

## Supporting Information

### **An easy functionalizable oligo(oxyethylene)- and ester-substituted poly(3,4-propylenedioxythiophene) derivative exhibiting alkali metal ion response**

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**Fig. S1** NMR spectra of monomer ProDOT-EO-ester **2** in CDCl<sub>3</sub>: a) chemical structure of ProDOT-EO-ester **2** and numbering scheme; b) <sup>1</sup>H-NMR spectrum; c) <sup>13</sup>C-NMR spectrum.

**Fig. S2** <sup>1</sup>H-NMR spectra of ProDOT-EO-ester **2** (top) and P(ProDOT-EO-ester) (bottom) in CDCl<sub>3</sub>

## *Materials*

Sodium hydride (60% dispersion in mineral oil), sodium iodide (ACS reagent,  $\geq 99.5\%$ ), ethyl 4-hydroxybenzoate (99%), ammonium chloride (99.99%), anhydrous magnesium sulphate ( $\geq 99.5\%$ ), anhydrous iron(III) chloride ( $\geq 98\%$ ), tetrabutylammonium perchlorate (TBAP,  $\geq 99\%$ ), ammonium hydroxide solution (ACS reagent, 28.0-30.0%  $\text{NH}_3$  basis) and hydrazine hydrate (reagent grade,  $\text{N}_2\text{H}_4$  50-60 %) were purchased from Sigma-Aldrich (Germany). Toluene (HPLC grade), tetrahydrofuran (dried,  $\geq 99.8\%$  THF,  $\leq 10$  ppm  $\text{H}_2\text{O}$ ), 2-butanone (methyl ethyl ketone, MEK,  $\geq 99.5\%$ , p.a., ACS), *N,N*-dimethylformamide ( $\geq 99.5\%$ , DMF), chloroform (dried,  $\geq 99.8\%$   $\text{CHCl}_3$ ,  $\leq 50$  ppm  $\text{H}_2\text{O}$ ), *n*-heptane (HPLC), diethyl ether ( $\geq 99.5\%$ , p.a.), acetonitrile (ACN, HPLC grade) and ethyl acetate (GC grade) were purchased from Carl Roth (Germany). All reagents were used as received.

## *Instrumentation*

The  $^1\text{H}$ - and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker Avance III 400 spectrometer, operating at 400.1 and 100.6 MHz for  $^1\text{H}$  and  $^{13}\text{C}$  nuclei, respectively.  $^1\text{H}$  and  $^{13}\text{C}$  chemical shifts are reported in  $\delta$  units (ppm) relatively to the residual peak of the solvent ( $^1\text{H}$ :  $\text{CDCl}_3$ : 7.26 ppm;  $^{13}\text{C}$ :  $\text{CDCl}_3$ : 77.01 ppm).

Cyclic voltammetry (CV) was employed to obtain the polymer by electropolymerisation and to study the electrochemical behaviour of the polymer prepared either by chemical or electrochemical method deposited as thin film onto ITO electrode. Measurements were done using the AUTOLAB PGSTAT302N system (ECO CHEMIE, Utrecht, The Netherlands) with a single compartment electrochemical cell of 3 ml volume with a Ag/AgCl as the reference electrode, a Pt wire as the counter electrode and ITO as the working electrode.

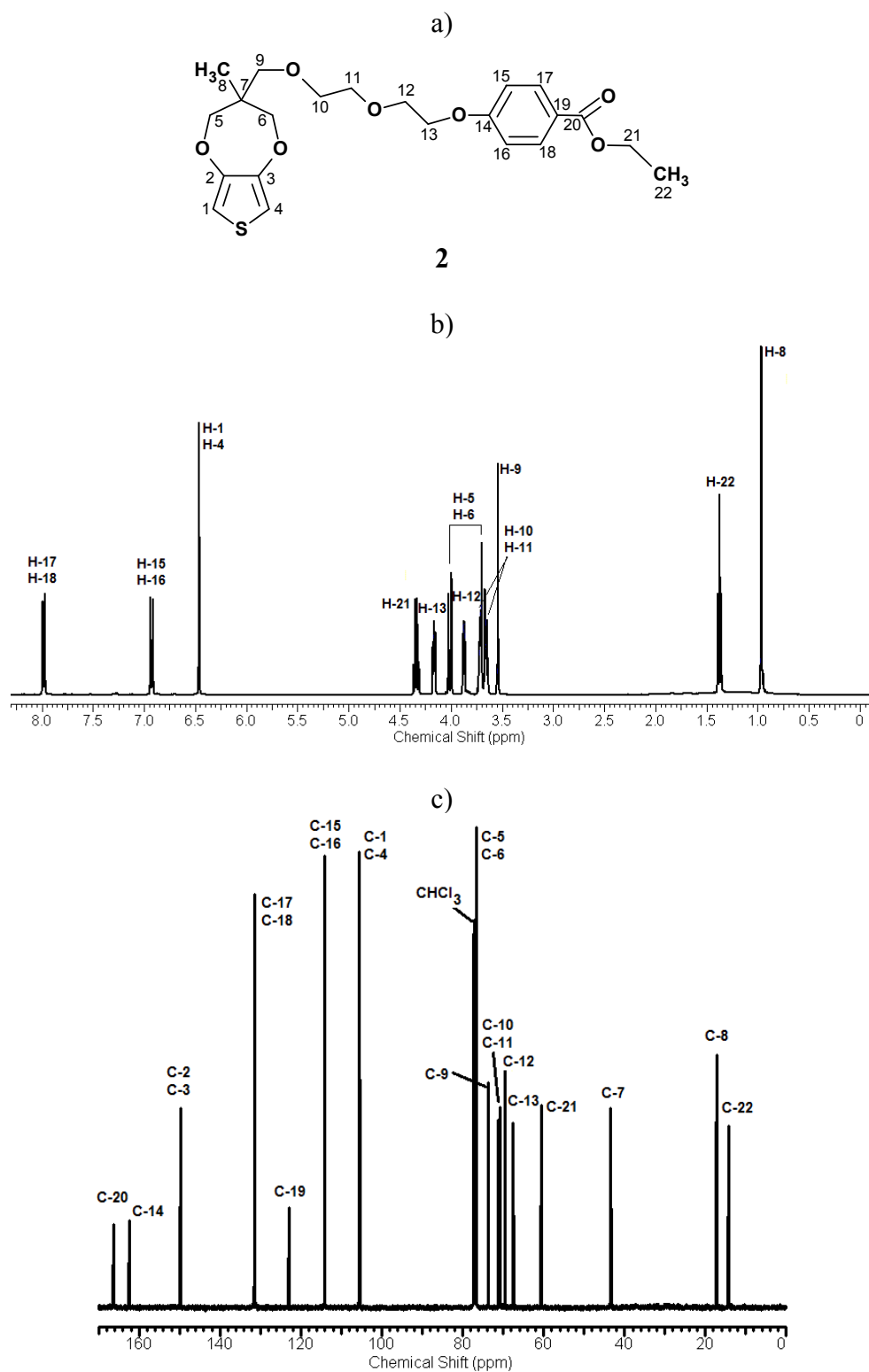
### *Synthesis of (ProDOT-EO-ester) 2*

In a 100 ml three-neck round bottom flask equipped with a reflux condenser with drying tube, dropping funnel, gas inlet and thermometer, 0.072 g (1.80 mmole) of sodium hydride was suspended in 10 mL of dry DMF under nitrogen. The suspension was cooled to 0°C and a solution of 0.20 g (1.21 mmole) of ethyl-4-hydroxybenzoate was added dropwise. After complete addition, the mixture was allowed to reach room temperature and it was stirred for 2h until the evolution of hydrogen stopped. Then, a solution of 0.48 g (1.21 mmole) of ProDOT iodo derivative **1** in 10 ml of dry DMF was added and the mixture was stirred for 6 h at 65°C. After cooling, the mixture was hydrolyzed using 5 mL of saturated aqueous NH<sub>4</sub>Cl and poured into 250 mL of water. The aqueous phase was extracted with 3 x 50 mL of diethyl ether. The organic extracts were combined and dried over Mg<sub>2</sub>SO<sub>4</sub>, followed by evaporation of the solvent. The crude product was purified by column chromatography on silica gel using *n*-heptane/ethyl acetate 2 : 1 as the eluent, giving 0.44 g (=83%) of **2** as a viscous colorless oil.

<sup>1</sup>H-NMR (CDCl<sub>3</sub>), δ (ppm): 7.99-7.96 (2H, dd, H-17, H-18), 6.93-6.91 (2H, dd, H-15, H-16), 6.46 (2H, s, H-1, H-4), 4.36-4.31 (2H, quartet, H-21), 4.18-4.15 (2H, t, H-13), 4.02-3.99 (2H, d, H-5, H6), 3.88-3.86 (2H, t, H-12), 3.73-3.64 (6H, m, H-5, H-6, H-10, H-11), 3.54 (2H, s, H-9), 1.39-1.36 (3H, t, H-22), 0.97 (3H, s, H-8).

<sup>13</sup>C-NMR (CDCl<sub>3</sub>), δ (ppm): 166.29 (C-9), 162.44 (C-14), 149.82 (C-23), 131.44 (C-17, C-18), 123.01 (C-19), 114.08 (C-15, C-16), 105.53 (C-1, C-4), 77.33-76.63 (C-5, C-6), 73.71 (C-9), 71.14-70.65 (C-10, C-11), 69.50 (C-12), 67.55 (C-13), 60.56 (C-21), 43.35 (C-7), 17.27 (C-8), 14.32 (C-22).

IR (cm<sup>-1</sup>): 3108, 2963-2873, 1707, 1607, 1510, 1484, 1449, 1366, 1274, 1251, 1168, 1101, 1057, 1021, 848, 769, 696.



**Fig. S1** NMR spectra of monomer ProDOT-EO-ester **2** in  $\text{CDCl}_3$ : a) chemical structure of ProDOT-EO-ester **2** and numbering scheme; b)  $^1\text{H}$ -NMR spectrum; c)  $^{13}\text{C}$ -NMR spectrum.

### *Chemical Polymerization of ProDOT-EO-ester 2*

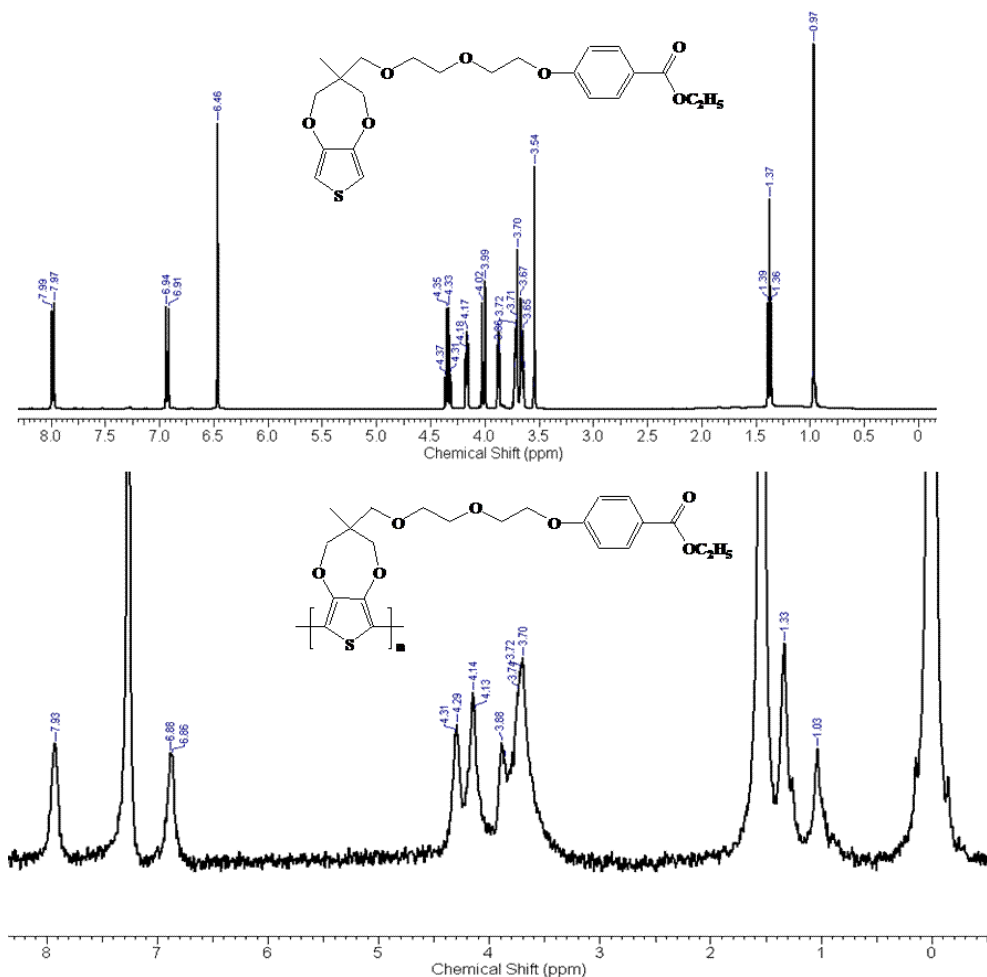
To a solution of 100 mg (0.229 mmole) of **2** in 15 mL of chloroform was added 170.6 mg (1.03 mmole) of anhydrous FeCl<sub>3</sub>. The mixture was stirred for 24 h under argon atmosphere. 2 mL of concentrated aqueous ammonium hydroxide was added to the reaction mixture and stirring was continued for another 12 h. After treating it with ammonium hydroxide, the reaction mixture was poured into 50 mL of methanol and precipitated out. The precipitate was filtered and vacuum-dried to get the crude undoped polymer, that was further purified by Soxhlet extraction with methanol to give 92 mg (= 92%) of the final polymer, P(ProDOT-EO-ester), as a dark purple powder. P(ProDOT-EO-ester) exhibits partial solubility in chloroform, THF and DMF, respectively, and only soluble fractions in these solvents were used for further investigations.

<sup>1</sup>H-NMR (CDCl<sub>3</sub>), δ (ppm): 7.94 (2H, s), 6.89 (2H, s), 4.31-4.15 (m, 6H), 3.89-3.71 (m, 10H), 1.34 (m, 3H), 1.06 (s, 3H), IR (cm<sup>-1</sup>): 3075, 2978-3867, 1704, 1605, 1509, 1470, 1434, 1362, 1275, 1250, 1167, 1101, 1043, 1022, 847, 769, 695.

### *Partial hydrazinolysis of the ester group in P(ProDOT-EO-ester)*

To a solution of 100 mg (0.229 mmole) of **2** in 15 mL of chloroform was added 170.6 mg (1.03 mmole) of anhydrous FeCl<sub>3</sub>. The mixture was stirred for 24 h under argon atmosphere. 2 mL of hydrazine monohydrate was added to the reaction mixture and stirring was continued for another 20 h. Then the reaction mixture was poured into 50 mL of methanol and the polymer precipitated. The precipitate was filtered and vacuum-dried to get the crude undoped hydrazide-functionalized copolymer CP(ProDOT). It was further purified by Soxhlet extraction with methanol and vacuum-dried to give 90 mg (=90%) of the pure copolymer CP(ProDOT) as a green-olive solid.

IR (cm<sup>-1</sup>): 3386, 3265, 2956-2779, 1664, 1605, 1510, 1470, 1435, 1349, 1276, 1253, 1195, 1168, 1099, 1046, 927, 847, 823, 769, 695.



**Fig. S2** <sup>1</sup>H-NMR spectra of ProDOT-EO-ester **2** (top) and P(ProDOT-EO-ester) (bottom) in CDCl<sub>3</sub>

### *Electropolymerization of ProDOT-EO-ester 2*

Electrochemical polymerization (electrocoating) was performed in acetonitrile (ACN) containing either 0.1 M TBAP or 0.1 M LiClO<sub>4</sub> and a concentration of 0.02 M of **2**, by cycling the potential between 0 and +1.4 V vs. Ag/AgCl at 100 mV/s scan rate. A three-electrode system employing indium tin oxide-coated glass (ITO) as working electrode, platinum wire as counter electrode, and Ag/AgCl as reference electrode was used. After electropolymerization, the polymer film was rinsed with fresh diethyl ether to remove the remaining monomer from the polymer films surface.