# **Supporting information**

# **PolyTCAQ in organic batteries: Enhanced capacity at constant cell potential using two-electron-redox-reactions**

Bernhard Häupler, René Burges, Tobias Janoschka, Thomas Jähnert, Andreas Wild, Ulrich S. Schubert\*

B. Häupler, R. Burges, T. Janoschka, T. Jähnert, Dr. A. Wild, Prof. Dr. U. S. Schubert Laboratory of Organic and Macromolecular Chemistry
Friedrich Schiller Universität Jena
Humboldtstr. 10, 07743 Jena, Germany
Fax: (+)49 3641 948202
E-mail: ulrich.schubert@uni.jena.de
Homepage: www.schubert-group.com

B. Häupler, R. Burges, T. Janoschka, T. Jähnert, Dr. A. Wild, Prof. Dr. U. S. Schubert Jena Center for Soft Matter (JCSM),
Friedrich Schiller Universität Jena,
Philosophenweg 7, 07743 Jena, Germany

## 1.) General remarks

Dichloromethane, tetrahydrofuran and toluene were dried with a PureSolv-EN<sup>TM</sup> Solvent Purification System (Innovative Technology). *N*,*N*-Dimethylformamide and benzene were distilled over calcium hydride and stored over mol sieves. 1,2-Dichloroethane was distilled over  $P_2O_5$  and stored over mol sieves.

All starting materials were purchased from commercial sources and were used as obtained unless otherwise noted. 2,2'-Azobis(*iso*-butyronitrile) (AIBN) was recrystallized from methanol prior to use.

Unless otherwise noted, all reactions were performed under inert atmosphere.

Reactions were monitored by TLC on 0.2 mm Merck silica gel plates (60 F254). Column chromatography was performed on silica gel 60 (Merck).

<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker AC 300 (300 MHz) spectrometer at 298 K. Chemical shifts are reported in parts per million (ppm,  $\delta$  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.

Cyclic voltammetry and galvanostatic experiments were performed using a Biologic VMP 3 potentiostat at room temperature.

Size exclusion chromatography 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, temperature: 40 °C, column: PSS GRAM guard/1000/30 Å)

## 2.) Syntheses

#### Synthesis of 2-vinylanthraquinone (3):

А flask charged with 2-bromoanthraquinone 5.22 was (1.5)mmol), g, bis(dibenzylideneacetone)palladium(0) (0.060)g, 0.104 biphenyl-2-yldi-tertmmol), butylphosphine (0.062 g, 0.209 mmol), tetrahydrofuran (10.5 mL) and 5.75 mL of a 1 M tetrabutylammonium fluoride solution in tetrahydrofuran. The mixture was purged with nitrogen and 2,4,6,8-tetramethyl-2,4,6,8-tetravinyl-1,3,5,7,2,4,6,8-tetraoxatetrasilocane (0.902 mL, 2.61 mmol) was added dropwise. The reaction mixture was heated to 80 °C for eight hours under nitrogen. The reaction mixture was allowed to cool to room temperature and was poured into 250 mL of ethanol. The precipitate was separated by filtration and washed twice with hexane. After drying in vacuum, almost pure 2-vinylanthraquinone (1.175 g, 5.02 mmol, 96%) as pale yellow powder, which was suitable for the next reaction, was obtained. An analytically pure sample was obtained by column chromatography (silica gel, hexane/dichloromethane 1/1). Anal. Calcd for C<sub>16</sub>H<sub>10</sub>O<sub>2</sub>: C, 81.90; H, 4.30. Found: C, 81.85; H, 4.31. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz, ppm): δ 5.54 (d, 1H), 6.05 (d, 1H), 6.87 (dd, 1H), 7.80 (m, 3H), 8.32 (m, 4H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz, ppm): δ 183.2, 182.6, 143.2, 135.4, 134.1, 134.0, 133.8, 133.6, 133.5, 132.5, 131.4, 128.3, 127.8, 127.2, 124.8, 118.4.

#### Synthesis of 2-vinyl-11,11,12,12-tetracyanoanthraquinonedimethane (4):

2-Vinylanthraquinone (1 g, 4.27 mmol) and malononitrile (0.85 g, 0.81 mL, 12.81 mmol) were dissolved in 71 mL chloroform under argon atmosphere. Pyridine (2.07 mL, 25.6 mmol) and titaniumtetrachloride (1.41 mL, 12.81 mmol) were added successively dropwise to the reaction mixture within five minutes. The mixture was heated to 80 °C for 14 h under nitrogen. The reaction mixture was allowed to cool to room temperature and extracted twice with water and once with brine. The organic layer was dried over sodium sulfate, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography (silica gel, chloroform) to yield 700 mg (2.12 mmol, 50%) as yellow powder. Anal. Calcd for C<sub>22</sub>H<sub>10</sub>N<sub>4</sub>: C, 80.00; H, 3.10, N, 16.90. Found: C, 79.94; H, 3.08, N 16.91. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 300 MHz, ppm):  $\delta$  5.61 (d, 1H), 6.06 (d, 1H), 6.88 (dd, 1H), 7.77 (m, 3H), 8.27 (m, 4H).<sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>, 75 MHz, ppm):  $\delta$  160.5, 160.0, 141.8, 134.5, 132.4, 130.8, 130.4, 130.2, 129.7, 129.0,128.01, 127.5, 124.93, 119.3, 113.1.

General procedure for the polymerization of monomer 4:

A flask was charged with 50 mg of the monomer **4** (0.15 mmol), and a sufficient amount of solvent (see Table 1) was added to dissolve the monomer completely. Subsequently 1.24 mg AIBN (0.0076 mmol, 5 mol %), was added and the reaction mixture was purged with nitrogen for 5 minutes. The mixture was heated to 80 °C for 18 hours. After the polymerization, the solution was poured into dichloromethane to precipitate the product which was purified by reprecipitation from DMF into dichloromethane to yield the polymer **5** as a yellow powder. Anal. Calcd for  $C_{22}H_{10}N_4$ : C, 80.00; H, 3.10, N, 16.90. Found: C, 79.96; H, 3.13, N 16.95. <sup>1</sup>H NMR (DMF-d7, 300 MHz, ppm):  $\delta$  8.83 to 7.48 (br, 7H), 2.62 to 1.31 (br, 3H).

Table S1: Analytical data for polymers prepared by free radical polymerization of 4.

Entry	solvent / concentration	<b>PDI</b> <sup>a</sup>	<b>M</b> <sub>n</sub> [g∕mol] <sup>a</sup>	yield [%]
1	benzene 0.25 M	1.25	$1.31 \times 10^4$	37
2	1,2-dichloroethane 0.5 M	1.82	$1.00  imes 10^4$	79
3	THF 0.25 M	1.98	$1.70  imes 10^4$	52
4	toluene 0.25 M	1.55	$1.16  imes 10^4$	42
5	DMF 1 M	1.87	$2.67  imes 10^4$	85

a) Determined by SEC (DMF, 0.1% LiCl, PS standard).

#### Electrochemical analysis:

For cyclic voltammetry a three electrode setup was used (WE: glassy carbon, RE: Ag/AgNO<sub>3</sub> in CH<sub>3</sub>CN, CE: Pt). The redox couple of Fc/Fc<sup>+</sup> was utilized as internal standard. All electrolytes were degassed with dry nitrogen and all measurements were performed under nitrogen atmosphere. Cyclic voltammograms of the polymers were obtained employing the composite electrode as working electrode (RE: Ag/AgNO<sub>3</sub> in CH<sub>3</sub>CN, CE: Pt).

#### Preparation of electrodes:

Electrodes were prepared by adding a solution of polyTCAQ in NMP (*N*-methyl-2-pyrrolidone) (10 mg/mL) to a mixture of vapor grown carbonfibers (VGCF; Sigma Aldrich) as conducting additives and poly(vinylidenefluoride) (PVDF; Sigma Aldrich) as a binder (ratio: 10/80/10 *wt* %). These materials were mixed in a montar for 10 minutes, and the thus-obtained paste was coated on graphite foil (Alfa Aesar) applying a doctor blading method. Next, NMP was removed heating the electrodes at 100 °C for 24 h.Subsequently the electrochemical experiments were performed.

#### Preparation of coin cells:

Electrodes for coin type cells were prepared as follows. A solution of polyTCAQ in NMP (Nmethyl-2-pyrrolidone) (10 mg/mL) was added to of vapor grown carbonfibers (VGCF; Showa-Denko) and Super P<sup>®</sup> as conducting additives and poly(vinylidenefluoride) (PVDF; Sigma Aldrich) as a binder (ratio: 20/30/30/10 wt %). These materials were mixed in a motar for 10 minutes, and the thus-obtained paste was coated on aluminium foil (thickness 0.015 mm, MTI Corporation) applying a doctor blading method. Next, the NMP was removed at 100 °C for 24 h. The amount of active material on the electrode was determined on the basis of the weight of the dried electrodes. The two electrode coin cells (type 2032) were manufactured under argon atmosphere. Suitable round composite electrodes (15 mm diameter) were cut with a MTI Corporation Precision Disc Cutter T-0.6. Thereby, the crude electrode was sandwiched between two sheets of paper. This electrode employed as cathode was placed into the bottom cell case and separated from the lithium anode by a porous polypropylene membrane (celgard, MTI Corporation). On top of the lithium anode a stainless steal space (diameter: 15.5 mm, thickness: 0.3 mm, MTI Corporation) and a stainless steal wave spring (diameter: 14.5 mm, thickness: 5 mm) were placed. The cell was filled with electrolyte (propylene carbonate, 0.1 lithium perchlorate) and the top cell case was placed onto the electrode. The cell was sealed with an electric crimper machine (MTI Corporation MSK-100D). Electrochemical measurements were performed after an equilibration time of 24 h.

Charge-discharge experiments:

All experiments were performed at room temperature. The charge/discharge capacities were determined based on the weight of poly(TCAQ) in the electrode.



**Figure S1:** Cyclic voltammogram of a composite electrode of **5**, 10/80/10 **5**/VCGF/PVdF. Scan speed of 20 mV/s, 100 cycles. Electrolyte: Propylene carbonate 0.1 M lithium perchlorate.