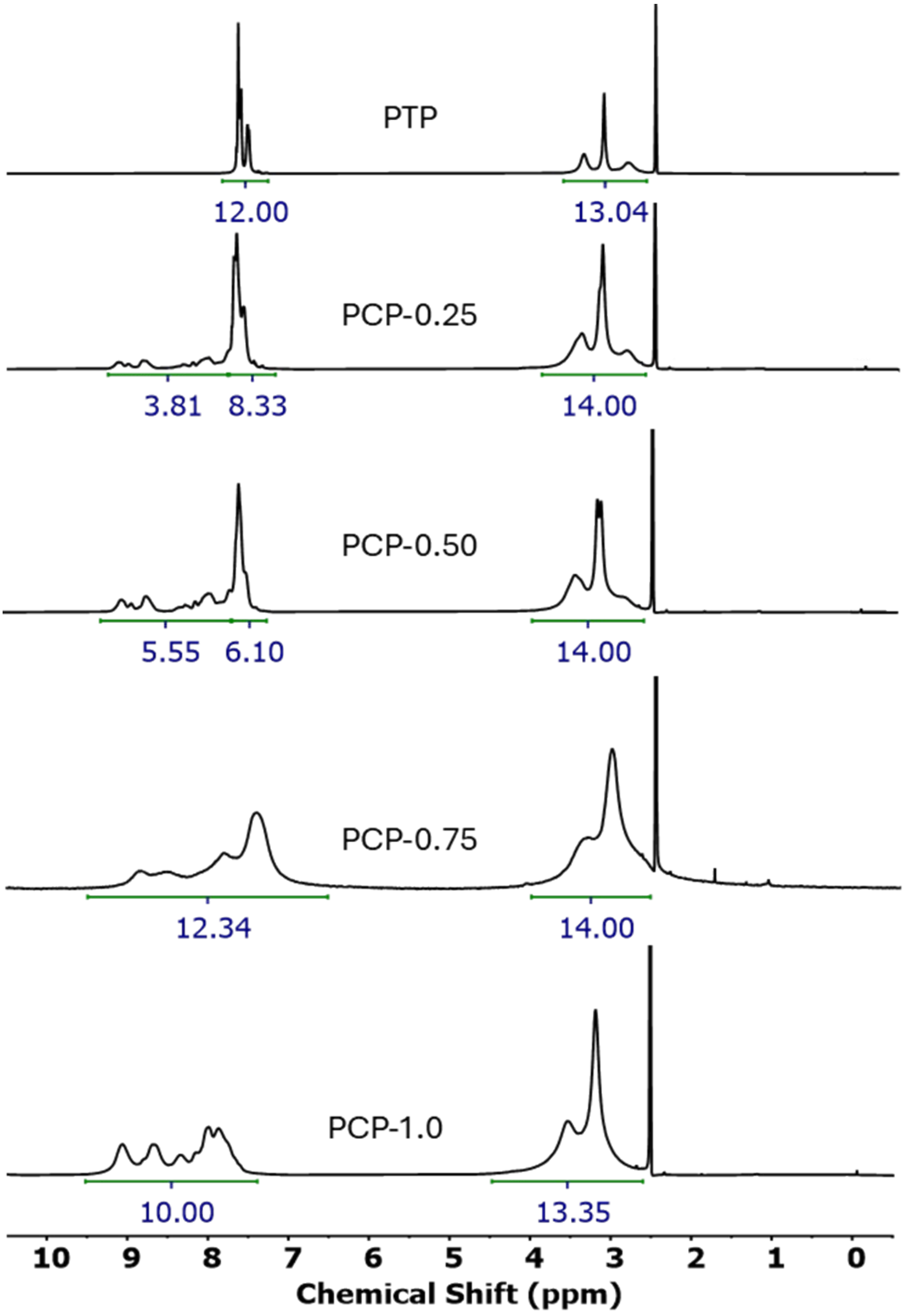


Figure S1. ^{1}H NMR spectra of the piperidinium-functionalized PTP and the PCP-*x* series of copolymers with different chrysene contents.

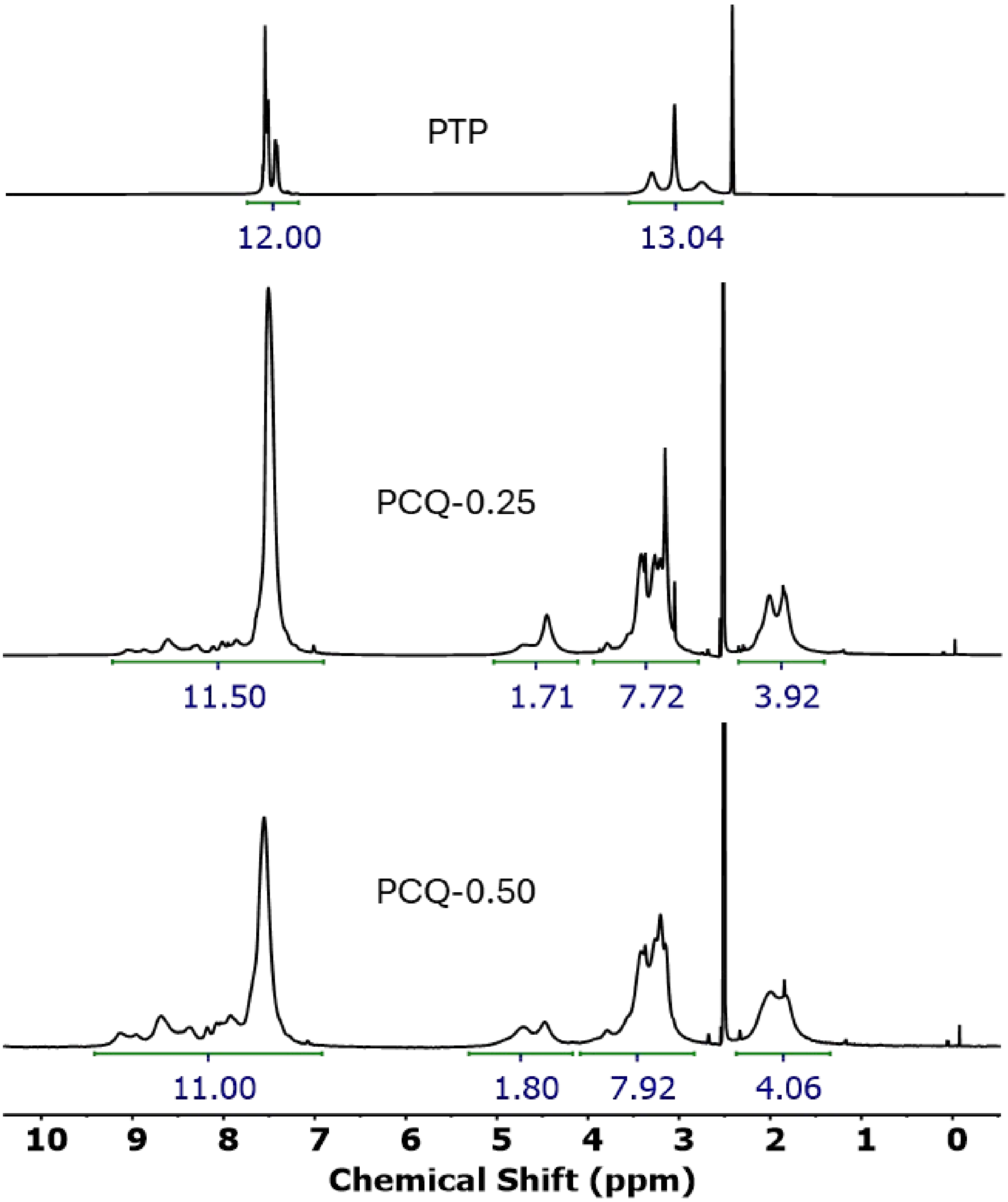


Figure S2. ^{1}H NMR spectra of the piperidinium-functionalized PTP and the quinuclidinium-functionalized PCQ-*x* series of copolymers with different chrysene contents.

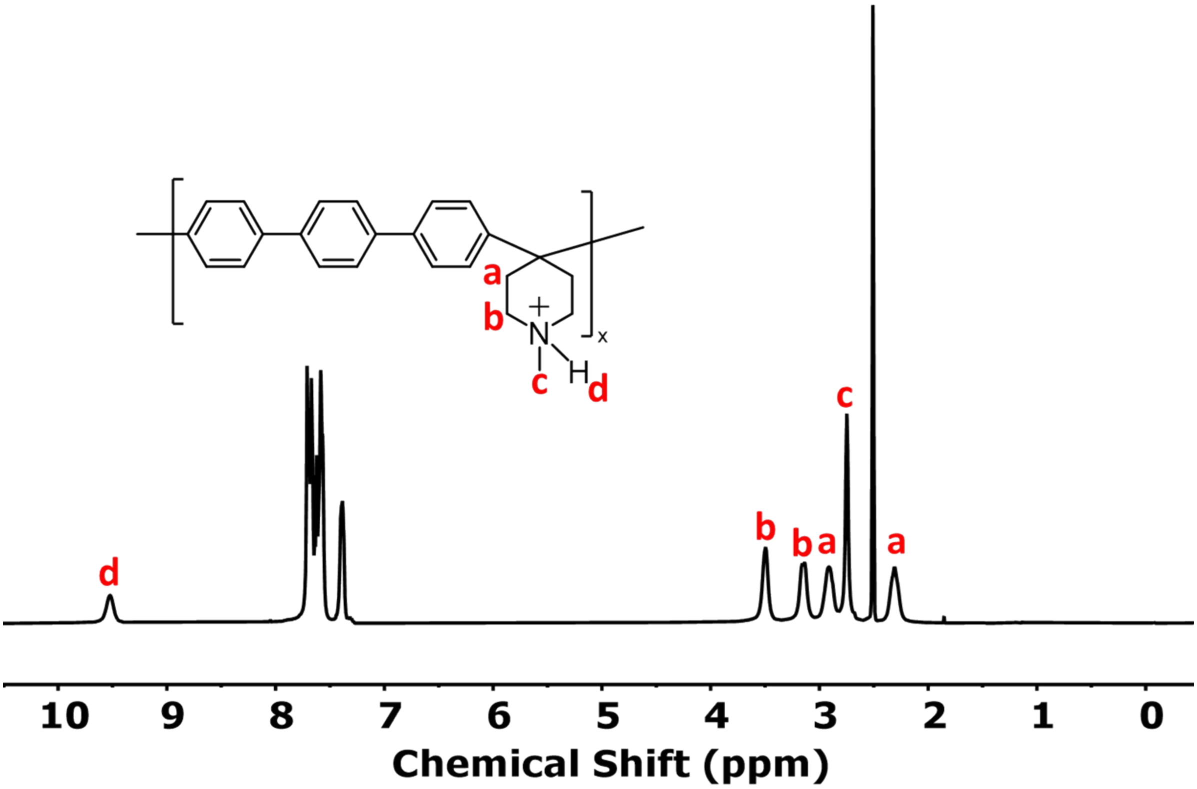


Figure S3. ^{1}H NMR spectrum of *pre*-PCP-0 in DMSO-d_6 with 5 vol% TFA.

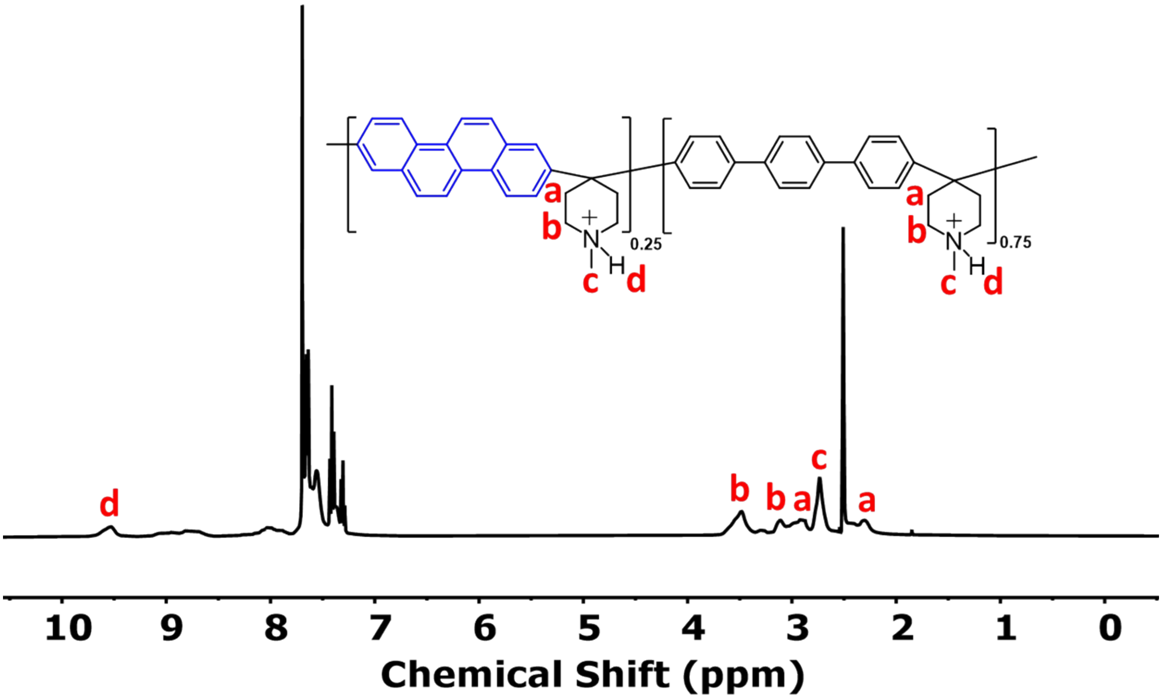


Figure S4. ^{1}H NMR spectrum of *pre*-PCP-0.25 in DMSO-d_6 with 5 vol% TFA.

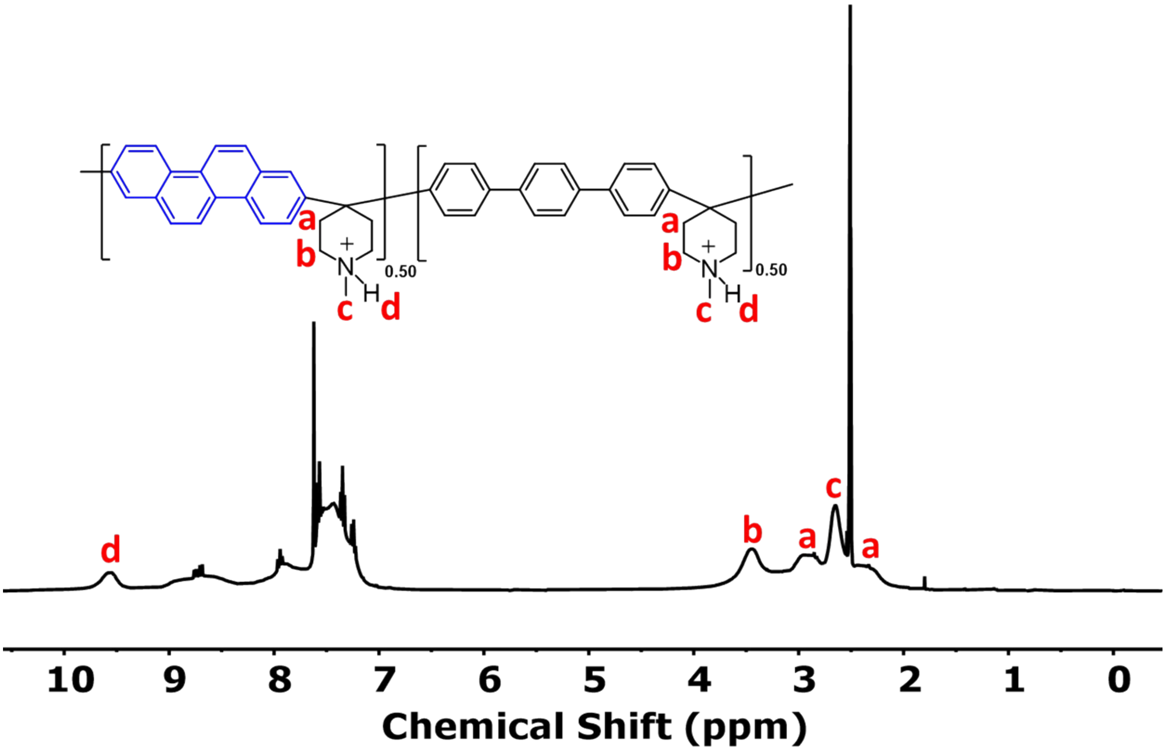


Figure S5. ^{1}H NMR spectrum of *pre*-PCP-0.50 in DMSO-d_6 with 5 vol% TFA.

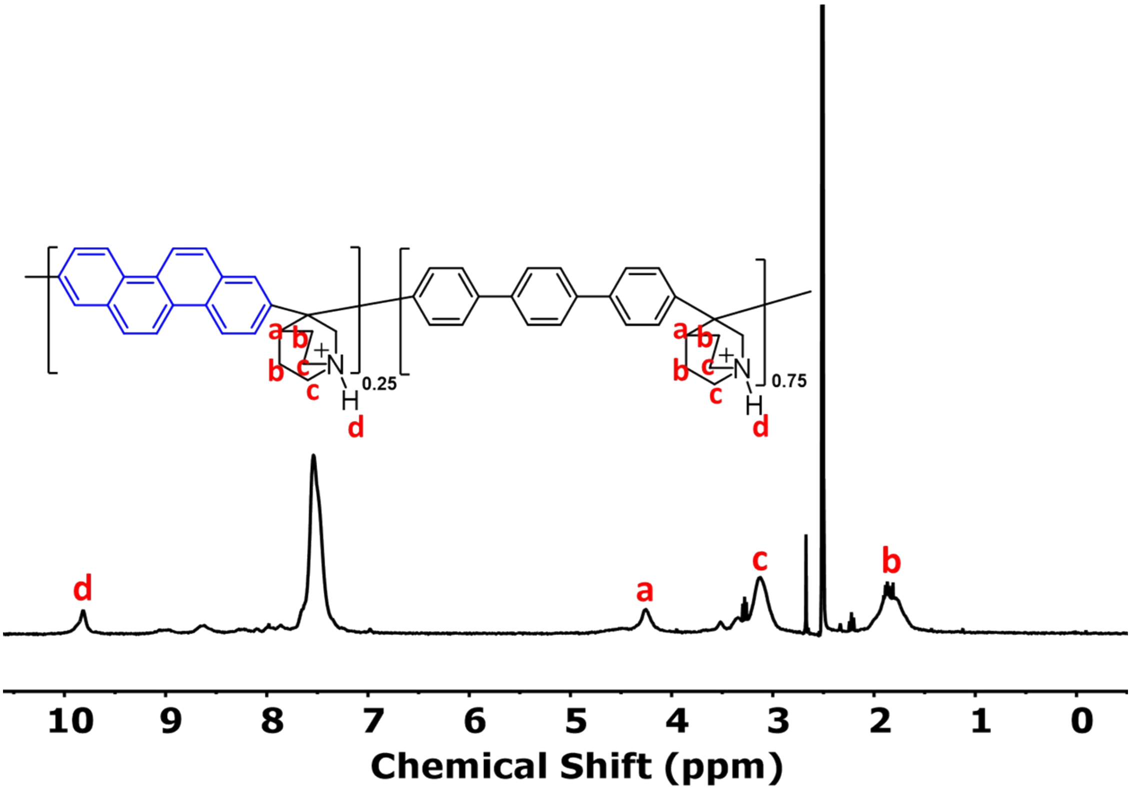


Figure S6. ^{1}H NMR spectrum of *pre*-PCQ-0.25 in DMSO-d_6 with 5 vol% TFA.

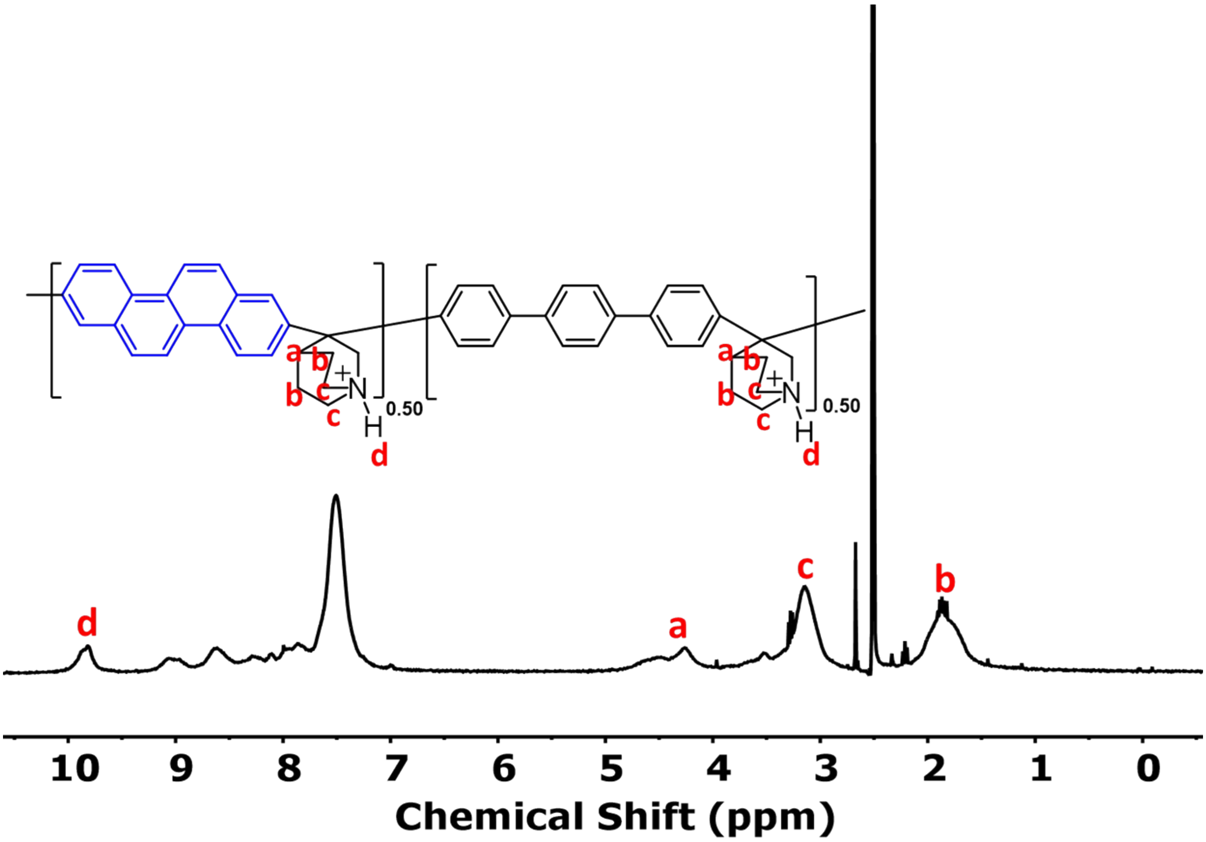


Figure S7. ^{1}H NMR spectrum of *pre*-PCQ-0.50 in DMSO-d_6 with 5 vol% TFA.

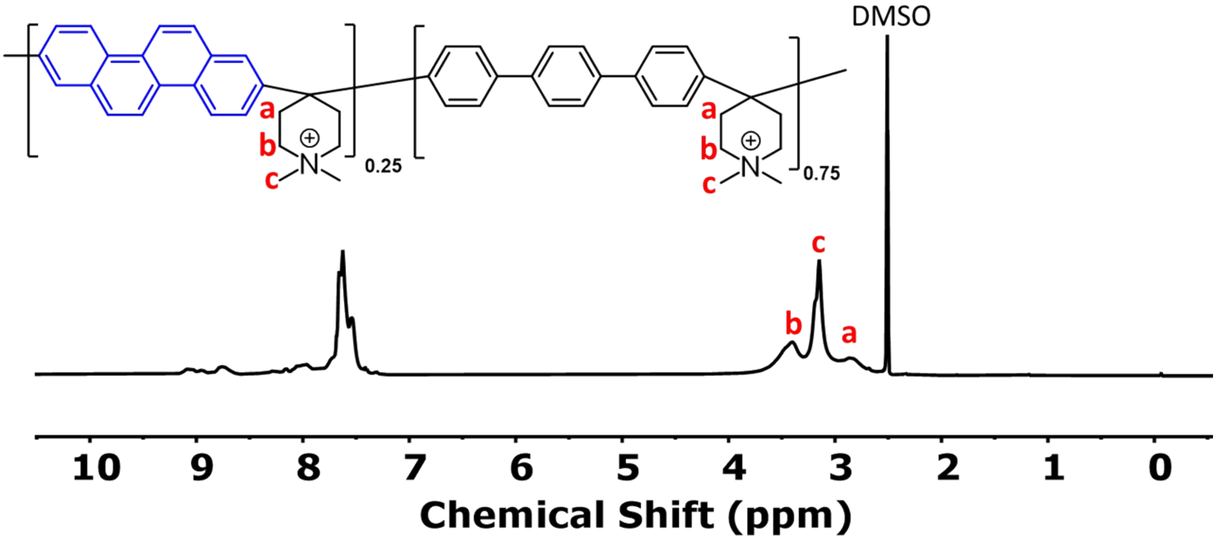


Figure S8. ^{1}H NMR spectrum of PCP-0.25 in DMSO-d_6 with 5 vol% TFA.

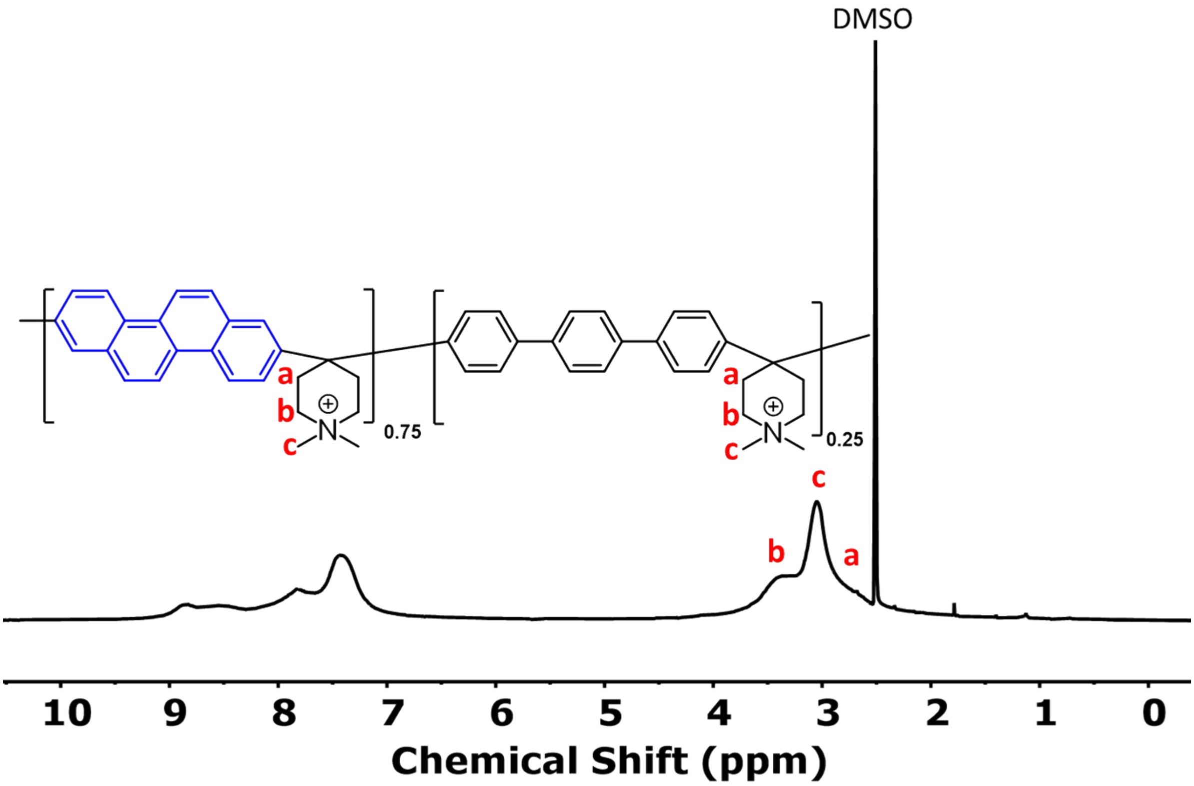


Figure S9. ^{1}H NMR spectrum of PCP-0.75 in DMSO-d_6 with 5 vol% TFA.

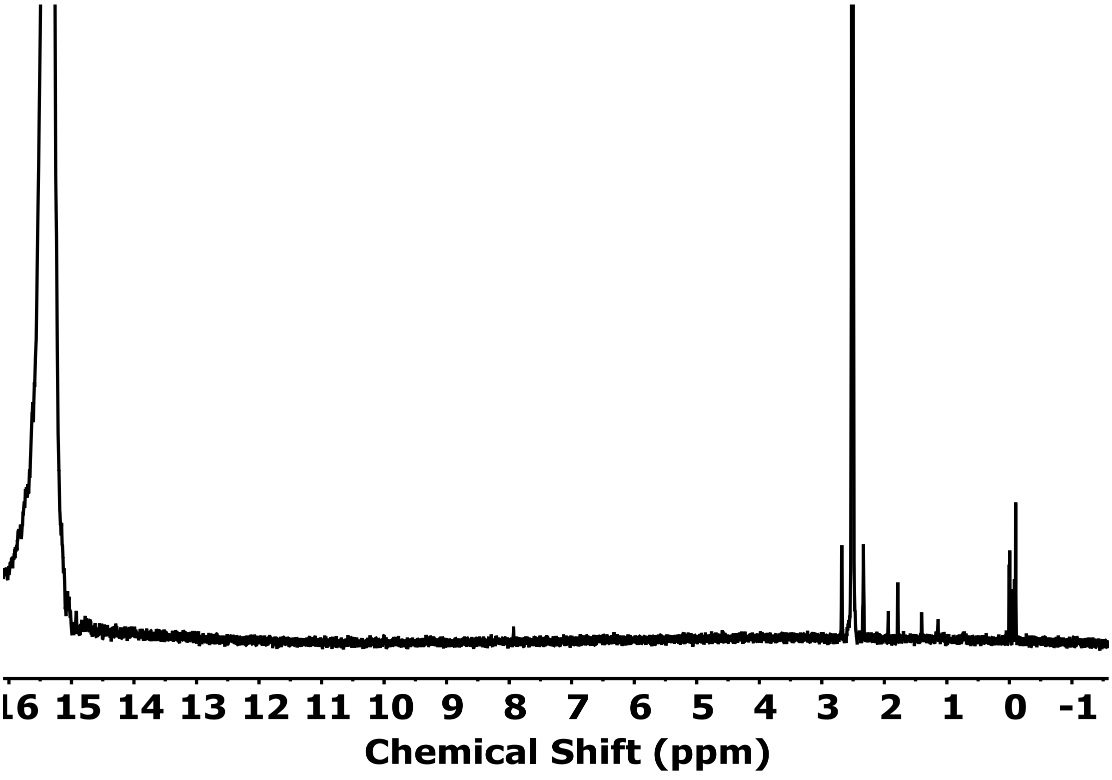


Figure S10. ^{1}H NMR spectrum of TFA in DMSO-d_6.

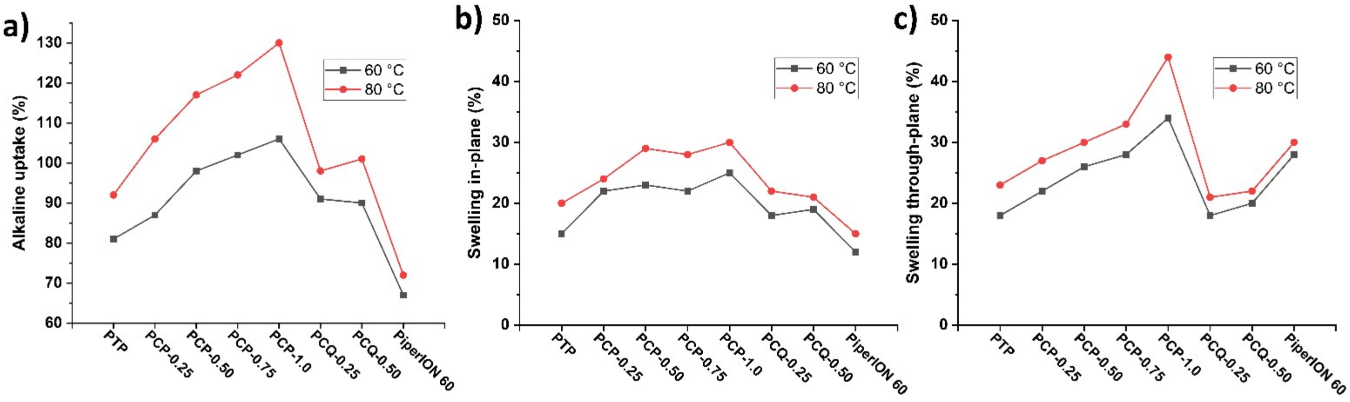


Figure S11. a) Alkaline uptake, **b)** in-plane swelling, and **c)** through-plane swelling of AEM samples in 2 M KOH at 60 °C and 80 °C, respectively.

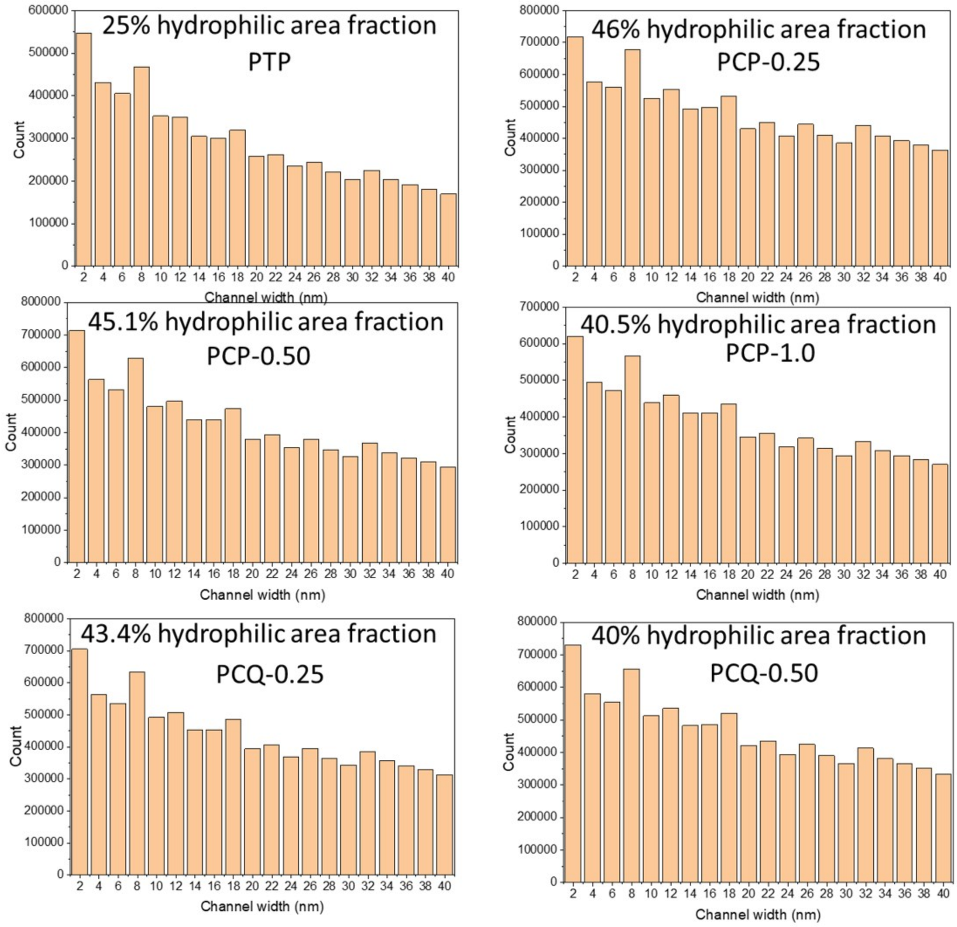


Figure S12. Hydrophilic channel width distribution and the hydrophilic area fraction of dry AEMs in the bromide form

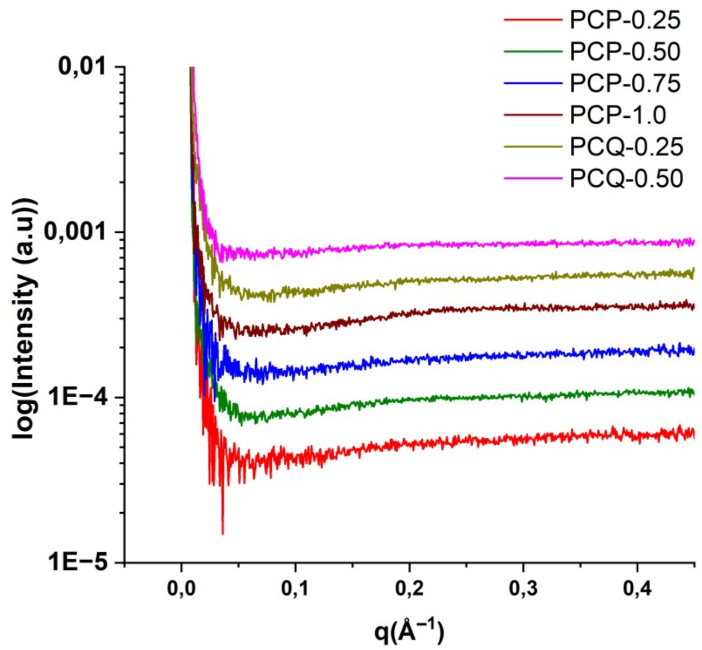


Figure S13. SAXS profiles of dry AEMs in the bromide form.

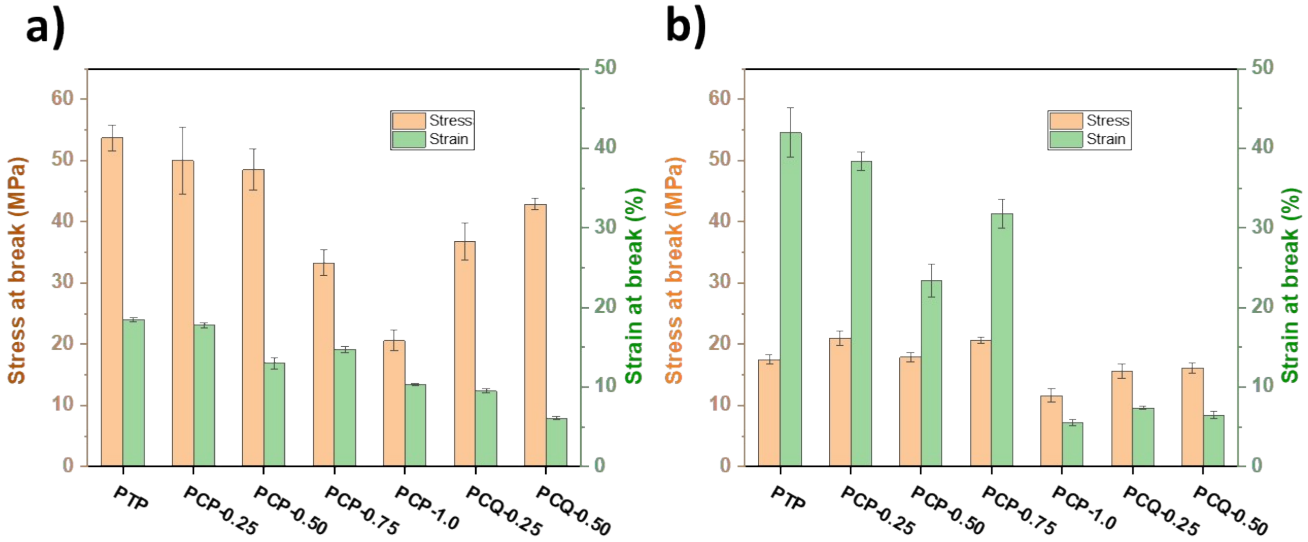


Figure S14. Stress at break and strain at break data of the AEM samples in the **a)** dry state and **b)** wet state.

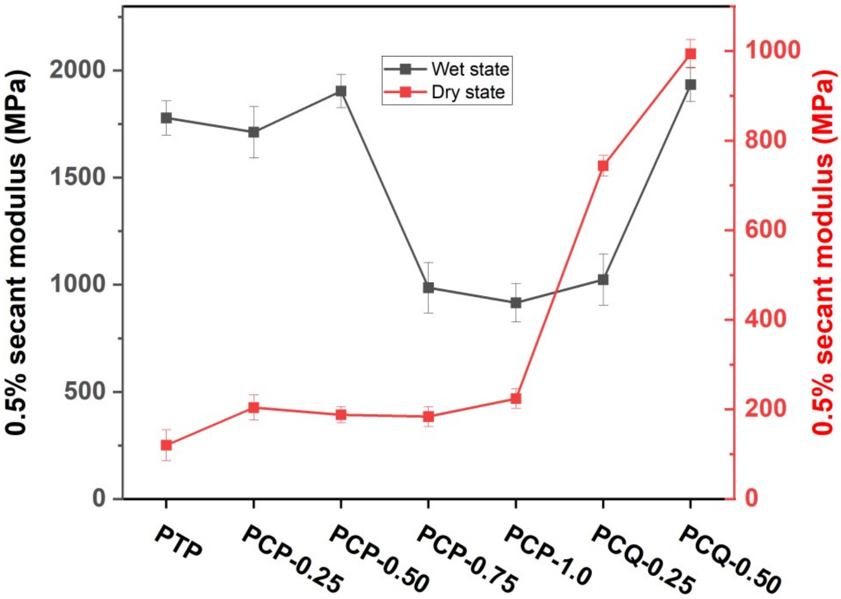


Figure S15. The 0.5% secant modulus of the AEM samples in the wet and dry state.

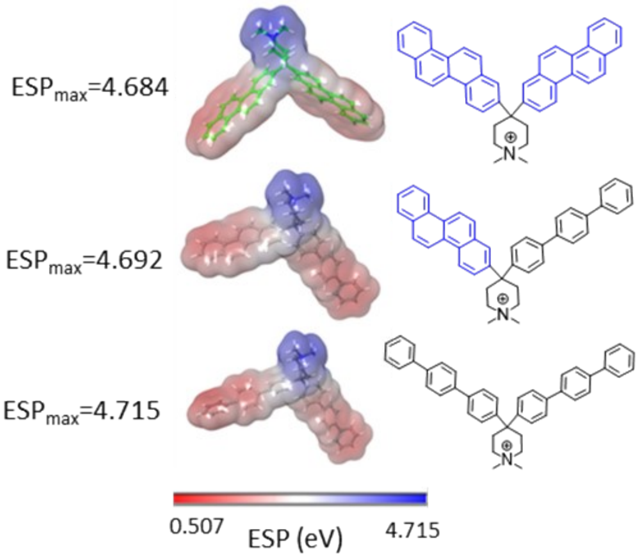
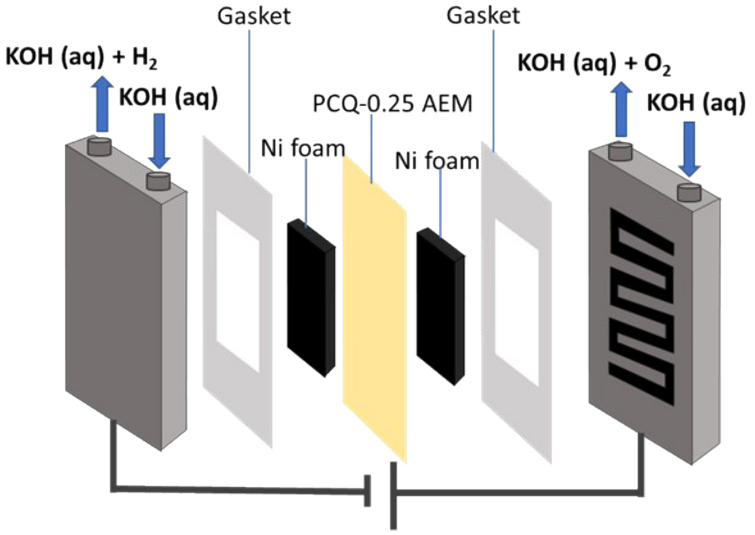


Figure S16. Electrostatic potentials (ESP) diagrams of chrysene-containing model compounds.



Scheme S1. Scheme of the AEMWE cell assembled with the PCQ-0.25 AEM.

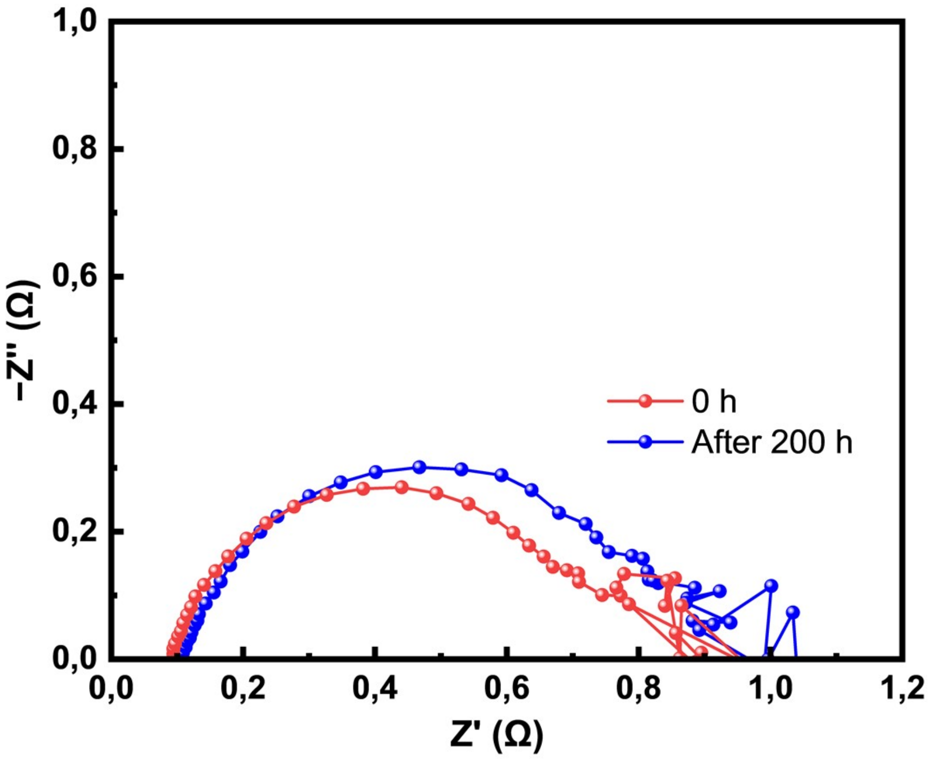


Figure S17. Nyquist plots of the EIS data of the AEMWE cell assembled with membrane PCQ-0.25 before (0 h) and after the 200 h durability test applying a current density of 500 mA cm^{-2} with a 2 M KOH feed at 90 °C.

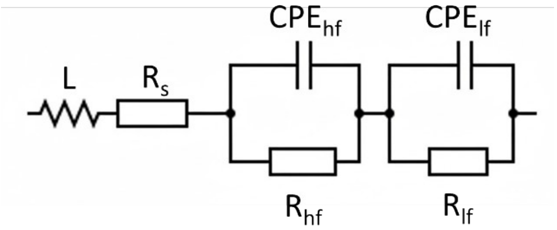


Figure S18. The equivalent circuit for EIS fitting.

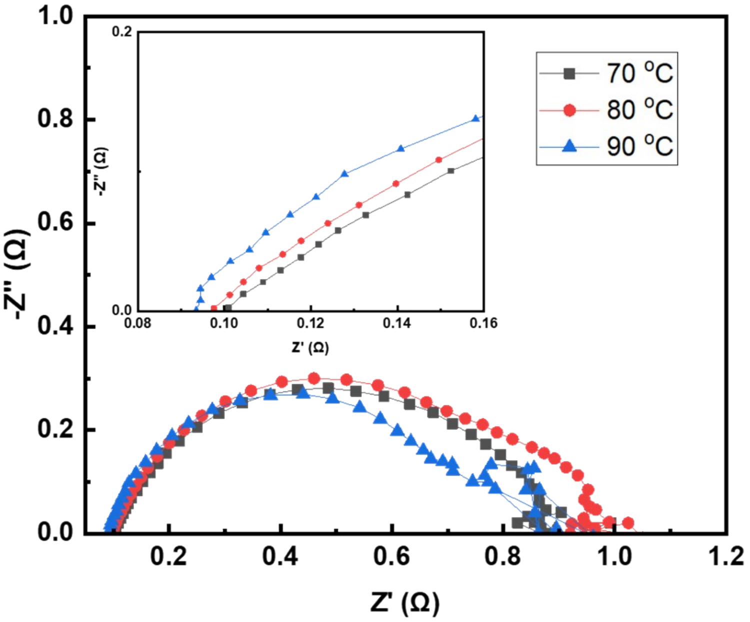


Figure S19. Nyquist plots of the EIS data of the AEMWE cell assembled with membrane PCQ-0.25 with a 2 M KOH feed at different temperatures.

Table S1. General properties of PiperION® (IEC_{OH^-} = 2.35 mequiv/mol).

Water uptake (%)[a]		Conductivity (mS/cm)		Swelling in-plane (%)[b]		Swelling through-plane (%)[c]	
20 °C	80 °C	20 °C	80 °C	20 °C	80 °C	20 °C	80 °C
48	116	58	149	19	23	46	53

[a, b, c] Measured in the fully hydrated state in OH^- form (immersed in water).