Supporting Information for:

**Thianthrene-functionalized polynorbornenes as high-voltage materials for organic cathode-based dual-ion batteries**

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1 Experimental section

1.1 Materials

Chemicals were obtained from commercial suppliers and used without further purification. Experiments with water- or oxygen-sensitive substances were carried out under an argon atmosphere using glassware dried by heating under vacuum and standard Schlenk-techniques. Anhydrous solvents were obtained from a solvent purification system (MB-SPS) by M-Braun. All other solvents were distilled prior to use.

1.2 Analytical methods

$^1$H and $^{13}$C($^1$H)NMR spectra were recorded on Bruker Avance dpx 400 and dmx 500 spectrometers at rt and referenced to the residual proton or carbon resonance of the deuterated solvent. $^1$ EI-MS spectra were recorded on a MAT 90 or a MAT 95 XL sector field device from Thermo Finnigan. Polymer molecular weights were determined using a GPC unit by Agilent Technologies. As eluent THF was used with a flow rate of 1 mL/min, and measurements were calibrated against polystyrene standards by PSS Polymer Standard Service GmbH. For thermal gravimetric analysis a TGA/STAA851 was used and for differential scanning calorimetry a DSC823°, both by Mettler Toledo.

1.3 Synthetic procedures

2-Bromothianthrene (2) and thianthrene-2-carbaldehyde (3) were synthesized according to literature procedures.

Thianthren-2-ylmethanol (4). NaBH$_4$ (269 mg, 7.10 mmol) was added to a solution of thianthrene-2-carbaldehyde (3, 3.48 g, 14.2 mmol) in a mixture of THF (50 mL) and H$_2$O (1.7 mL) at 0 °C. The resulting mixture was stirred at rt until TLC indicated completion of the reaction (1 h). H$_2$O (50 mL) was added, and the mixture was extracted with Et$_2$O. The organic extracts were washed with brine and dried (MgSO$_4$). Column chromatography (silica gel, cyclohexane/Et$_2$O: 5/1 to 2/1) afforded 4 (3.15 g, 90%) as a colorless solid. $R_f$: 0.19 (cyclohexane/Et$_2$O: 2/1); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.48-7.43 (m, 4H), 7.26-7.19 (m, 3H), 4.64 (s, 2H), 1.83 (s, 1H); $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 140.9, 136.0, 135.6, 135.5, 134.7, 128.9, 128.8, 127.8, 127.2, 126.4, 64.5; MS (EI+): m/z 246.0 [M$^+$], 229.0 [M-OH]$^+$, 216.0 [M-CH$_2$O]$^+$, 184.0 [M-S-CH$_2$O]$^+$; HRMS (EI+): m/z calcld for C$_{13}$H$_{10}$OS$_2$: 246.0173 [M$^+$], found 246.0171; elemental analysis: calcld (%) for C$_{13}$H$_{10}$OS$_2$: C 63.38, H 4.09, S, 26.03; found: C 63.55; H 4.27; S 25.74.

(1S,2R,4S)-Thianthren-2-ylmethyl bicyclo[2.2.1]hept-5-ene-2-carboxylate (5). DCC (710 mg, 3.44 mmol) and 4-DMAP (87.0 mg, 712 mmol) were successively added to a suspension of exo-5-norbornene-2-carboxylic acid (351 mg, 2.54 mmol). Thianthren-2-ylmethanol (4, 700 mg, 2.84 mmol) was added in a mixture of dry NEt$_3$ (0.44 mL, 3.16 mmol) and dry CH$_2$Cl$_2$ (5 mL) at -30 °C. The reaction mixture was vigorously stirred at 0 °C for 1 h and at rt for 6 d. 20 mL CH$_2$Cl$_2$ were added, and the solution was washed with 0.3 M HCl, H$_2$O, and brine and dried (MgSO$_4$). Column chromatography (silica gel, cyclohexane/CH$_2$Cl$_2$: 2/1) afforded 5 (554 mg, 59%) as a colorless, viscous oil. $R_f$: 0.34 (cyclohexane/CH$_2$Cl$_2$: 2/1); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.50-7.44 (m, 4H), 7.26-7.22 (m, 3H), 6.14 (dd, J = 5.6, 2.9 Hz, 1H), 6.10 (dd, J = 5.6, 3.0 Hz, 1H), 5.09 (s, 1H), 3.06 (ddddd, J = 2.2, 1.5, 0.8 Hz, 1H), 2.94-2.93 (m, 1H), 2.29-2.26 (m, 1H), 1.96-1.91 (m, 1H), 1.54-1.51 (m, 1H),
1.42-1.36 (m, 2H); $^{13}$C NMR (101 MHz, CDCl$_3$): δ 176.0, 138.2, 136.3, 136.0, 135.8, 135.6, 135.4, 135.4, 128.8, 128.8, 128.4, 127.9, 127.8, 127.6, 65.4, 46.7, 46.5, 43.2, 41.8, 30.5; MS (EI+): m/z 366.1 [M$^+$], 300.1 [M-C$_3$H$_6$]$^+$, 229.1 [M-C$_3$H$_7$O$_2$]$^+$; HRMS (EI+) m/z calcd for C$_{21}$H$_{19}$O$_4$S$_2$ 366.0748 [M$^+$], found 366.0748; elemental analysis: calcd (%) for C$_{21}$H$_{19}$O$_4$S$_2$: C 68.82, H 4.95, S, 17.50; found: C 68.66; H 4.71; S 17.42.

$(1R,2S,3R,4S)$-Bis(thianthren-2-ylmethyl) bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate (6). CMPI (592 mg, 2.28 mmol) and 4-DMAP (279 mg, 0.76 mmol) were successively added to a solution of thianthren-2-ylmethanol (4, 1.03 g, 4.18 mmol) and 5-norbornene-2,3-dicarboxylic anhydride (312 mg, 1.90 mmol) in a mixture of NEt$_3$ (0.32 mL, 2.28 mmol) and dry CH$_2$Cl$_2$ (15 mL) at 0 °C. The mixture was stirred at 0 °C for 1 h and at rt for 18 h. 15 mL CH$_2$Cl$_2$ were added, and the solution was washed with 0.3 M HCl, H$_2$O, and brine and dried (MgSO$_4$). Column chromatography (silica gel, cyclohexane/EtOAc: 10/1 to 5/1) afforded 6 (1.11 g, 91%) as a colorless, viscous oil. $R_t$ 0.41 (cyclohexane/EtOAc: 5/1); $^1$H NMR (500 MHz, CDCl$_3$): δ 7.47-7.41 (m, 4H), 7.38 (d, J = 7.9 Hz, 2H), 7.37 (d, J = 1.8 Hz, 2H), 7.23-7.18 (m, 4H), 7.08 (dd, J = 8.0, 1.8 Hz, 2H), 6.25 (dd, J = 1.9, 1.9 Hz, 2H), 4.93 (d, J = 12.5 Hz, 2H), 4.83 (d, J = 12.5 Hz, 2H), 3.32-3.31 (m, 2H), 3.17 (q, J = 1.7 Hz, 2H), 1.48 (ddd, J = 8.7, 1.9 Hz, 1H), 1.31 (ddd, J = 8.8, 1.5 Hz, 1H); $^{13}$C NMR (126 MHz, CDCl$_3$): δ 172.3, 135.9, 135.9, 135.6, 135.4, 135.3, 135.1, 128.8, 128.8, 128.7, 127.9, 127.9, 127.8, 65.5, 48.9, 48.4, 46.5; MS (EI+): m/z 639.0 [M$^+$], 638.0 [M$^+$], 572.0 [M-C$_3$H$_7$]$^+$, 229.0 [M-C$_{22}$H$_9$O$_7$]$^+$; HRMS (EI+): m/z calcd for C$_{33}$H$_{28}$O$_4$S$_4$ 638.0713 [M$^+$], found 638.0716. The endo-configuration of 6 was determined by NOE spectroscopy.

2-((1S,4S)-Bicyclo[2.2.1]hept-5-ene-2-yl)thianthrene (7). 2-Bromothianthrene (2, 1.20 g, 4.06 mmol), freshly distilled norbornadiene (1.67 mL, 16.3 mmol), PdCl$_2$(PPh$_3$)$_2$ (144 mg, 0.16 mmol), and formic acid (0.48 mL, 8.13 mmol) were dissolved in a mixture of NEt$_3$ (1.80 mL, 12.2 mmol) and DMF (1.9 mL) and degassed by purging with argon for 15 min. The resulting mixture was stirred at 80 °C for 6 h and cooled to rt. Toluene (10 mL) and HCl (10 wt% in H$_2$O) were added, and the organic layer was separated. The aq. layer was extracted with toluene. The combined organic extracts were washed with H$_2$O and brine and dried (MgSO$_4$). Column chromatography (silica gel, cyclohexane) followed by two successive Kugelrohr distillation steps and another column chromatography step (silica gel, cyclohexane) afforded 7 (724 mg, 58%) as a colorless solid. $R_t$ 0.41 (cyclohexane); $^1$H NMR (400 MHz, CDCl$_3$): δ 7.50-7.46 (m, 2H), 7.41-7.40 (m, 1H), 7.39 (d, J = 8.1 Hz, 1H), 7.25-7.21 (m, 2H), 7.15 (ddd, J = 8.1, 2.0, 0.7 Hz, 1H), 6.24 (dd, J = 5.7, 3.1 Hz, 1H), 6.17 (dd, J = 5.7, 2.9 Hz, 1H), 2.98-2.95 (m, 1H), 2.89-2.86 (m, 1H), 2.69-2.65 (m, 1H), 1.71-1.66 (m, 1H), 1.65-1.60 (m, 1H), 1.54-1.51 (m, 1H), 1.45-1.42 (m, 1H); $^{13}$C NMR (101 MHz, CDCl$_3$): δ 146.5, 137.6, 137.2, 136.0, 135.9, 135.6, 132.2, 128.9, 128.8, 128.6, 127.9, 127.7, 127.4, 48.3, 45.9, 43.5, 42.4, 33.9; MS (EI+): m/z 308.1 [M$^+$], 242.0 [M-C$_3$H$_6$]$^+$; HRMS (EI+): m/z calcd for C$_{19}$H$_{16}$S$_2$ 308.0693 [M$^+$], found 308.0693.

Synthesis of P1 by ROMP. A degassed solution of (1S,2R,4S)-thianthren-2-ylmethyl bicyclo[2.2.1]hept-5-ene-2-carboxylate (5, 728 mg, 1.99 mmol) in 4.6 mL CH$_2$Cl$_2$ was rapidly added to a stirred and degassed solution of G3 (4.4 mg, 5.0 μmol) in 2.4 mL CH$_2$Cl$_2$. The resulting solution was stirred at rt for 21 h. Ethylvinylenether (1.5 mL) was added, and the solution was stirred at rt for 2 h. The polymer was precipitated into methanol and isolated by filtration. The polymer was purified by twofold dissolution in CHCl$_3$ and precipitation from MeOH. P1 (627 mg, 86%) was isolated as a white powder. $^1$H NMR (400 MHz, CDCl$_3$): δ 7.40 (br s, 4H), 7.17-7.06 (m, 3H), 5.35-5.16 (m, 2H), 5.01-4.93 (m, 2H), 3.07-2.96 (m, 1H), 2.67-2.51
(m, 2H), 2.06-1.91 (m, 2H), 1.59 (br s, 1H), 1.11-0.98 (m, 1H); GPC (eluent THF, polystyrene standard): $M_n$ 2.04 × 10^5, $M_w/M_n$ 1.35; DSC (10 °C/min, N₂): $T_g$ 83 °C; TGA (10 °C/min, N₂): $T_{d10\%}$ 382 °C.

Synthesis of P₂ by ROMP. A degassed solution of (1R,2S,3R,4S)-bis(thianthren-2-ylmethyl)bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate (6, 1.19 g, 1.87 mmol) in 3.8 mL CH₂Cl₂ was rapidly added to a stirred and degassed solution of G₃ (8.3 mg, 9.34 µmol) in 2.4 mL CH₂Cl₂. The resulting solution was stirred at rt for 23 h. Ethylvinylether (2 mL) was added, and the solution was concentrated in vacuo. The residue was dissolved in CHCl₃, and the polymer was precipitated into methanol and isolated by filtration. This procedure was repeated once, yielding P₂ (861 mg, 72%) as a white powder. $^1$H NMR (400 MHz, CDCl₃): δ 7.32 (br s), 7.22 (br s), 7.11 (br s), 7.01 (br s), 6.89 (br s), 5.48 (br s), 5.32 (br s), 4.92 (br s), 4.73 (br s), 3.10 (br s), 3.01 (br s), 2.88 (br s), 2.53 (br s), 1.72 (br s); GPC (eluent THF, polystyrene standard): $M_n$ 1.10 × 10^5, $M_w/M_n$ 1.23; DSC (10 °C/min, N₂): $T_g$ 112 °C; TGA (10 °C/min, N₂): $T_{d10\%}$ 372 °C.

Synthesis of P₃ by ROMP. A degassed solution of G₃ (1.1 mg, 1.26 µmol) in 0.33 mL CH₂Cl₂ was rapidly added to a stirred and degassed solution of (2-((1S,4S)‑bicyclo[2.2.1]hept‑5‑ene‑2‑yl)thianthrene (7, 38.9 mg, 0.126 mmol) in 0.5 mL CH₂Cl₂. The resulting solution was stirred at rt for 2 h. Ethylvinylether (0.4 mL) was added, and the solution was concentrated in vacuo. The residue was dissolved in CHCl₃, and the solution was filtered through a short pad of Al₂O₃. The solution was concentrated in vacuo to a small volume, and the polymer was precipitated into methanol and isolated by filtration, yielding P₃ (26 mg, 67%) as a white powder. $^1$H NMR (400 MHz, CDCl₃): δ 7.44 (br s), 7.36 (br s), 7.18 (br s), 6.99 (br s), 5.13 (br s), 2.68 (br s), 2.58 (br s), 2.44 (br s), 2.04 (br s), 1.86 (br s), 1.19 (br s); GPC (eluent THF, polystyrene standard): $M_n$ 2.94 × 10⁴, $M_w/M_n$ 1.63; DSC (10 °C/min, N₂): $T_g$ 130 °C; TGA (10 °C/min, N₂): $T_{d10\%}$ 417 °C.

### 1.4 ROMP of monomers 5, 6 and 7

Table S1. Ring Opening Metathesis Polymerizations of Monomers 5, 6, and 7 using Catalysts G₂ and G₃.₆
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<th>Entry</th>
<th>Monomer (M)</th>
<th>Polymer</th>
<th>Catalyst (C)</th>
<th>[M]/[C]</th>
<th>$M_n$theo [kDa]</th>
<th>$M_n$obs [kDa]</th>
<th>PDI</th>
<th>Yield [%]</th>
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<tbody>
<tr>
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<td>5</td>
<td>P1</td>
<td>G2</td>
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<tr>
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<td>5</td>
<td>P1</td>
<td>G3</td>
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<td>48.5</td>
<td>1.22</td>
<td>60</td>
</tr>
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<td>G3</td>
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<td>G3</td>
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<td>30.8</td>
<td>29.4</td>
<td>1.63</td>
<td>67</td>
</tr>
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</table>

*a*Polymerizations in CH$_2$Cl$_2$ at rt; *b*estimated by GPC in THF against polystyrene standard; *c*performed on a large scale (1.2-2.0 mmol).

1.5 Preparation of composite electrodes

Cell assembly and electrode preparation were performed in a dry room with < 0.02% water content. Composite electrodes were prepared by dispersing polymer, hard carbon or carbon black Super P Li (Imerys), and polyvinylidene fluoride (PVdF) binder (Kynar Flex, Arkema) in NMP with an Ultra-Turrax® T25 digital by IKA at 5000 rpm for 1 h. The resulting suspension was cast on etched alumina foil (30 µm, Schlenk) using a doctor blade (200 µm wet film thickness). Electrodes with 12 mm diameter were cut out and dried in a vacuum oven (BÜCHI B-585) at 80 °C and 10^-5 mbar for 48 h.

1.6 Electrochemical measurements

Cyclic voltammograms (CVs) in solution were measured inside a glovebox using a PGSTAT128N by Metrohm Autolab. As working, counter, and reference electrode a glassy carbon disc electrode (2 mm diameter), a platinum rod, and a Ag/AgNO$_3$ electrode containing a silver wire immersed in an inner chamber filled with 0.1 M AgNO$_3$ and 0.1 M $n$-Bu$_4$NPF$_6$ were used, respectively. The ferrocene/ferrocenium redox couple was used as internal reference. Composite electrodes were tested in Swagelok® type T-cells with a three-electrode setup. Lithium foil (500 µm, Rockwood Lithium) was used as counter and reference electrode, and Freudenberg polypropylene separators (FS2190) were employed soaked with 120 µL of 1 M LiPF$_6$ in EC/DMC (1:1). CVs were measured at 20 °C using a Biologic VMP3 potentiostat. Each measurement was preceded by an open circuit potential step of 6 h to ensure sufficient wetting of the electrodes and separator. Galvanostatic investigations were performed on a MACCOR® 4000 series battery cycler at 20 °C in an environmental chamber. A rest step of 12 h was applied before starting the constant current cycling experiment.
1.7 Rate capability measurements of the P1 composite electrode

Figure 1. Constant current cycling data of a P1 composite electrode at different C rates (P1/Super P Li/PVdF (50:47:3 wt%), EC/DMC (1:1), 1 M LiPF₆, Li counter/reference electrode, potential range 3.3-4.4 V vs. Li/Li⁺).
2 NMR spectra

Figure S1: 400 MHz $^1$H NMR and 101 MHz $^{13}$C{H} NMR spectrum of thianthren-2-ylmethanol (4) in CDCl$_3$. 
Figure S2: 400 MHz $^1$H NMR and 101 MHz $^{13}$C{H} NMR spectrum of (1S,2R,4S)-thianthren-2-ylmethyl bicyclo[2.2.1]hept-5-ene-2-carboxylate (5) in CDCl$_3$. 
Figure S3: 500 MHz $^1$H NMR and 126 MHz $^{13}$C{H} NMR spectrum of (1R,2S,3R,4S)-bis(thianthren-2-ylmethyl) bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate (6) in CDCl$_3$. 
Figure S4: 500 MHz NOE difference $^1$H NMR spectrum of (1R,2S,3R,4S)-bis(thianthren-2-ylmethyl) bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate (6) in CDCl$_3$ (irradiation at H2 (3.31 ppm)).

Figure S5: HH COSY spectrum of (1R,2S,3R,4S)-bis(thianthren-2-ylmethyl) bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate (6) in CDCl$_3$. 
Figure S6: 400 MHz $^1$H NMR spectrum of 2-((1S,4S)-bicyclo[2.2.1]hept-5-en-2-yl)thianthrene (7) in CDCl$_3$. 
Figure S7: 101 MHz $^{13}\text{C}\{\text{H}\}$ NMR and DEPT-135 spectrum of 2-((1S,4S)-bicyclo[2.2.1]hept-5-en-2-yl)thianthrene (7) in CDCl$_3$. 
Figure S8: HH-COSY and HMQC spectrum of 2-((1S,4S)-bicyclo[2.2.1]hept-5-en-2-yl)thianthrene (7) in CDCl$_3$. 
Figure S9: 400 MHz $^1$H NMR spectrum of P1 in CDCl$_3$.

Figure S10: 400 MHz $^1$H NMR spectrum of P2 in CDCl$_3$. 
Figure S11: 400 MHz $^1$H NMR spectrum of P3 in CDCl$_3$. 
3 References


