

Supporting Information to

“Nitrogen-doped carbon fibers and membranes by carbonization of electrospun poly(ionic liquid)s”

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Materials

1-Vinylimidazole (Aldrich 99 %) was purified by vacuum distillation. 4,4'-Azobis(4-cyanovaleric acid (Aldrich 98 %), poly(4-vinylpyridine) (Aldrich, average $M_w \sim 160,000$ g/mol), 1-allyl bromide (Aldrich 97 %), 2,6-di-tert-butyl-4-methylphenol (BHT) (Aldrich 99 %) and trimethylolpropane tris(3-mercaptopropionate (Aldrich) were received without purification. All solvents used were of analytic degree. Silver dicyanamide was prepared similarly according to previous literature (Paraknowitsch, J. P.; Zhang, J.; Su, D.; Thomas, A.; Antonietti, M. *Adv. Mater.* 2010, 22, 87-92.).

Synthesis of poly(1-vinylimidazole)

50 g of 1-vinylimidazole and 60 mg of AIBN was dissolved in 120 mL of DMF. The solution was bubbled by argon for 30 minutes and placed in an oil bath at 70 °C for 24 h. After cooling down to room temperature, the polymer was precipitated into 1 L of acetone. 30 g of white solid was obtained as product.

Quaternization of poly(1-vinylimidazole) and poly(4-vinylpyridine)

6.42 g of g of poly(1-vinylimidazole) or poly(4-vinylpyridine) and 0.67 g of BHT were dissolved in 200 mL of DMF. The solution was heated to 90 °C, at which 15.5 g of 1-allyl bromide was added dropwise. Precipitate appeared and was redissolved by continuous stirring. In the case of poly(4-vinylpyridine), 50 mL of ethylene glycol was added additionally to achieve a clear solution. After complete addition of 1-allyl bromide, the clear solution was heated to 100 °C overnight. After cooling down to room temperature, the polymer was precipitated in 2 L of diethyl ether and dried at 40 °C under high vacuum. Yield: 85 %.

Anion exchange process

8 g of poly(3-allyl-1-vinylimidazolium bromide) was dissolved in 100 mL of aqueous methanol solution (water/methanol = 1/1). An aqueous solution of silver dicyanamide (6.8 g in 50 mL of water) was added dropwise into the polymer solution under dark environment. The reaction mixture was stirred for 48 h at 40 °C. After cooling down to room temperature, the insoluble precipitate was removed by centrifugation and the upper clear solution was collected. -Yield: 75 %. The same procedure was conducted to poly(1-allyl-4-vinylpyridinium bromide)

Electrospinning and crosslinking of poly(ionic liquid)s

(A) poly(3-allyl-1-vinylimidazolium dicyanamide)

In a vial (2 mL) equipped with a magnetic stirrer, 250 mg of poly(3-allyl-1-vinylimidazolium dicyanamide) was dissolved in 0.9 mL of a mixture of acetonitrile/methanol (volume ratio: 1/1) by gentle heating. 160 mg of 4,4'-azobis(4-cyanovaleric acid) (**ACVA**) and 90 mg of 4-(3-mercaptopropyl)-1,7-heptandithiol (**TRIS**) were added and stirred sequentially. After complete dissolution (20 min), 0.3 mL of the solution was loaded into a syringe (1 mL) in a syringe pump and the electrospinning process started. The rest solution in the vial was immediately cooled down to -15 °C and kept frozen until the previously withdrawn aliquot was totally electrospun. Aliquots of 0.3 mL of the polymer solution were subsequently withdrawn for electrospinning, and the cooling process was repeated until the whole solution was consumed.

Electrospinning conditions: Injection flow rate: 1.0 mL/h

Voltage: 28 kV - 30 kV.

Collector distance: 12 cm

Relative humidity: 9 - 15 %

Temperature: 21 °C.

(B) poly(1-allyl-4-vinylpyridinium dicyanamide).

The same as that of poly(3-allyl-1-vinylimidazolium dicyanamide), except that after addition of ACVA and TRIS, the mixture was stirred at room temperature for 10 minutes before the electrospinning process started.

Electrospinning conditions: Injection flow rate: 0.5 mL/h

Voltage: 26 kV - 28 kV.

Collector distance: 12 cm

Relative humidity: 9 - 15 %

Temperature: 21 °C

Carbonization Process

Electrospun fiber mats were first dried under vacuum overnight and cured at 80 °C under vacuum for 2 days. The cured fiber mats were first heated in air to 280 °C in 2 h and maintained at this temperature for 2 h; afterwards, they were heated under nitrogen in 5 h to 1000 °C and maintained at this temperature for 1 h. Yields at 280°C and 1000 °C: 62 % and 16 % for poly(3-allyl-1-vinylimidazolium dicyanamide); 65 % and 19 % for poly(1-allyl-4-vinylpyridinium dicyanamide).

Analytical instrumentation

¹H- and ¹³C-NMR measurements were carried out at room temperature using a Bruker DPX-400 spectrometer operating at 400.1 MHz and 100.6 MHz, respectively. D₂O, DMSO-*d*₆ and CDCl₃ were used as solvents; signals were referenced to the signal of residual protonated solvent at $\delta = 4.79$ ppm, 2.50 ppm and 7.26 ppm, respectively. Size exclusion chromatography (SEC) with simultaneous UV and RI detection was performed in THF at 25 °C, flow rate: 1 mL/min, column set: two MZ-SDplus columns, 300 mm \times 8 mm (dimensions), 5 μ m (particle size), 103 Å and 105 Å (porosity). Calibration was done with 1,2-polybutadiene standards (PSS, Mainz, Germany). Size exclusion chromatography (SEC) with simultaneous UV and RI detection was

performed in DMSO at 70 °C using a column set of two 300 × 8 mm PSS-GRAM columns with porosities of 10² Å and 10³ Å, respectively. Calibration was done with poly(methyl methacrylate) standards. Elemental analysis was performed for carbon, hydrogen and nitrogen using a Vario EL Elemental Analyzer. Fourier-transform infrared (FT-IR) spectroscopy was done at room temperature with a BioRad 6000 FT-IR spectrometer equipped with a Single Reflection Diamond ATR. Scanning electron microscopy (SEM) pictures were taken with a GEMINI LEO 1550 microscope at 3 kV. DSC measurements were done by Netzsch DSC 200 at 10 K/min heating/cooling rate under nitrogen. Powder X-ray diffraction was measured in reflection mode by Nonuis diffractometer (Inel, France) using CuK_α radiation and a position sensitive detector.

The conductivity of the nitrogen-doped carbon was determined by potentiostatic DC-resistivity measurements (Keithley, 6430) and confirmed by additional AC-impedance measurements (Biologic, SP300). A lateral geometry was used for the measurements. Fig. S2 shows a representative Bode plot of the AC data. The scattering in the data at low and medium frequencies is very small, and thus, the determined resistances are quite precise. Since it is difficult to fix electrodes to single fibers, the measurements were performed at spin coated nitrogen-doped carbon films (thickness 150 nm) on a quartz glass substrate. Gold was applied by thermal heating as electrode material with an edge length of 5 mm, the horizontal spacing between both electrodes was 5 mm. The film thicknesses were measured with a profilometer (LOT-Oriel, Alpha-Step IQ Surface Profiler).

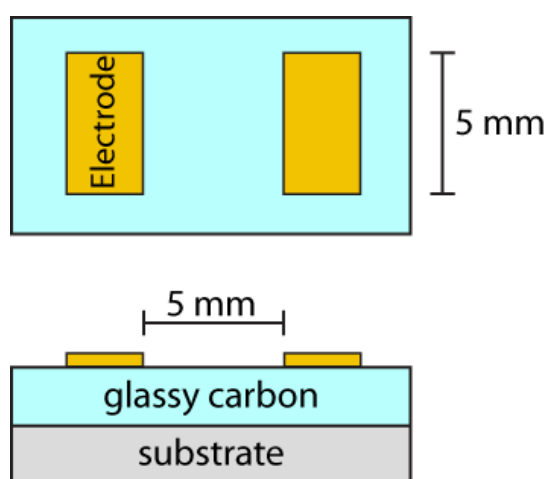


Figure S1. Measurement setup for the determination of the resistivity of nitrogen-doped carbon thin film.

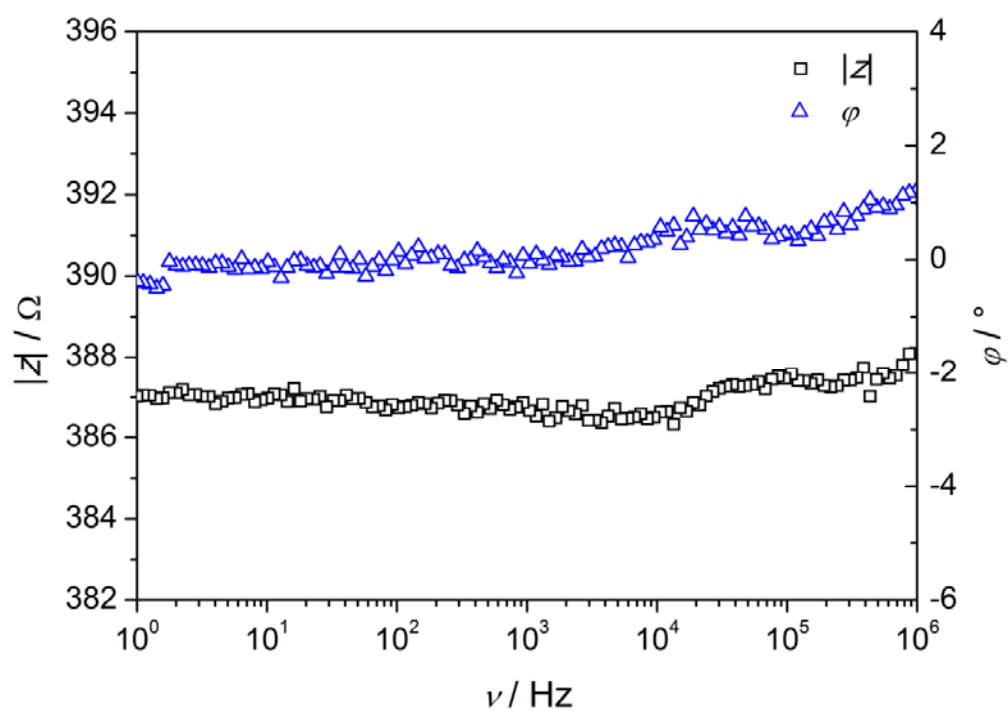
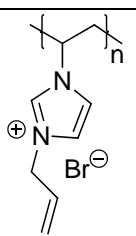
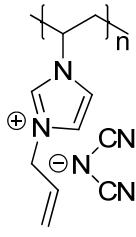
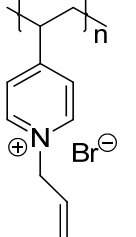
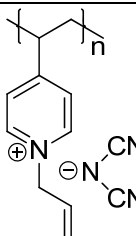


Figure S2. Representative Bode plot of the impedance at room temperature of the nitrogen-doped carbon films.

Table S1. Elemental analysis of PILs before and after anion exchange process

		C%	N%	C/N
	Found	44.67	13.03	3.43
	Calculated	42.27	12.27	3.44
	Found	57.77	33.03	1.75
	Calculated	59.68	34.81	1.71
	Found	50.44	5.72	8.47
	Calculated	53.09	6.19	8.58
	Found	24.45	63.29	2.59
	Calculated	26.40	67.90	2.57

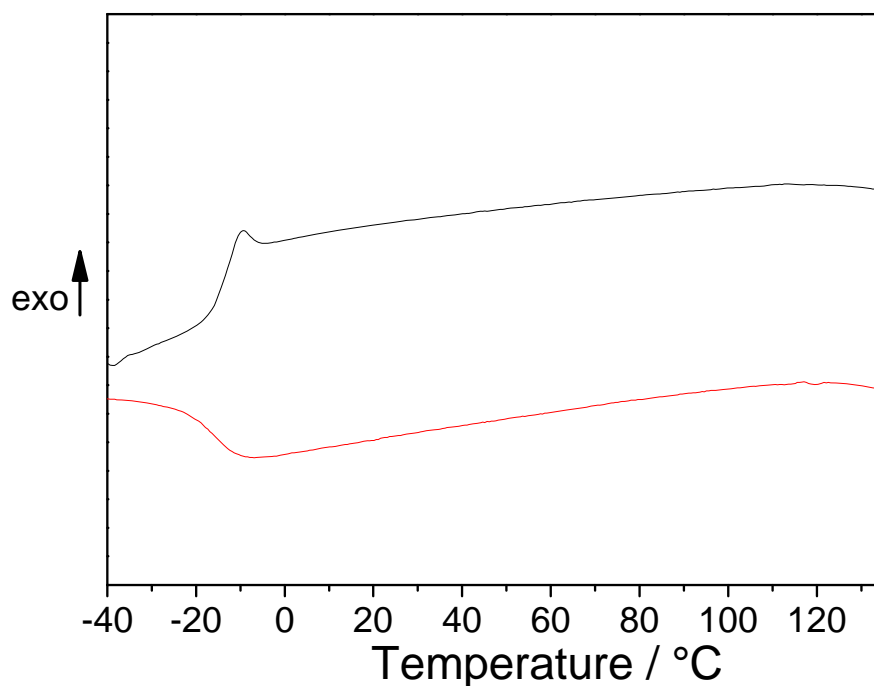


Figure S3. DSC curve of poly(3-ethyl-1-vinylimidazolium dicyanamide). Its glass transition temperature was determined to be $-15\text{ }^{\circ}\text{C}$.

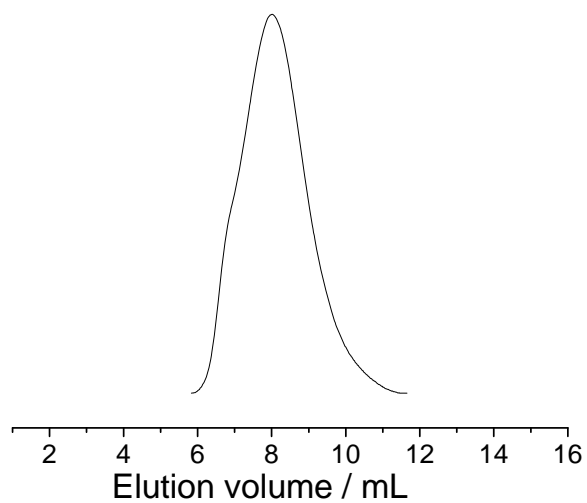


Figure S4. GPC trace of poly(1-vinylimidazole). Its molecular weight $M_n = 85,1000\text{ g/mol}$ was determined from GPC using DMSO as eluent and PMMA standard.

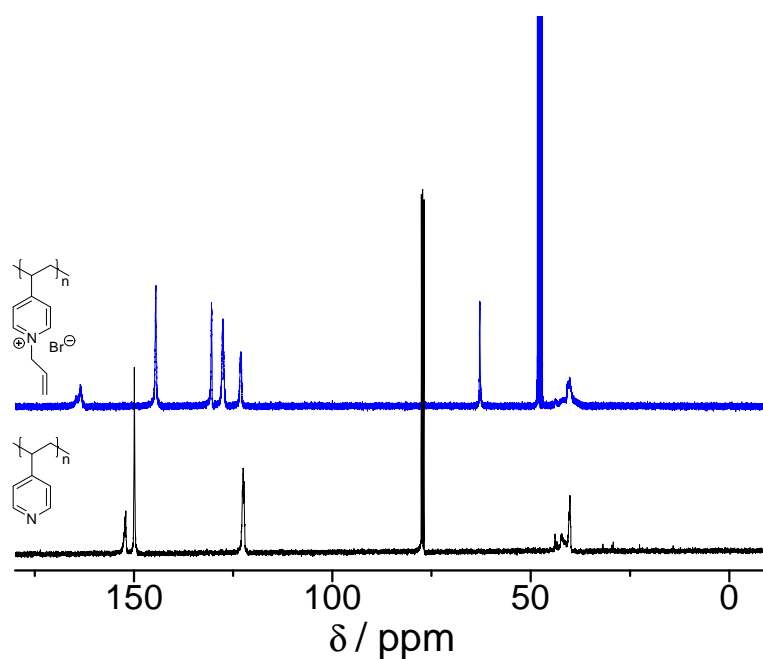


Figure S5. ¹³C-NMR spectra of poly(4-vinylpyridine) (black curve) in CDCl₃ and poly(1-allyl-4-vinylpyridinium bromide) in DMSO-*d*₆ (blue curve). The carbon signals of the phenyl ring in P4VP at 150 ppm and 152 ppm completely vanished after the quaternization and shifted to 164 ppm and 144 ppm. Thus, the quaternization reached 100 %.

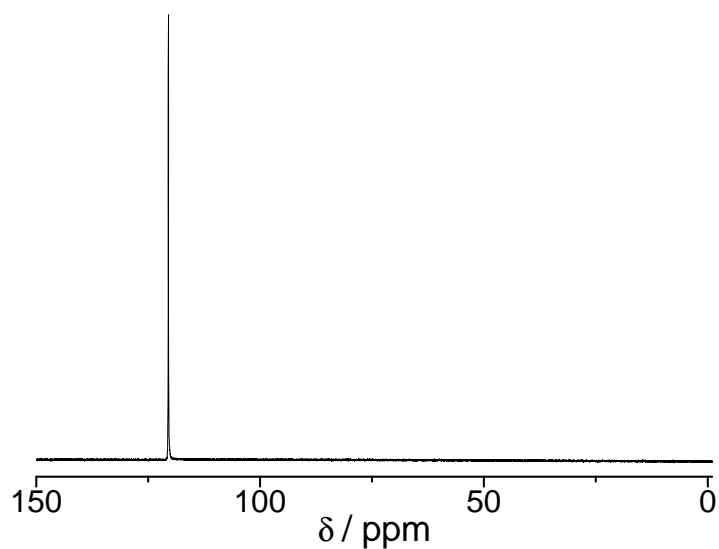


Figure S6. ¹³C-NMR spectrum of NaN(CN)₂ in D₂O. Only one signal was observed at 119 ppm, attributed to the dicyanamide anion.

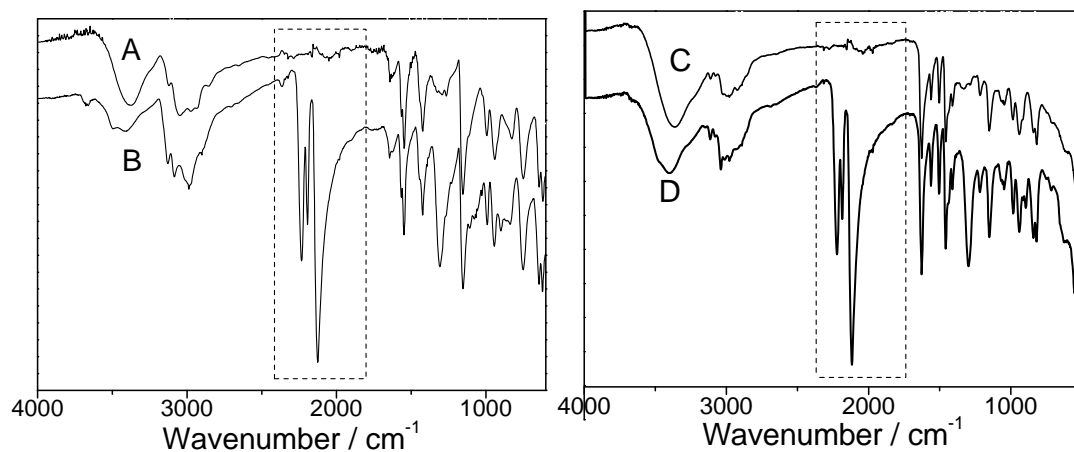


Figure S7. FTIR spectra of (A) poly(3-allyl-1-vinylimidazolium bromide), (B) poly(3-allyl-1-vinylimidazolium dicyanamide), (C) poly(1-allyl-4-vinylpyridinium bromide) and (D) poly(1-allyl-4-vinylpyridinium dicyanamide). The triple bonds in the range of 2100 cm^{-1} - 2300 cm^{-1} are characteristic of dicyanamide function. It proves the anion exchange between brom anion and dicyanamide anion indeed took place in the reaction.

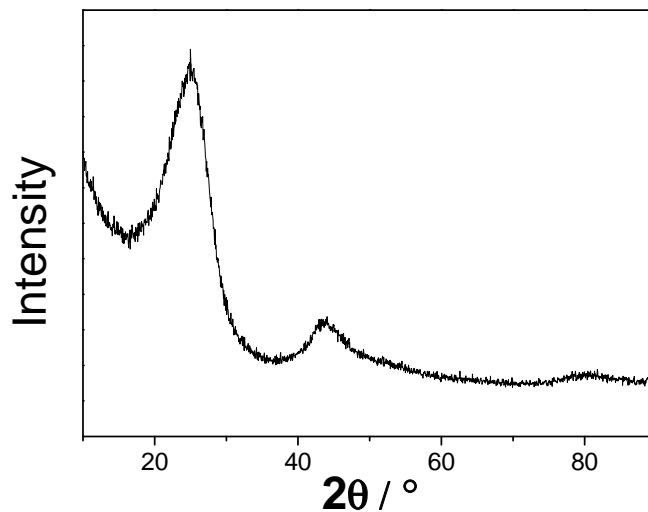


Figure S8. XRD pattern of the carbon membranes prepared from the carbonization of electrospun poly(3-allyl-1-vinylimidazolium dicyanamide) fibers. The bands at 25.5° , 43.7° and 80.3° are indicative of the existence of graphitic phase in the nitrogen-doped carbon membrane.