

Supporting information

pNTQS: Easily Accessible High-Capacity Redox-Active Polymer for Organic Battery

Electrodes

*Simon Muench,^{1,2} Jan Winsberg,^{1,2} Christian Friebe,^{1,2} Andreas Wild,^{1,2} # Johannes C. Brendel,^{1,2} Alexandra Lex-Balducci,^{1,2} Ulrich S. Schubert.^{1,2}**

¹ Laboratory of Organic and Macromolecular Chemistry (IOMC), Friedrich Schiller University Jena, Humboldtstraße 10, 07743 Jena, Germany, Fax: (+)49 3641 948202, E-mail: ulrich.schubert@uni-jena.de, Homepage: www.schubert-group.de

² Center for Energy and Environmental Chemistry Jena (CEEC Jena), Friedrich Schiller University Jena, Philosophenweg 7a, 07743 Jena, Germany

Current adress: Evonik Creavis GmbH, Paul-Baumann-Straße 1, 45772 Marl, Germany

Experimental

1.1. Materials and equipment

All starting materials were purchased from commercial sources and used as obtained. Dimethyl sulfoxide (DMSO), *N,N*-dimethylformamide (DMF), 1,3-dioxolane (DOL), and dimethoxyethane (DME) were purchased from Acros Organics in anhydrous quality. Lithium *bis*(trifluoromethane)sulfonimide (LiTFSI) 99.95% was purchased from Sigma-Aldrich. The progress of the reactions was monitored by thin-layer chromatography (TLC) on 0.2 mm Merck silica gel plates (60 F254). Column chromatography was performed on silica gel 60 columns (Macherey-Nagel 40 to 63 µm). ¹H and ¹³C NMR spectra were recorded on a Bruker AC 300 spectrometer at 298 K. Chemical shifts are reported in parts per million (ppm,

δ scale) relative to the residual signal of the deuterated solvent. Elemental analyses were carried out using a Vario ELIII – Elementar Euro and an EA – HekaTech. SEC was performed on an Agilent 1200 series system (degasser: PSS, pump: G1310A, auto sampler: G1329A, oven: Techlab, DAD detector: G1315D, RI detector: G1362A, eluent: DMAc + 0.21% LiCl, 1 mL min⁻¹, temperature: 40 °C, column: PSS GRAM guard/1000/30 Å) with a polystyrene calibration standard. CV and galvanostatic experiments were performed using a Biologic VMP 3 potentiostat at room temperature under an argon atmosphere. The homogenation of the polymer slurries was performed using a VMA-Getzmann lab dissolver LC30 with a 25 mm disc.

1.2. Synthesis

1-(4-vinylbenzyl)-1H-naphtho[2,3-d]triazole-4,9-dione (**3**). 0.71 mL (5.0 mmol) of *p*-vinylbenzylchloride (**1**) was dissolved in 5 mL of *N,N*-dimethylformamide (DMF) and 360 mg (5.5 mmol) of NaN₃ was added. The reaction mixture was stirred at room temperature for 2 h. 50 mL of diethyl ether was added and the mixture was washed twice with 25 mL of brine. Diethyl ether was added to the aqueous layers for extraction and the combined organic layers were dried over MgSO₄. 5 mL of DMF was added and the diethyl ether was removed under reduced pressure (50 mbar, 40 °C). The obtained solution was subsequently utilized in the next reaction step without isolation of the organic azide.

To the solution of *p*-vinylbenzylazide in DMF, 1.58 g (10.0 mmol) of 1,4-naphthoquinone (**2**) was added. The reaction mixture was stirred at 80 °C for 18 h. After cooling, 50 mL of ethyl acetate was added and the mixture was washed twice with 25 mL of brine. Ethyl acetate was added to the aqueous layers for extraction and the combined organic layers were dried over MgSO₄. The solvent was evaporated under reduced pressure and the residue was washed three

times with each 10 mL of MeOH. The residue was then purified *via* a short silica flash column with dichloromethane as eluent and recrystallized from EtOH/acetone/CHCl₃ (2/1/1) utilizing activated charcoal. 685 mg (2.2 mmol, 43%) of an off-white powder were obtained.

¹H NMR (300 MHz, CD₂Cl₂, δ in ppm): 8.24 (m, 2H, Ar); 7.83 (m, 2H, Ar); 7.42 (m, 4H, Ar); 6.68 (dd, 1H, C=CH); 6.00 (s, 2H, CH₂); 5.75 (d, 1H, C=CH₂); 5.26 (d, 1H, C=CH₂).

¹³C NMR (75 MHz, CD₂Cl₂, δ in ppm): 176.8; 175.4; 145.7; 138.2; 135.9; 135.2; 134.3; 133.5; 133.4; 133.2; 132.8; 128.7; 127.6; 127.2; 126.6; 114.7; 53.5. Elemental analysis calculated for C₁₉H₁₃N₃O₂: C: 72.37, H: 4.16, N: 13.33; found: C: 71.97, H: 3.94, N: 13.18.

poly(1-(4-vinylbenzyl)-1H-naphtho[2,3-d]triazole-4,9-dione) (**pNTQS**). 500 mg (1.59 mmol) of **3** and 26 mg (0.16 mmol, 10 mol%) of AIBN were added to 4.1 mL of dry dimethyl sulfoxide (DMSO) and deaerated under argon atmosphere. The mixture was heated to 75 °C, which allows the dissolution of the monomer, and the reaction mixture was stirred at this temperature for 18 h. After precipitation in cold acetonitrile, the product was separated by centrifugation, washed with acetonitrile, and dried under vacuum to give 195 mg (39%) of an off-white solid.

¹H NMR (300 MHz, CDCl₃, δ in ppm): 8.3-7.9 (b, 2H); 7.9-7.6 (b, 2H); 7.4-6.9 (b, 2H); 6.9-6.2 (b, 2H); 6.1-5.7 (b, 2H); 1.9-0.7 (b, 2H).

SEC (DMAc, 0.21% LiCl, PS standard): $M_n = 3900 \text{ g mol}^{-1}$, $M_w = 4900 \text{ g mol}^{-1}$, $D = 1.25$.

1.3. Electrochemical analysis

Cyclic voltammetry analysis: A three-electrode setup was used. Working electrode: Glassy carbon disk (diameter 2 mm); reference electrode: AgNO₃/Ag; counter electrode: Pt-wire; scan rates: 25 to 500 mV s⁻¹. The redox couple of ferrocenium/ferrocene (Fc⁺/Fc) was utilized as internal standard.

Galvanostatic charge/discharge experiments were performed after an equilibration time of 24 h. All experiments were carried out at room temperature. The charge/discharge capacities were determined based on the weight of the active material in the electrode.

1.4. Cell manufacturing

The slurries for the coin cell experiments were formulated utilizing a lab dissolver. A solution of **pNTQS** and poly(vinylidene fluoride) (PVdF, M_w 534,000 g mol⁻¹, Sigma-Aldrich) in *N*-methyl-2-pyrrolidone (NMP) was added to SuperP[®] (Alfa Aesar) as conducting additive (**pNTQS**/PVdF/SuperP[®] 10/10/80 or 25/10/65 (*m/m/m*)). The resulting paste was homogenized for 30 min at 4000 rpm. The slurry was coated on aluminum foil (thickness: 15 μm; MTI) applying the doctor blading method. Subsequently, the solvent was removed at 80 °C for 20 h. After drying, round composite electrodes (15 mm diameter) were cut with a MTI Precision Disc Cutter T-0.6. The composite loading on the electrodes amounted between 0.9 and 1.2 mg. Coin cells (type 2032) with a polymer composite cathode, a lithium metal anode and a poly(propylene) separator (Celgard, MTI) were manufactured under an argon atmosphere. 1 M LiTFSI in DOL/DME 1/1 (v/v) was used as electrolyte. The cells were sealed with an electric crimper machine (MTI MSK-100D).

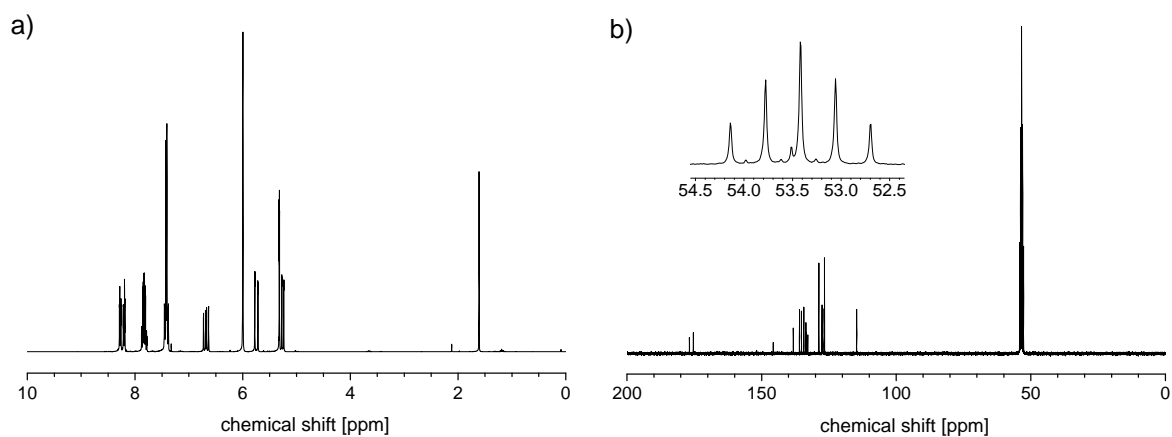


Figure S1: a) ^1H and b) ^{13}C NMR spectra of **3** (CD_2Cl_2 , 300 MHz).

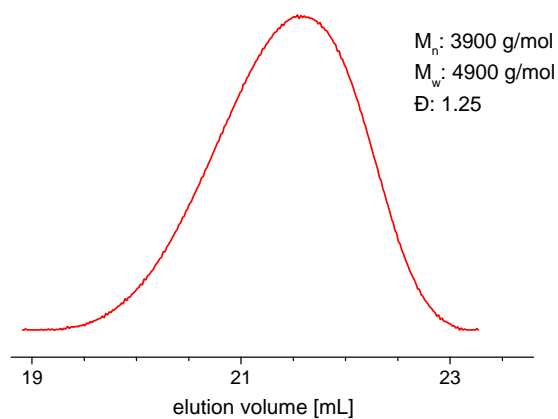


Figure S2: Size-exclusion chromatography of **pNTQS** polymerized in DMSO with 10 mol% AIBN (DMAc, 0.21% LiCl with poly(styrene) standard).

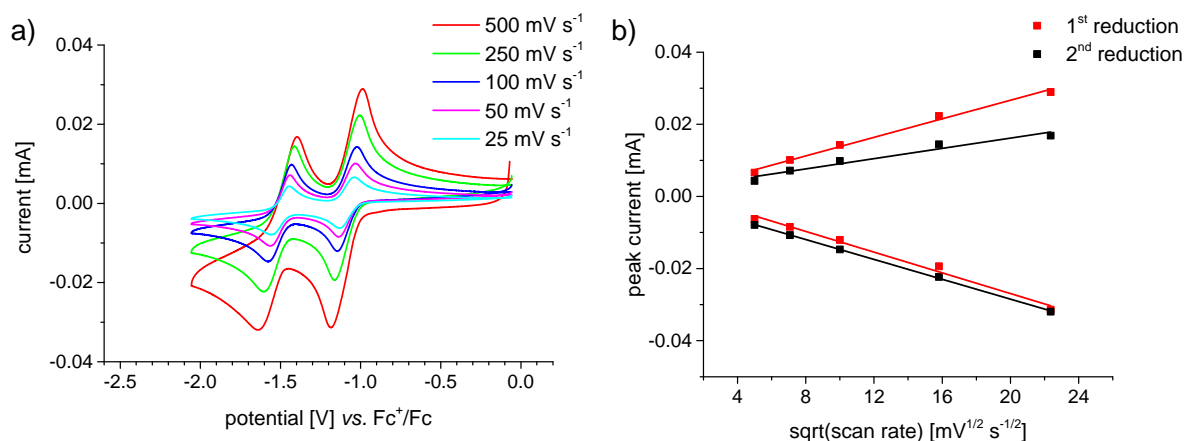


Figure S3: a) Variation of the scan rate for the cyclic voltammetry of **3** with DMF/0.1 M LiClO₄ as electrolyte and b) the corresponding square-root dependence of the peak current on the scan rate.

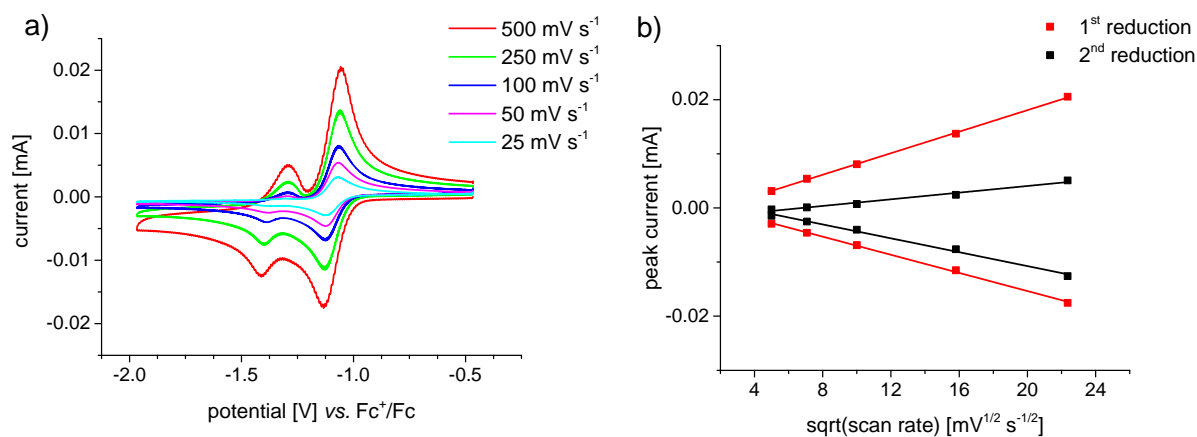


Figure S4: a) Variation of the scan rate for the cyclic voltammetry of **pNTQS** with DMF/0.1 M LiClO₄ as electrolyte and b) the corresponding square-root dependence of the peak current on the scan rate.

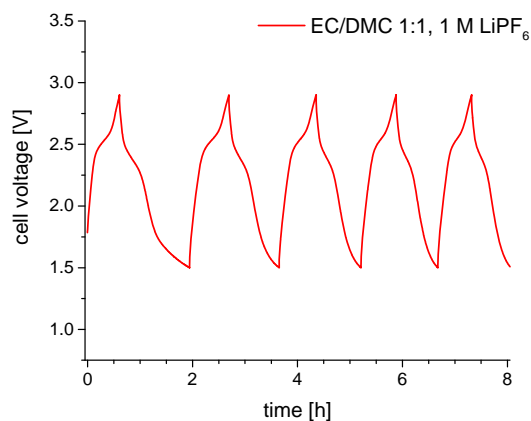


Figure S5: Voltage profile of a charge/discharge experiment of a **pNTQS** vs. Li cell at 1C with 1 M LiPF₆ in EC/DMC 1/1 (v/v).

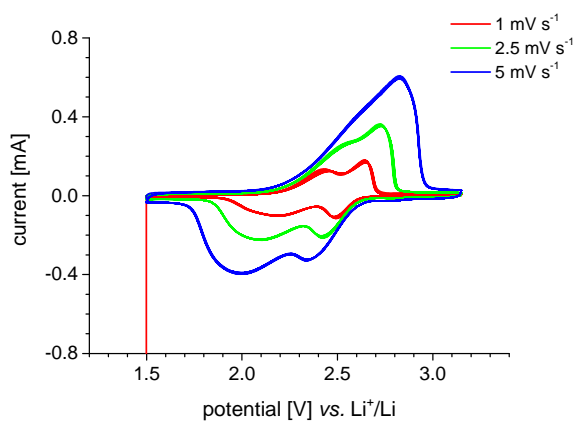


Figure S6: Cyclic voltammetry of **pNTQS** in a coin cell at different scan rates (**pNTQS**/PVdF/SuperP[®] 10/10/80 (m/m/m) vs. Li with 1 M LiTFSI in DOL/DME 1/1 (v/v), 10 cycles each).