

# Covalent Cross-linking of Porous Poly(Ionic Liquid) Membranes via a Triazine Network

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## Materials and characterization methods

Vinylimidazole, bromoacetonitrile, AIBN, sodium dicyanamide, poly(acrylic acid) (Mw: 450 kDa) and ammonium hydroxide solution 28% in water were obtained from Sigma-Aldrich and used without further purification. Dimethyl sulfoxide (DMSO) was of analytical grade.

Scanning electron microscopy (SEM) was performed using a GEMINI LEO 1550 microscope at 3 kV, and samples were coated with gold before examination. ATR-FTIR spectra were collected with a Nicolet iS5 FT-IR instrument from ThermoFisher Scientific equipped with a single-reflection ATR diamond with a working range from 4000  $\text{cm}^{-1}$  to 500  $\text{cm}^{-1}$  with 64 scans per spectrum and 128 scans for the background with a resolution of 2  $\text{cm}^{-1}$ . Thermogravimetric measurements were performed with a TG 209 F1 Libra thermomicrobalance from Netzsch. The samples were analyzed in a platinum crucible at a heating rate of 10  $\text{K min}^{-1}$  under a  $\text{N}_2$  flow of 30  $\text{mL min}^{-1}$ . The FT-IR set-up used to study the cross-linking mechanism of the membranes consisted of a FT-IR 600 Linkam stage cell connected to a Bruker Vertex 70 FT-IR spectrometer. The membrane is placed in the FTIR cell and is heated at a rate of 5  $\text{K min}^{-1}$  from 25  $^\circ\text{C}$  to 260  $^\circ\text{C}$  under nitrogen flow (150  $\text{mL min}^{-1}$ ). FT-IR spectra are recorded every 10 s during the heating of the sample.  $^1\text{H}$  NMR and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra were collected using a Bruker DPX-400 spectrometer in  $\text{D}_2\text{O}$  as solvent. Solid-state NMR spectra were recorded with a Bruker Avance 400 MHz spectrometer operating at 100.56 MHz for  $^{13}\text{C}$  and 399.88 MHz for  $^1\text{H}$  and  $^1\text{H}$ - $^{13}\text{C}$  cross-polarization magic angle spinning (CP-MAS) NMR experiments were carried out at a MAS rate of 10 kHz using a 4 mm diameter MAS HX double-resonance probe. The  $^1\text{H}$   $\pi/2$  pulse length was 3.1  $\mu\text{s}$  and two pulse phase modulation (TPPM) heteronuclear dipolar decoupling was used during acquisition. The spectra were measured using contact time of 2.0 ms for  $^{13}\text{C}$  and recycle delays of 2 s. All  $^{13}\text{C}$  spectra are referenced to external TMS at 0 ppm using adamantane as a secondary reference. Pore size distribution of the membrane was analyzed on membrane cross-section SEM images by means of Adobe Photoshop CS5 software. All the data were elaborated using OriginPro2015 software.

## Synthesis of poly(3-cyanomethyl-1-vinylimidazolum dicyanamide)

Poly(3-cyanomethyl-1-vinylimidazolium bromide) was prepared according to our previous method (J. Am. Chem. Soc. 2012, 134, 11852–11855). Afterwards, this polymer undergoes anion exchange towards dicyanamide following this procedure: a solution of sodium dicyanamide (0.917 g, 10.3 mmol) in water (30,0 mL) was slowly dropped on a solution of poly(3-cyanomethyl-1-vinylimidazolium bromide) (2 g) in water (60,0 mL). The obtained poly(3-cyanomethyl-1-vinylimidazolium dicyanamide) (PCMVIm-DCA) precipitated in water due to the presence of excess charge in solution.

The PIL was filtered off and dried until constant weight. The polymer yield of the anion exchange is 92,7%. The EDX shows a bromine content of 34.8 wt% in poly(3-cyanomethyl-1-vinylimidazolium

bromide) and of 13.5 wt% for poly(3-cyanomethyl-1-vinylimidazoiium dicyanamide); therefore, it is possible to calculate an anion exchange rate of 61 mol%. For the purpose of membrane fabrication, this anion exchange amount has proven to be sufficiently high.

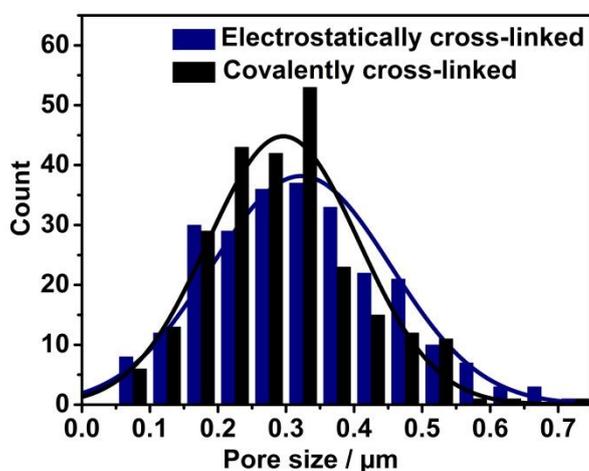
#### Synthesis of initial electrostatically cross-linked PIL membrane

A homogeneous solution of poly(3-cyanomethyl-1-vinylimidazoiium dicyanamide) (0.200 g, 1 mmol of repeating unit) and poly(acrylic acid) (PAA) (0.072 g, 1 mmol of repeating unit) in DMSO (2 mL) is cast onto a glass plate and the solvent is evaporated at 80 °C. The obtained dry PCMVIm-DCA/PAA blend film, coated on the glass plate, is immersed in an aqueous NH<sub>3</sub> solution (~0.2 % w/w, 10 mL) for 2 h. During this period, ammonia solution slowly penetrated into the polymers film, neutralizes PAA into the charged poly(ammonium acrylate) salt and activates the electrostatic cross-linking between PIL and poly(ammonium acrylate). It should be noticed that the inter-polyelectrolyte complexation is an entropy-driven process, in which the complexation proceeds only to a certain extent. Thus, the DCA anions remain in a significant amount in the PIL. After two hours, the electrostatically cross-linked membrane was washed with water in order to remove the excess of NH<sub>4</sub>OH and the formed NH<sub>4</sub>DCA, and it was then dried in a vacuum oven for 2 hours.

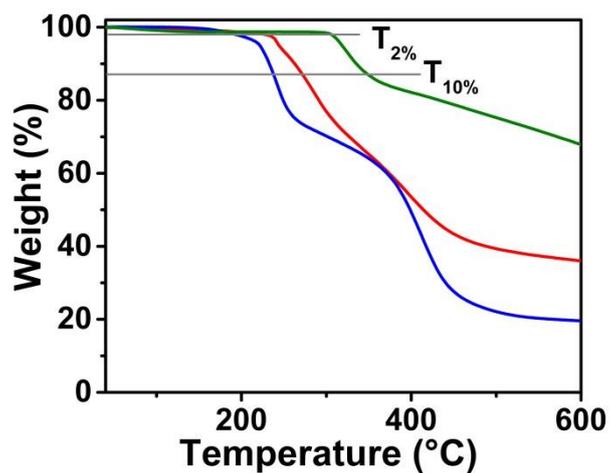
#### Synthesis of electrostatically and covalently cross-linked membrane

The obtained initial electrostatic cross-linked membrane was annealed at 200 °C for 2 h under a nitrogen atmosphere, in order to form the additional covalent cross-links. The resulting electrostatically and covalent cross-linked membrane was used without any further clean-up or drying.

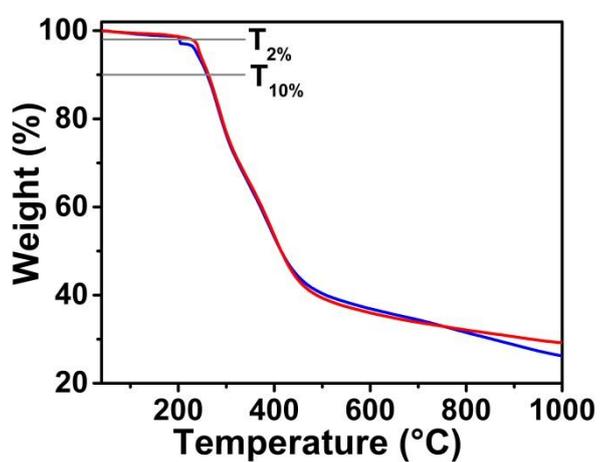
#### Characterization Data



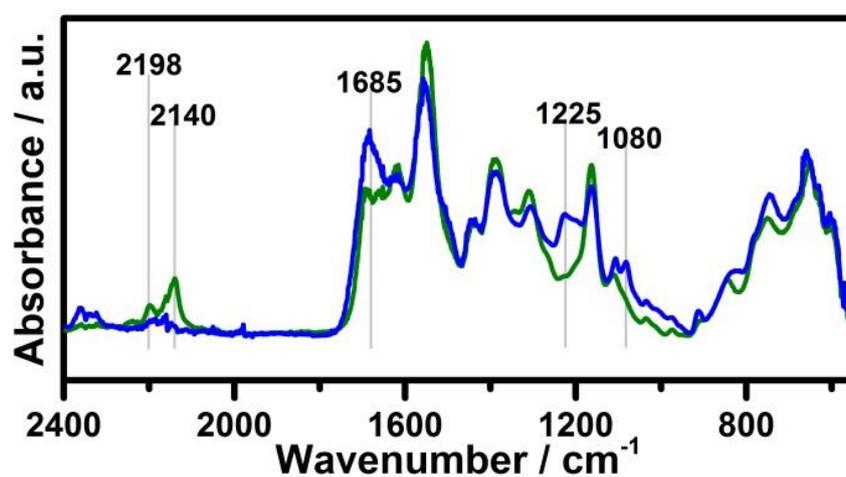
**Figure S1.** Pore size distribution of porous membrane before (blue columns) and after annealing (black columns).



**Figure S2.** Thermogravimetric profiles of: PAA (blue curve), PCMVIm-DCA (green curve) and of the membrane originating from their electrostatic complexation (red curve).



**Figure S3.** Thermogravimetric profiles of electrostatic cross-linked membrane (red curve) compared with the one of covalently cross-linked membrane (blue curve).



**Figure S4.** FTIR-ATR spectra of PCMVIm-DCA before (green curve) and after annealing process at 200 °C (blue curve).

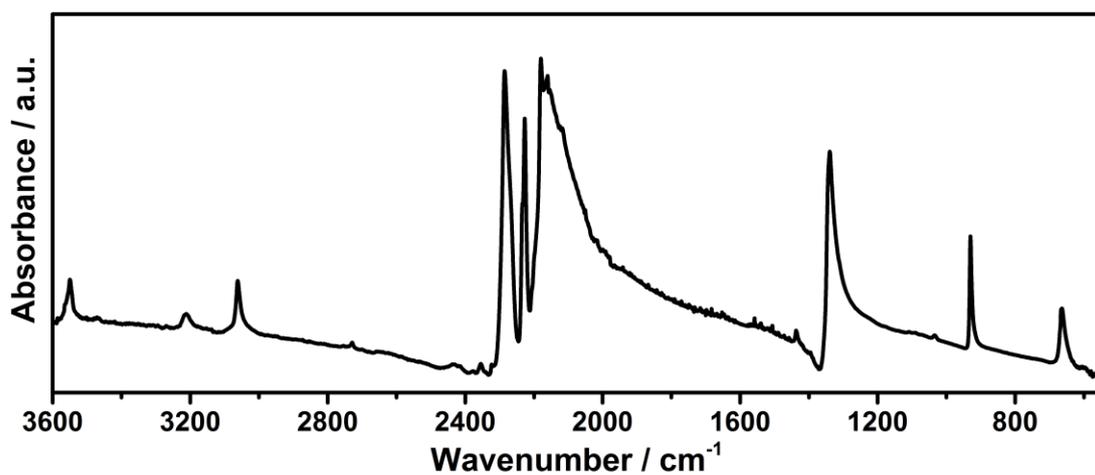


Figure S5. ATR-FTIR spectrum of sodium dicyanamide.

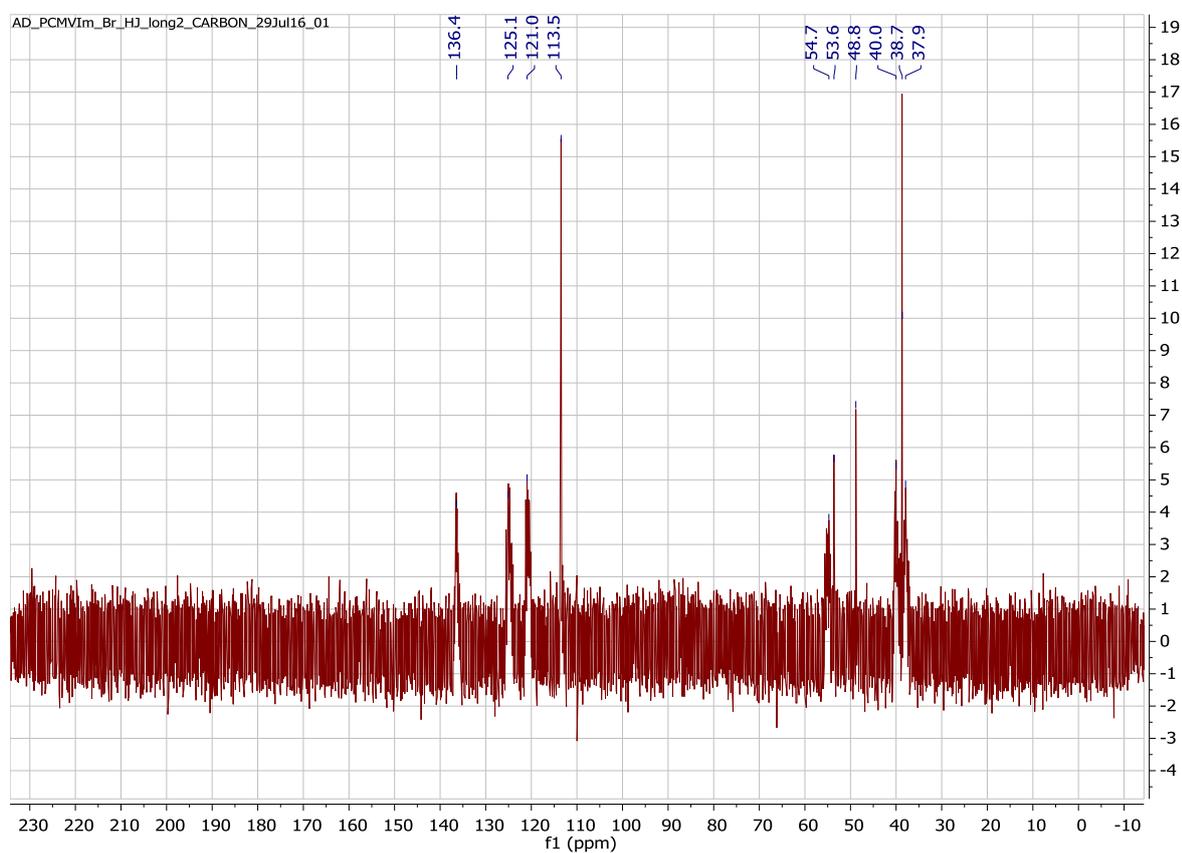


Figure S6.  $^{13}\text{C}$ -NMR spectra of Poly(CMVIIm-Br) in  $\text{D}_2\text{O}$

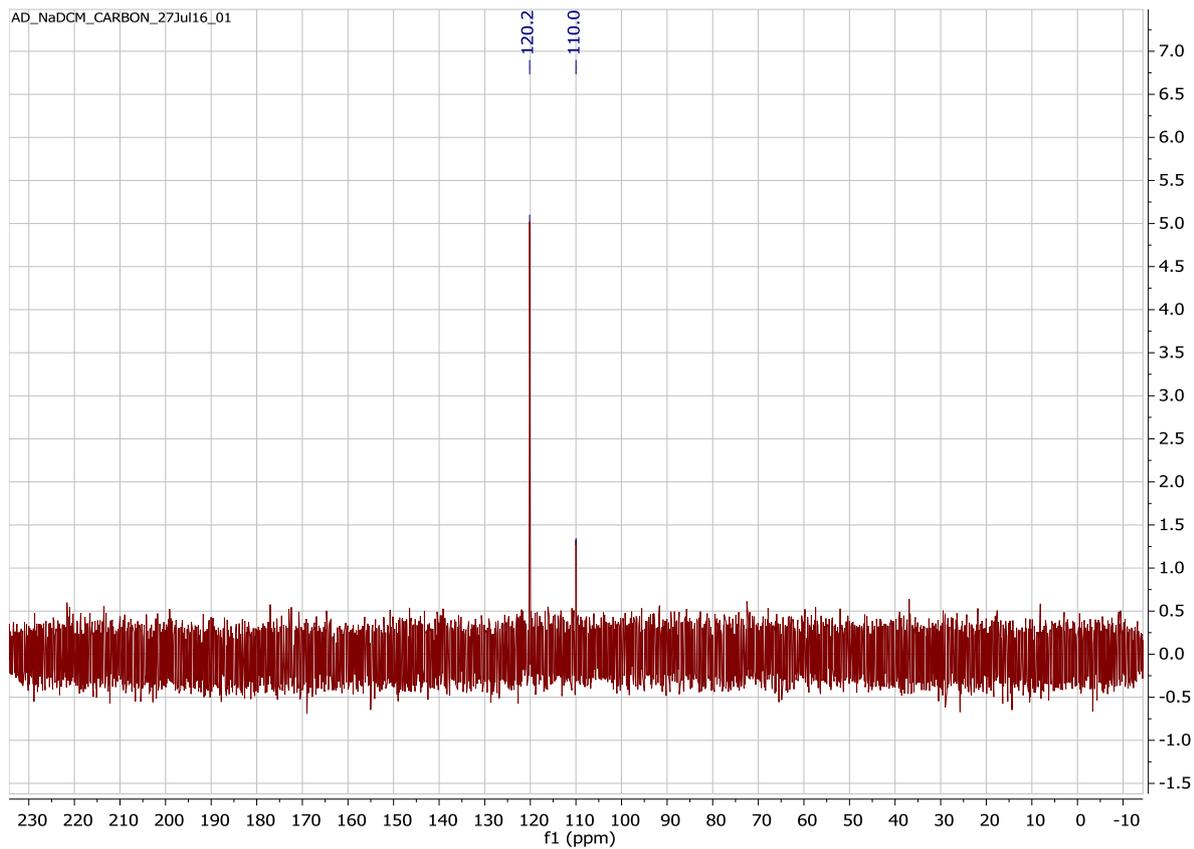


Figure S7.  $^{13}\text{C}$ -NMR spectra of sodium dicyanamide in  $\text{D}_2\text{O}$

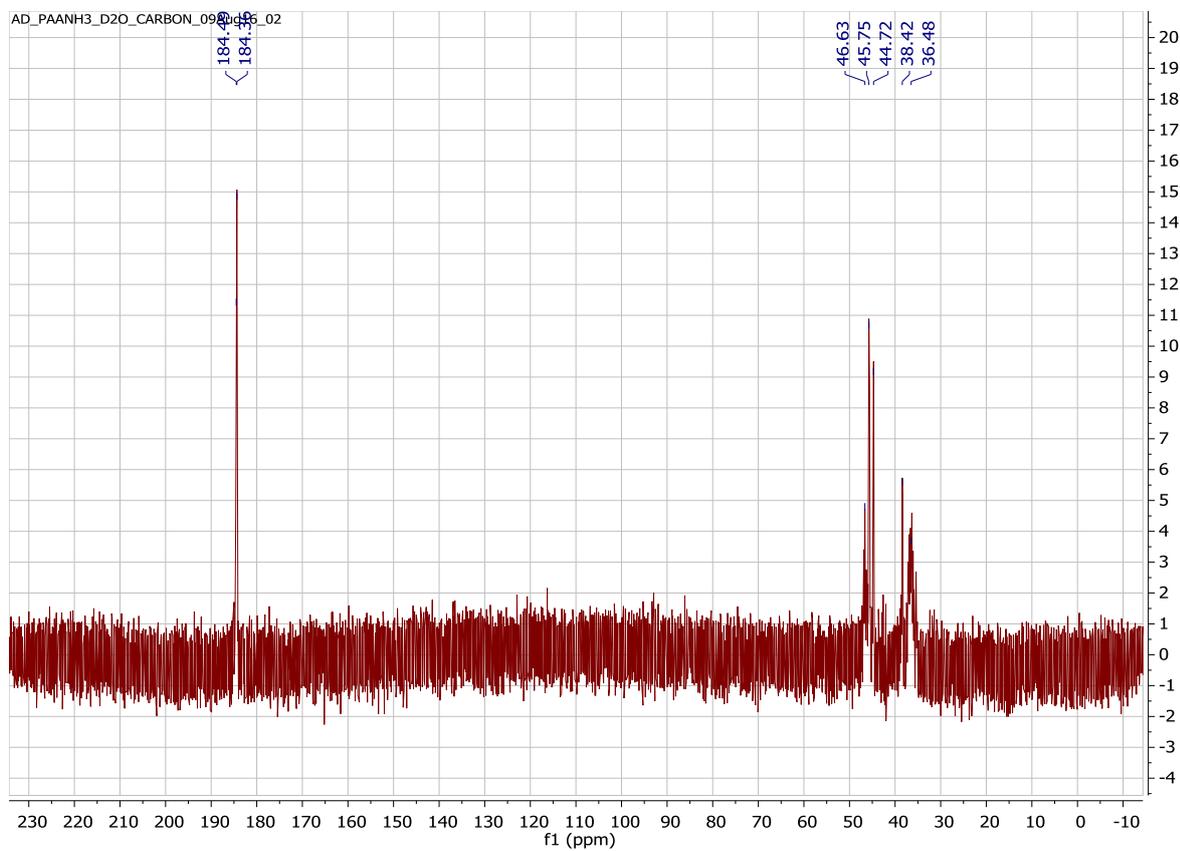
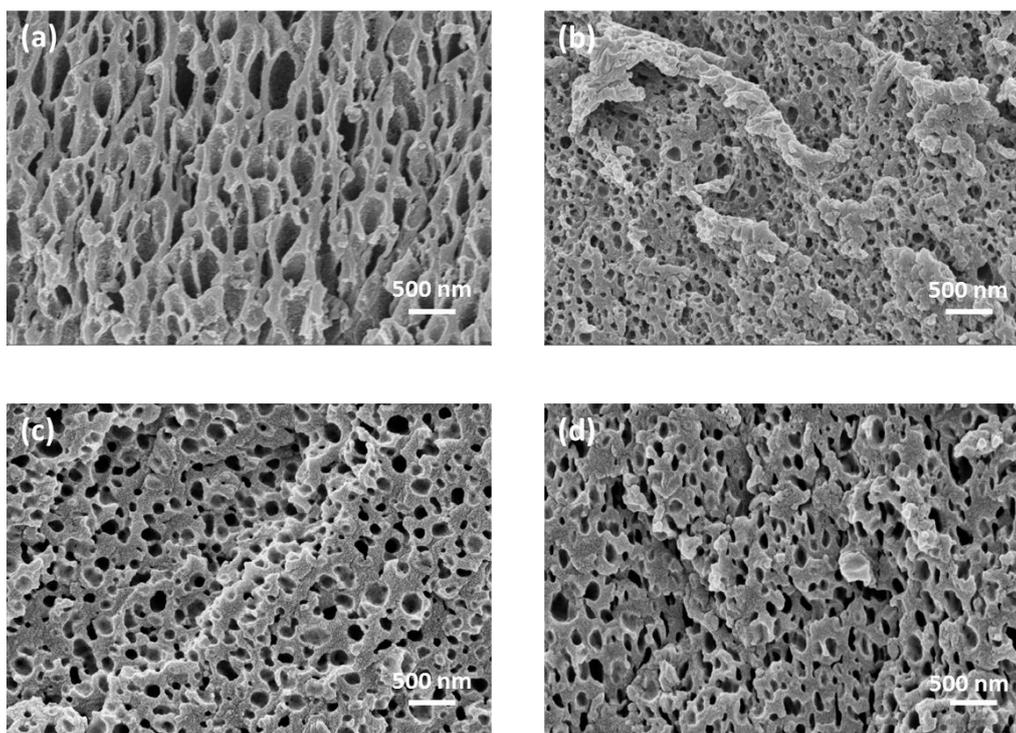


Figure S8.  $^{13}\text{C}$ -NMR spectra of poly(acrylic acid) ammonium salt solution in  $\text{D}_2\text{O}$ .



**Figure S9.** a) SEM images of the initial non-annealed membrane after treatment with  $\text{LiTf}_2\text{N}$  solution in water; b)-d) SEM images of annealed membranes after salt treatment: b)  $\text{LiTf}_2\text{N}$  in water; c)  $\text{KPF}_6$  in water; d)  $\text{LiPF}_6$  in ethylene carbonate/dimethyl carbonate (1:1 v/v).

**Table S1.** Average pore size distribution and standard deviation of electrostatical and covalent cross-linked membranes before and after treatment with salt solution.

membrane	treatment	average pore size nm	standard deviation nm
Initial electrostatically cross-linked membrane	Before $\text{LiTf}_2\text{N}$ solution soaking	120	60
	After $\text{LiTf}_2\text{N}$ solution soaking	500	300
Electrostatically and covalently cross-linked membrane	Before $\text{LiTf}_2\text{N}$ solution soaking	170	20
	After $\text{LiTf}_2\text{N}$ solution soaking	140	10
	Before $\text{KPF}_6$ solution soaking	300	100
	After $\text{KPF}_6$ solution soaking	260	100
	Before $\text{LiPF}_6$ solution soaking	170	70
	After $\text{LiPF}_6$ solution soaking	180	70