

Electronic Supplementary Information for:

A crosslinked conducting polymer with well-defined proton trap  
function for reversible proton cycling in aprotic environments

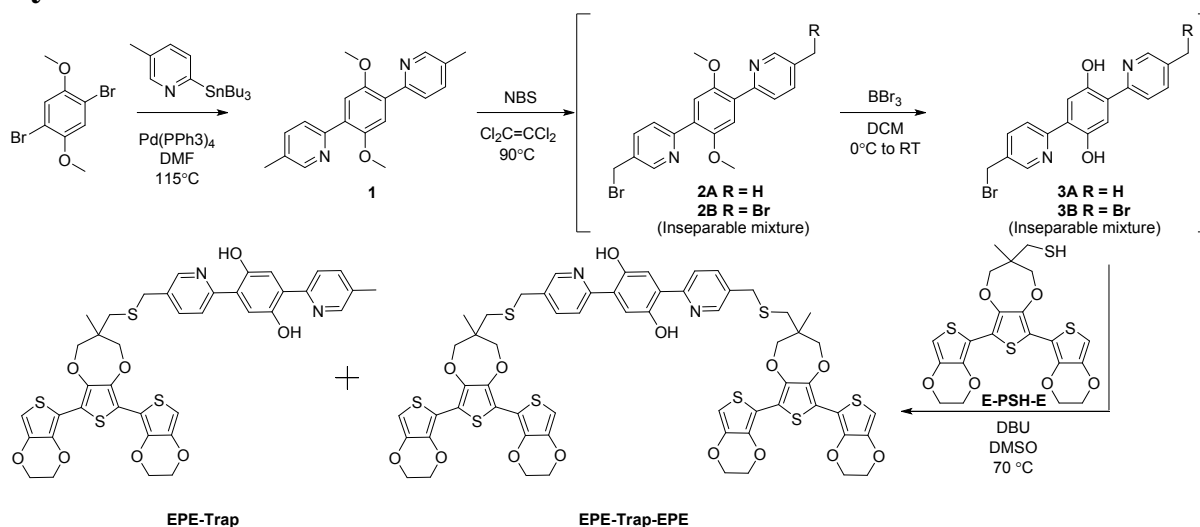
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## Synthesis and characterization



**Scheme S 1.** Synthesis of the trap unit and the coupling to an EDOT-ProDOT-EDOT (EPE) trimer base to form the trap-CRPs (**EPE-trap** and **EPE-trap-EPE**).

### General synthetic information

All reactions were performed in flame dried glassware under an argon atmosphere unless otherwise noted. Room temperature (RT) refers to 22 °C. Reagents were purchased from commercial sources and used without further purification. Anhydrous *N,N*-dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) was obtained from Sigma-Aldrich/Merck. Analytical thin layer chromatography was performed using pre-coated Merck Silica 60 F254 plates, and compound visualization was achieved with UV light (254 nm). Trimeric compounds darkens under prolonged exposure to UV light and requires no extra visualization aid, other compounds were visualized using potassium permanganate stain and heated when needed. Flash chromatography was performed on a Grace REVELERIS® X2 flash chromatography system using pre-packed silica cartridges (12 or 40 g, 40–63 μm). Dry loading was used in all cases and the crude was loaded onto silica using a suitable solvent which was subsequently removed under vacuum. The silica was then packed in a dry loading cartridge and eluted using the specified gradient and solvent combination. 2-Tributylstannyl-5-methylpyridine<sup>1</sup> and E-PSH-E<sup>2</sup> was prepared as previously reported.

### Instrumentation

**Nuclear magnetic resonance (NMR) spectroscopy:** NMR spectra were recorded using an Agilent 400-MR (<sup>1</sup>H at 400 MHz, <sup>13</sup>C at 101 MHz) equipped with a OneNMR probe, or using a Bruker Avance Neo (<sup>1</sup>H at 500 MHz, <sup>13</sup>C at 126 MHz) equipped with a TXO (CRPHe TR-<sup>13</sup>C/<sup>15</sup>N/<sup>1</sup>H 5 mm-Z) cryoprobe. Chemical shifts are reported using the residual solvent signal as an indirect reference to TMS (CHCl<sub>3</sub>: δ<sub>H</sub> = 7.26 ppm, δ<sub>C</sub> = 77.16 ppm, DMSO-d<sub>6</sub>: δ<sub>H</sub> = 2.50 ppm, δ<sub>C</sub> = 39.52 ppm). Coupling constants (*J*) are reported in Hz and the following abbreviations (or combination thereof) were used to explain multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad.

**High resolution mass spectrometry:** High-resolution mass spectra were acquired on a Waters LCT PREMIER operating in ES+ or ES- mode.

CONDITIONS FOR ES+

Capillary Voltage: 2 kV

Sample Cone Voltage: 30 V

Desolvation Temperature: 350 °C

Source Temperature: 120 °C

Cone Gas Flow (Nitrogen): 10 l/hr

Desolvation Gas Flow (Nitrogen): 400 l/hr

MCP Voltage: 2.1 kV

CONDITIONS FOR ES-

Capillary Voltage: 2.5 kV

Sample Cone Voltage: 150 V

Desolvation Temperature: 350 °C

Source Temperature: 120 °C

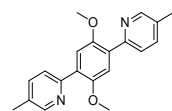
Cone Gas Flow (Nitrogen): 10 l/hr

Desolvation Gas Flow (Nitrogen): 400 l/hr

MCP Voltage: 2.1 kV

Samples referenced against leucine-enkephalin or sulfadimethoxine (depending on mass). MassLynx version 4.1 was used to analyze the results, this version of software does not account for the electron and all the calibrations/references are calculated accordingly.

**Experimental details**



6,6'-(2,5-dimethoxy-1,4-phenylene)bis(3-methylpyridine) (**1**)

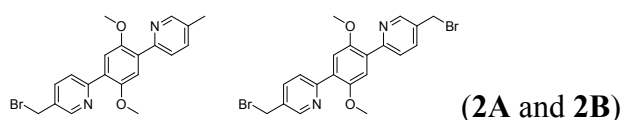
1,4-dimethoxy-2,5-dibromobenzene (3.45 g, 11.65 mmol, 1 eq) and 5-methyl-2-(tri-n-butylstannyl)pyridine (9.8 g, 25.6 mmol, 2.2 eq) was dissolved in a round-bottomed flask containing DMF (60 mL) and thoroughly degassed by bubbling N<sub>2</sub> (g) through the reaction mixture for 15 min. Pd(PPh<sub>3</sub>)<sub>4</sub> (1.0 g, 0.75 mmol, 7.5 mol%) was added and the solution was lowered into a pre-heated metal block (115 °C) and heated at that temperature for 18 h. After cooling to RT most of the DMF was removed under reduced pressure resulting in formation of a grey precipitate. Et<sub>2</sub>O (50 mL) was added and the solution was sonicated for 5 min. The precipitate was filtered off using a Buchner funnel and was washed with more Et<sub>2</sub>O (25 mL). The fine powder was subsequently dried under vacuum to give **1** as a grey powder.

Yield: 2.3 g, 62 %

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.55 (2H, m), 7.85 (2H, d, *J* = 8.1 Hz), 7.54 (2H, s), 7.53 (2H, m), 3.90 (s, 6H), 2.38 (6H, s).

<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 152.9, 151.5, 150.0, 136.5, 131.5, 129.7, 124.5, 56.5, 18.4.

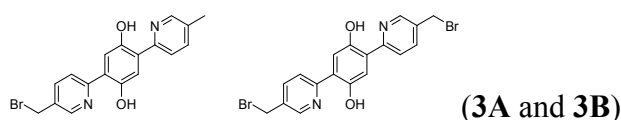
HRMS (ES+ TOF) calcd for [C<sub>20</sub>H<sub>20</sub>N<sub>2</sub>O<sub>2</sub> + H, M + H]<sup>+</sup>: 321.1603; found: 321.1602.



**1** (4.56 g, 14.23 mmol, 1 eq) was suspended in a round-bottomed flask containing tetrachloroethylene (350 mL) together with NBS (3.29 g, 18.5 mmol, 1.3 eq) and AIBN (230 mg, 1.4 mmol, 0.1 eq). The reaction flask was lowered into a pre-heated metal block (90 °C) and stirred at that temperature for 16 h. After cooling to RT the resulting succinimide precipitate was filtered. The organic layer was washed with NaHCO<sub>3</sub> (100 mL x 2), water (100 mL), brine (100 mL) and subsequently dried over MgSO<sub>4</sub>. Removal of solvent under reduced pressure gave a solid containing a mixture of mono- (**2A**) and dibrominated product (**2B**) as well as unreacted **1**. Dissolving the filtered succinimide precipitate in DCM (100 mL) and washing the organic layer with NaOH (1 M, 50 mL) gave, after drying over MgSO<sub>4</sub> and removal of solvent, more of unreacted **1** (0.5 g). The products were not separable on silica nor were crystallization successful. The materials were thus used in the next step without further purification.

Yield: 4.5 g containing dibrominated **2B**, monobrominated **2A** and **1** in a 0.15:1:0.25 mol ratio based on <sup>1</sup>H NMR.

Characteristic <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) signals are for **2A**: δ 4.54 (2H, s, CH<sub>2</sub>Br) and for **2B**: 4.65 (4H, s, CH<sub>2</sub>Br).



The mixture containing **2A**, **2B** and **1** (3 g) was dissolved in DCM (250 mL) and cooled to 0 °C. BBr<sub>3</sub> (10.4 g, 4 mL, 41.6 mmol) was added dropwise. Upon addition a precipitate formed and the solution was stirred to RT overnight. Ice was added to carefully quench the reaction resulting in more precipitate. NaHCO<sub>3</sub> (sat) was added and the pH adjusted to 8 while stirring. The resulting precipitate was vacuum filtered and air dried giving 1.0 g of a yellow solid. The organic layer was separated, washed with NaHCO<sub>3</sub> (100 mL), brine (100 mL) and dried over MgSO<sub>4</sub>. Thereafter, the solvent was removed under vacuum to give a yellow solid (1.6 g). The solids contained the same ratio as found in the starting material. Recrystallization from boiling acetone removed a small amount of polymeric material but yielded no enrichment of any of the components. The materials were thus used in the next step without further purification.

Yield: 2.3 g containing dibrominated **3B**, monobrominated **3A** and deprotected **1** in a 0.13:1:0.25 mol ratio based on <sup>1</sup>H NMR.

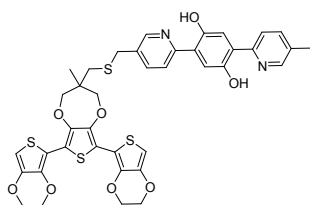
Characteristic <sup>1</sup>H NMR (500 MHz, D<sub>6</sub>-DMSO) signals are for **3A**: δ 13.41 (1H, br s, OH), 13.00 (1H, br s, OH), 4.83 (2H, s, CH<sub>2</sub>Br) and for **3B**: 13.40 (2H, br s, OH), 4.90 (4H, s, CH<sub>2</sub>Br).

**3A**: HRMS (ES+ TOF) calcd for [C<sub>18</sub>H<sub>15</sub>N<sub>2</sub>O<sub>2</sub>Br + H, M + H]<sup>+</sup>: 371.0400; found: 371.0395.

**3B**: HRMS (ES+ TOF) calcd for  $[C_{18}H_{14}N_2O_2Br_2 + H, M + H]^+$ : 448.9500; found: 448.9489.

### Terthiophene trimers containing the proton trap

The mixture of **3A**, **3B** and deprotected **1** (400 mg) was dissolved in degassed DMSO (15 mL) and **E-PSH-E** (496 mg, 1.0 mmol) was added together with diazabicycloundecene (DBU, 152 mg, 0.15 mL, 1.0 mmol). The reaction was lowered into a pre-heated metal block and stirred at 70°C for 3h, thereafter it was allowed to reach RT overnight. The reaction mixture was diluted with EtOAc (100 mL) and filtered through celite. The organics was washed with water (2 x 50 mL), brine (50 mL) and dried over MgSO<sub>4</sub>. Silica was added and the solvents were removed under reduced pressure and the products were purified through column chromatography (Pentane:DCM containing 2 % Et<sub>3</sub>N), gradient from 15 % DCM:Et<sub>3</sub>N to 100 %). This separated **EPE-trap** from **EPE-trap-EPE**, fractions containing the products were identified via NMR, separately concentrated in vacuo, then re-dissolved in minimal amount of DCM and slowly added into a stirred solution of pentane (50 mL). The yellow precipitate was filtered and dried under vacuum.



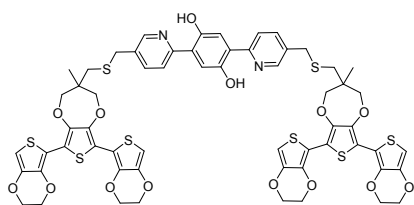
**EPE-trap**

Yield: 300 mg, yellow powder

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 13.60 (1H, s), 13.50 (1H, s), 8.51 (1H, s), 8.36 (1H, s), 7.87 (2H, m), 7.83 (1H, d, *J* = 8.4 Hz), 7.67 (1H, dd, *J* = 8.4, 1.7 Hz), 7.42 (1H, s), 7.41 (1H, s), 6.26 (2H, s), 4.35 (4H, m), 4.23-4.20 (6H, m), 3.88 (2H, s), 3.70 (2H, d, *J* = 11.9 Hz), 2.89 (2H, s), 2.40 (3H, s), 0.95 (3H, s).

<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 156.1, 154.6, 152.0, 151.8, 146.5, 146.3, 144.5, 141.4, 138.7, 138.6, 137.5, 133.0, 131.9, 121.9, 119.7, 119.5, 114.8, 114.7, 113.8, 110.3, 98.3, 78.1, 65.3, 64.8, 43.4, 36.9, 35.0 18.6, 18.4.

HRMS (ES+ TOF) calcd for  $[C_{39}H_{35}N_2O_8S_4 + H, M + H]^+$ : 787.1276; found: 787.1284.



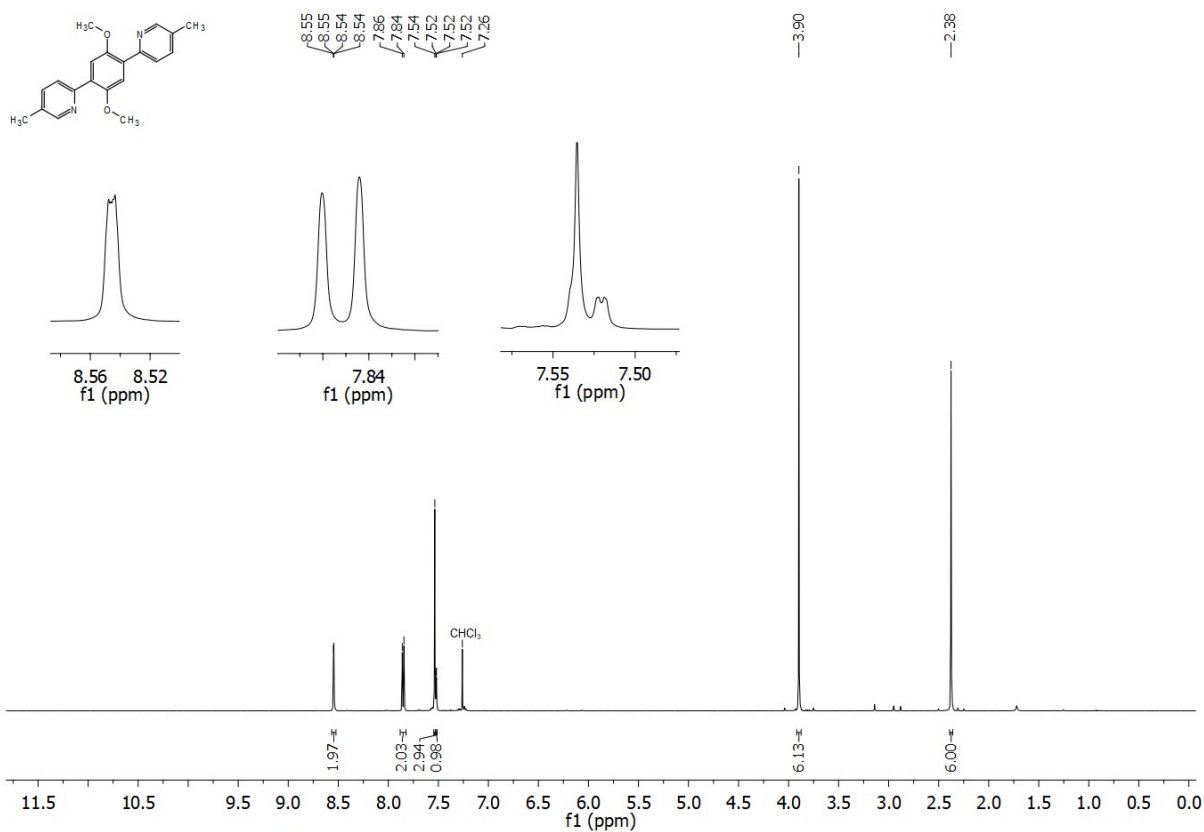
**EPE-trap-EPE**

Yield: 75 mg, yellow powder

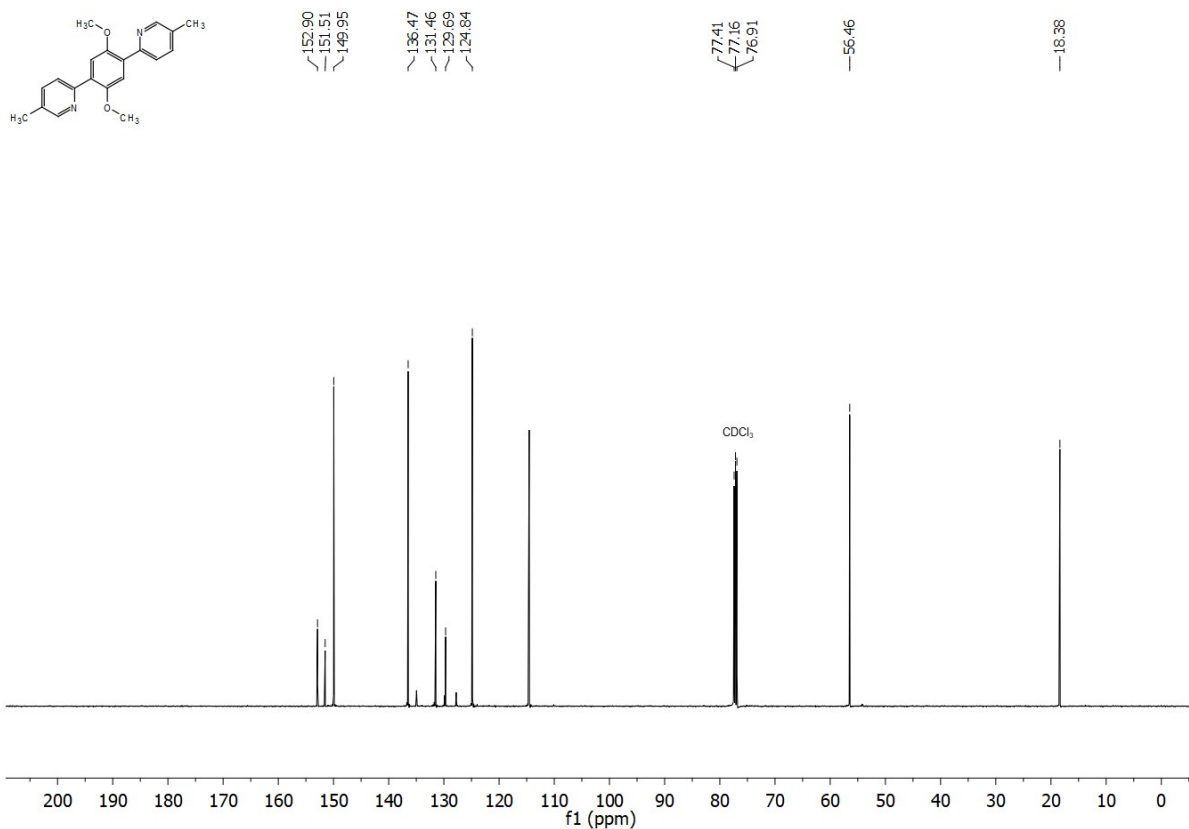
$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  13.50 (2H, s), 8.50 (2H, s), 7.86 (4H, s), 7.40 (2H, s), 6.26 (4H, s), 4.34 (8H, m), 4.23-4.20 (12H, m), 3.87 (4H, s), 3.70 (4H, d,  $J = 11.9$  Hz), 2.88 (4H, s), 0.94 (6H, s).

$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  156.0, 152.0, 146.5, 144.5, 141.4, 138.5, 137.5, 133.0, 121.6, 119.8, 114.9, 113.8, 110.3, 92.3, 78.1, 65.3, 64.8, 43.4, 36.8, 34.9, 18.6.

HRMS (ES+ TOF) calcd for  $[\text{C}_{60}\text{H}_{52}\text{N}_2\text{O}_{14}\text{S}_8 + \text{H}, \text{M} + \text{H}]^+$ : 1281.1263; found: 1281.1285.



**Fig. S 1**  $^1\text{H}$  NMR spectrum (500 MHz,  $\text{CDCl}_3$ , RT) of **1**.



**Fig. S 2**  $^{13}\text{C}$  NMR spectrum (126 MHz,  $\text{CDCl}_3$ , RT) of **1**.

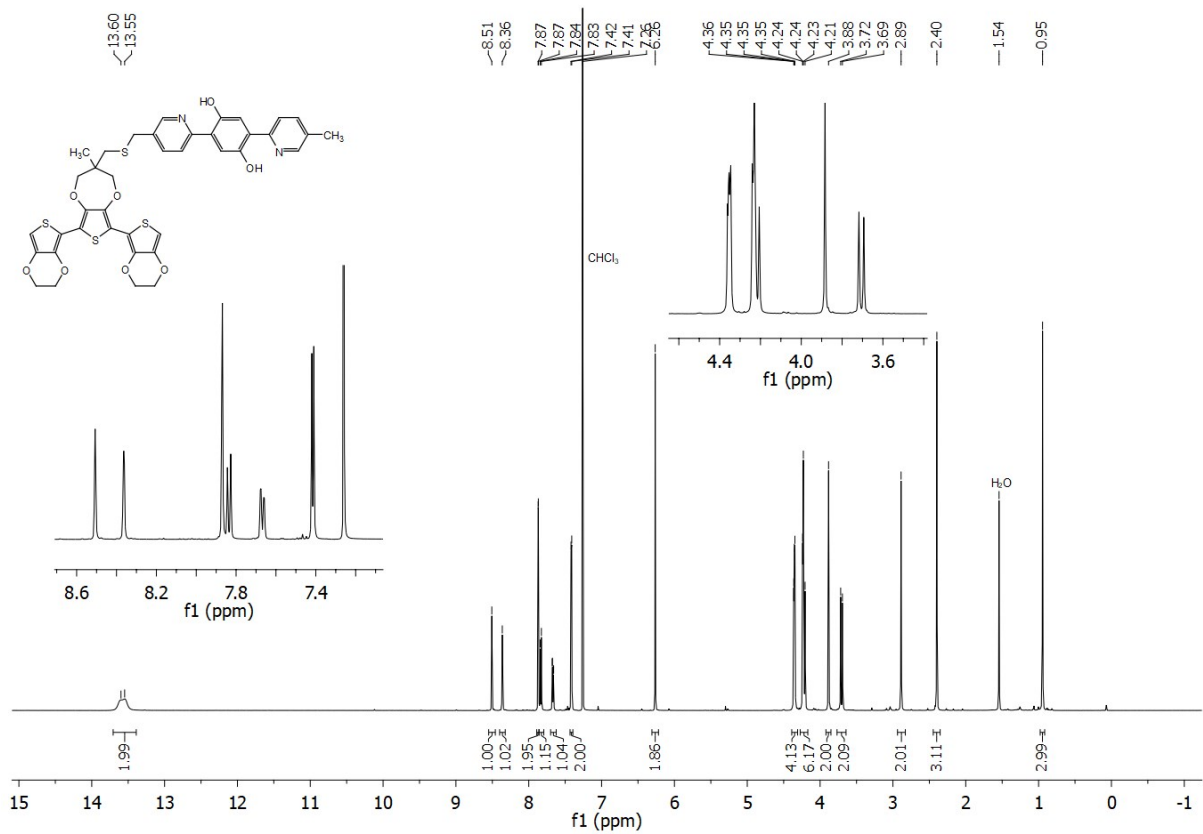


Fig. S 3  $^1\text{H}$  NMR spectrum (500 MHz,  $\text{CDCl}_3$ , RT) of EPE-trap.

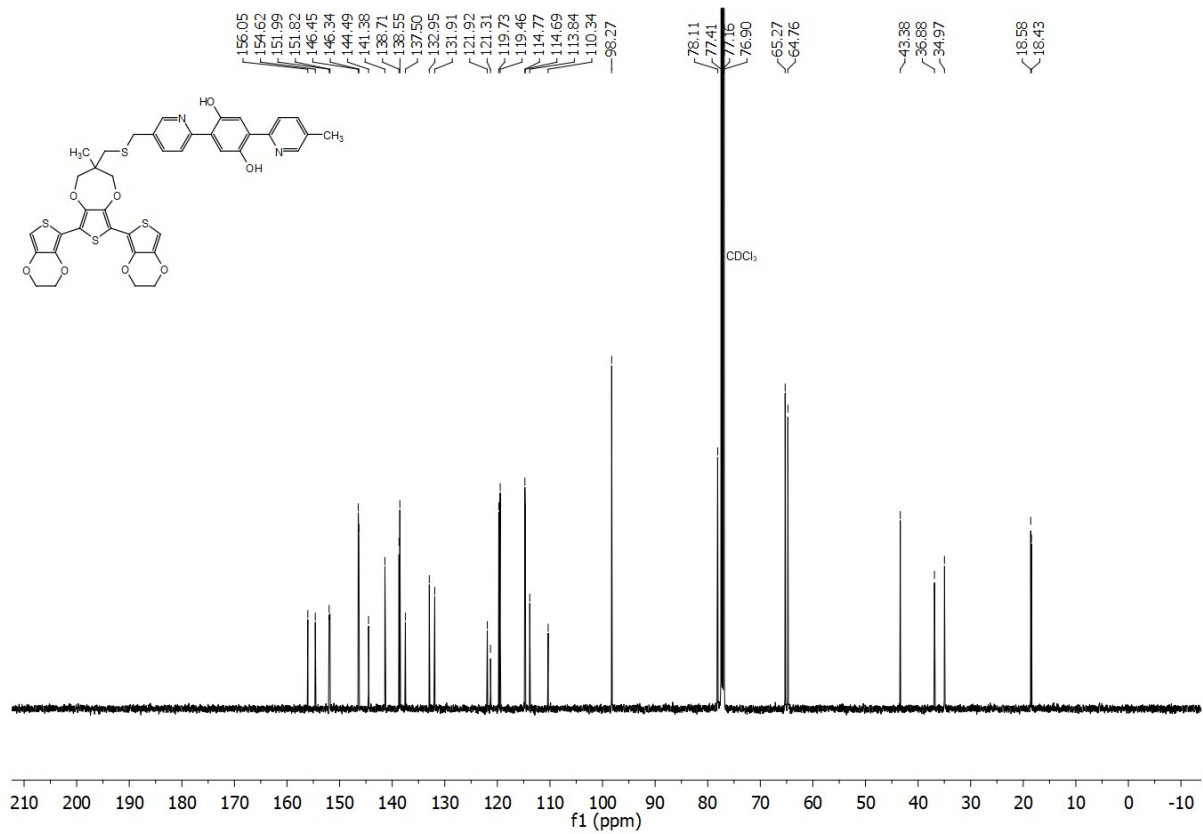
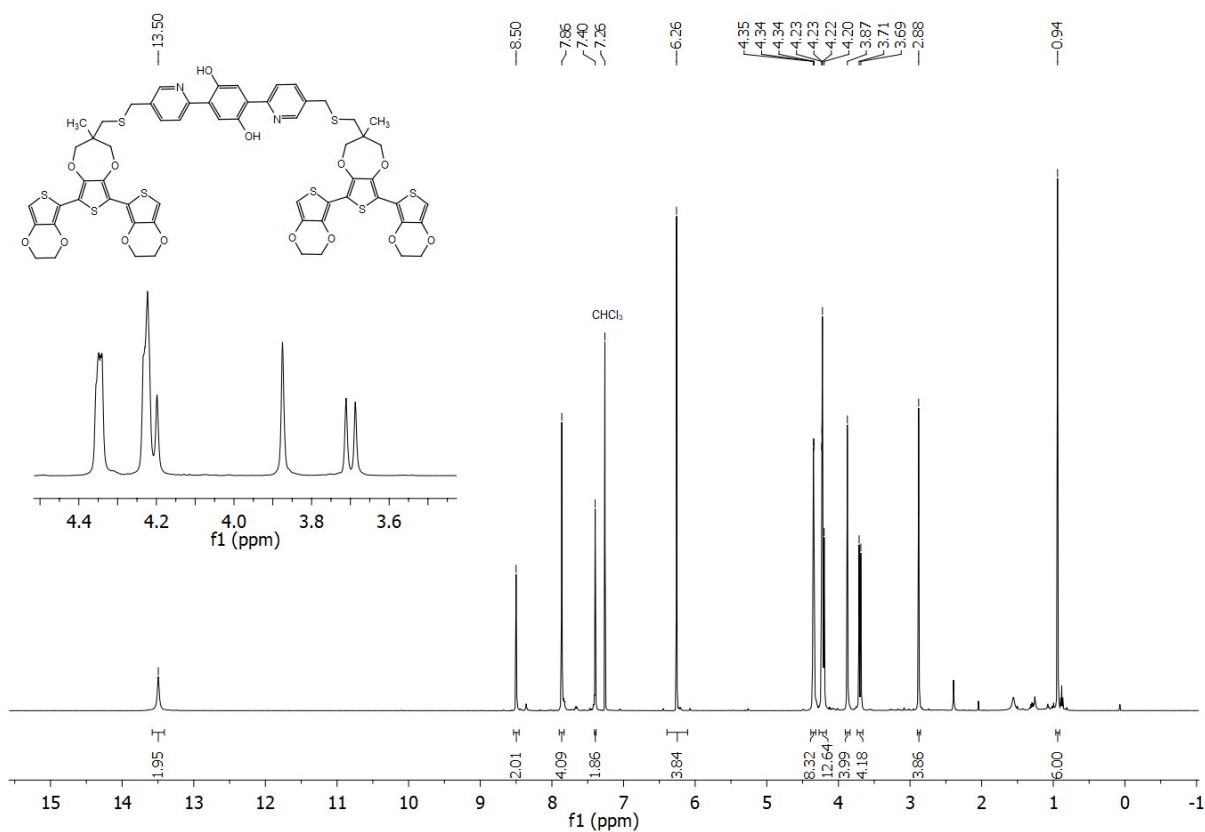
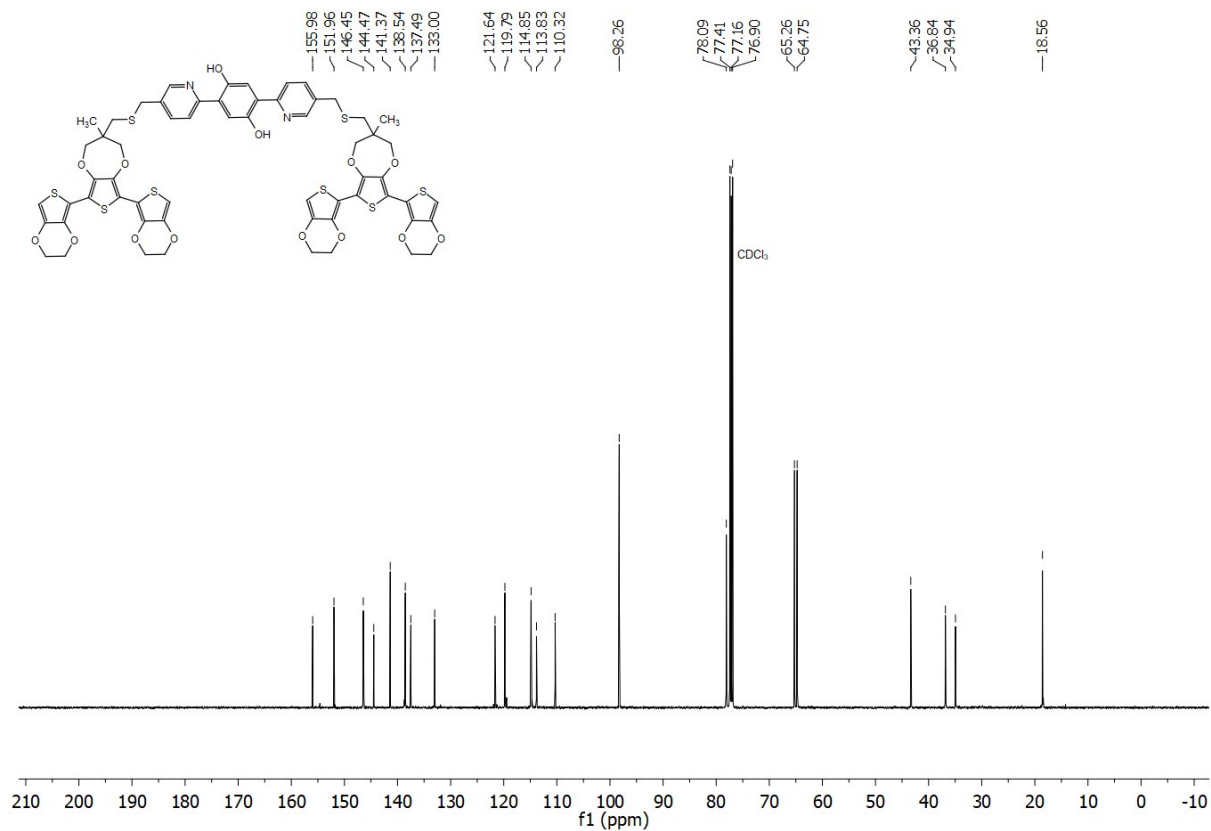


Fig. S 4  $^{13}\text{C}$  NMR spectrum (126 MHz,  $\text{CDCl}_3$ , RT) of EPE-trap.





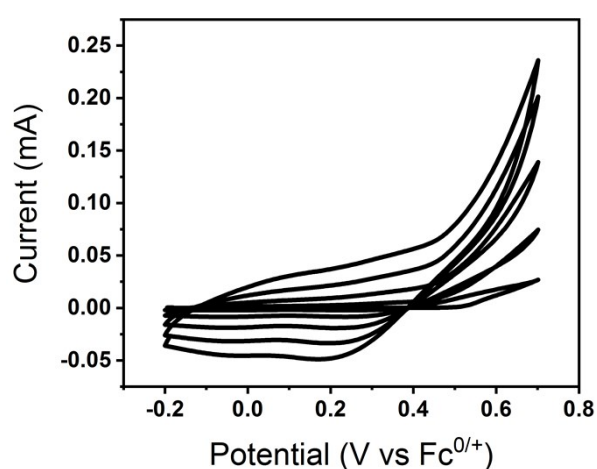
**Fig. S 5**  $^1\text{H}$  NMR spectrum (500 MHz,  $\text{CDCl}_3$ , RT) of EPE-trap-EPE.



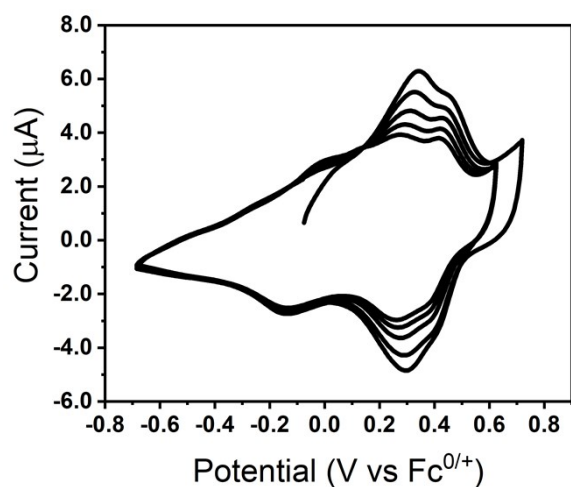
**Fig. S 6**  $^{13}\text{C}$  NMR spectrum (126 MHz,  $\text{CDCl}_3$ , RT) of EPE-trap-EPE.

## Polymerization

Polymerization was performed in aqueous electrolyte to inhibit dissolution. Fig. S 7 shows a standard polymerization CV of **EPE-trap-EPE** to **p(EPE-trap-EPE)**. For battery electrodes, which had a higher mass loading, this procedure proved to be insufficient on a reasonable time scale. Hence the procedure was modified so that polymerization could be reached relatively fast without dissolution of the material, which resulted in a 9:2 volume ratio between MeCN and H<sub>2</sub>O with TBAPF<sub>6</sub> as supporting electrolyte.



**Fig. S 7** polymerization CV (25 mV/s for 5 scans between -0.2 - 0.7 V vs Fc<sup>0+</sup>) of **EPE-trap-EPE** in a buffered electrolyte (0.5 M Na<sub>2</sub>SO<sub>4</sub>, buffered to pH 5.46).



**Fig. S 8** Characterization of the product with one trimer base, **p(EPE-trap)**, cycled at 10 mV/s in 0.1 M TBAPF<sub>6</sub>/MeCN.

## Conductance

To monitor the conductance variation during cyclic voltammetry measurements, interdigitated array (IDA) electrodes were coated with dissolved trimers and then dried. A bipotentiostat was applied with a voltage bias ( $E_{\text{bias}}$ ) set between the two sides of the IDA electrode, hence the current at the two working electrodes ( $i_1$  and  $i_2$ ) is composed of the current passing through the polymer in response to  $E_{\text{bias}}$  and the current resulting from the CV-measurement. For polymerization the voltage bias was set to 1 mV and during characterization the bias was adjusted to 10 mV. The conductance of the polymer,  $G_p$ , was calculated through Eq. S1, where  $\Delta i$  corresponds to the current difference between  $i_1$  and  $i_2$ .

$$G_p = \frac{\Delta i}{2E_{\text{bias}}} \quad (\text{Eq. S1})$$

The sum of currents ( $i_1$  and  $i_2$ ) corresponds to the current to and from the auxiliary electrode, which results from the potential variation relative to the external reference, i.e. the CV response originating from redox conversion of the polymer. Assuming that only material in the volume in-between the two working electrodes contribute to the conductance and that the entire volume is filled with polymer, the conductance can be converted to conductivity by dividing with the cross-sectional area ( $A = 7.08 \times 10^{-2} \text{ m}^2$ ) and multiplying with the distance ( $l$ ) between the electrodes ( $l = 1 \times 10^{-5} \text{ m}$ ).

## EQCM

Eq. S2 is derived from the Sauerbrey equation and applied to calculate the mass change from the EQCM measurements:

$$\Delta m = \Delta f \frac{A(\rho_q \times \mu_q)^{1/2}}{2Fq_2} \quad (\text{Eq. S2})$$

where  $\Delta m$  is the mass change,  $\Delta f$  is the measured frequency change,  $Fq$  is the reference frequency,  $A$  the area of the active surface,  $\rho_q$  is the quartz crystal density, and  $\mu_q$  is the AT-cut quartz constant. For a reliable value the mass change is converted into molar mass ( $M_w$ ) and calculated per charge ( $Q$ ) in linear regions, to evaluate the flux of specific species. Since one counter ion is needed per charge, the calculated  $M_w/Q$  must consist of the mass flux of available ions in the electrolyte (when solvent flux is disregarded):

$$\frac{M_w}{Q} = x * M_w(PF_6^-) - (1 - x) * M_w(TBA^+) \quad (\text{Eq. S3})$$

## Characterization of the trap unit

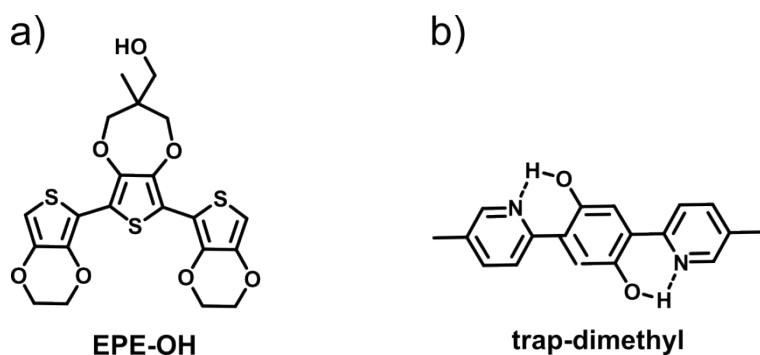


Fig. S 9 a) EPE-OH and b) trap-dimethyl (2,5-bis(4-methyl-2-pyridyl)1,4-hydroquinone).

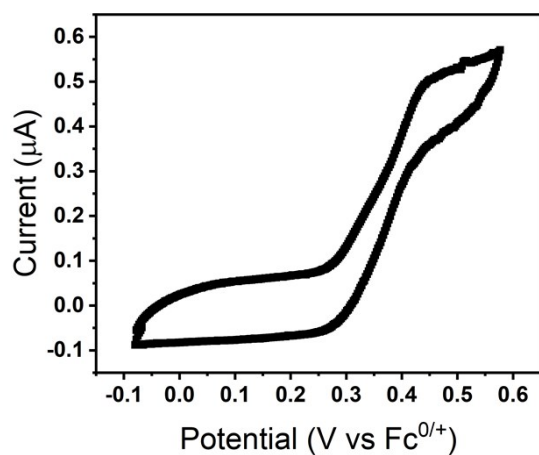


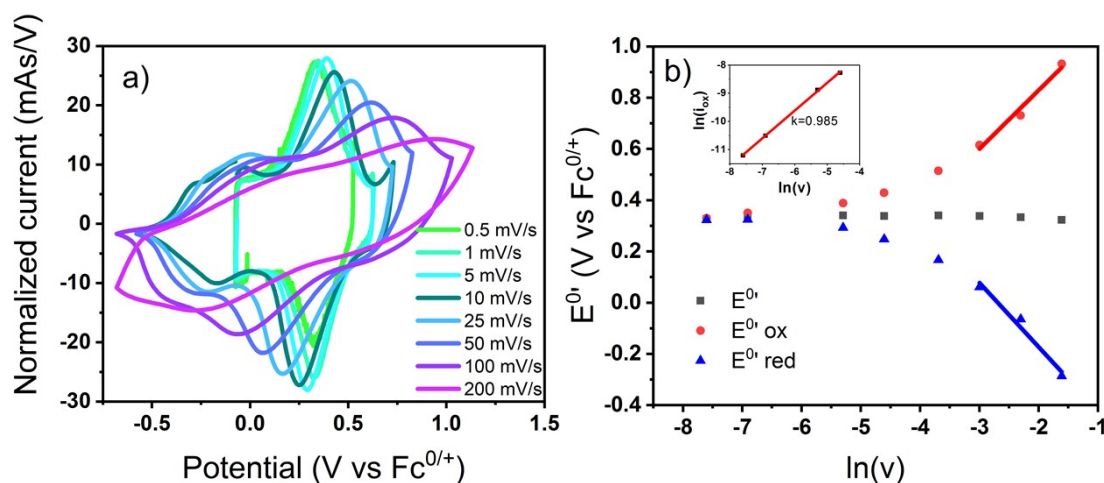
Fig. S 10 CV of trap-dimethyl in solution (0.1 M TBAPF<sub>6</sub>/MeCN).

## Scan rate dependence

The mechanisms governing electron transport can be investigated by scan rate dependence calculations. These mechanisms can differ depending on the thickness of the material, where diffusion is often limiting for thick materials and kinetic limitations are normally the origin for thin materials. For a reversible process the peak split often follows the  $\frac{56.5 \text{ mV}}{n}$ . When the oxidation and reduction peaks are differing  $>200 \text{ mV}$  the reaction is viewed as irreversible. In this region we can ignore the back reaction (reduction if you are looking at the oxidation) and by plotting the peak potential at different scan rates we can calculate the so called *apparent* rate constant,  $k^0$ , by Laviron's equation:

$$E_p = E^{0'} \pm \frac{RT}{\alpha z F} \times \ln\left(\frac{\alpha z F}{RT} * \frac{v}{k^0}\right) \quad (\text{Eq. S4})$$

where  $E^{0'}$  is the formal potential,  $R$  is the gas constant in  $\text{J mol}^{-1} \text{K}^{-1}$ ,  $T$  is the temperature in  $\text{K}$ ,  $F$  is the Faraday constant in  $\text{C mol}^{-1}$ ,  $z$  is the number of electrons involved,  $\alpha$  is the transfer coefficient and  $v$  is the scan rate in  $\text{V s}^{-1}$ .



**Fig. S 11 a)** Cyclic voltammograms with normalized current at scan rates 0.5-200 mV/s in 0.1 M TBAPF<sub>6</sub>/MeCN. **b)** Scan rate dependence of peak potential,  $E^{0'}$ , at 0.5-200 mV/s in 0.1 M TBAPF<sub>6</sub>/MeCN. The inset shows the peak current plot at low scan rates.

## UV/Vis

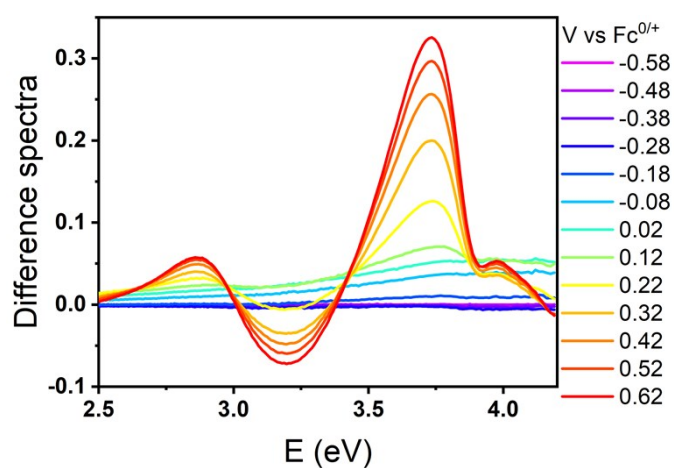


Fig. S 12 Difference spectra (relative to the spectrum at  $-0.58$  V vs  $Fc^{0/+}$ ) of trap-dimethyl in solution for an oxidation scan. When reaching above  $0.1$  V vs  $Fc^{0/+}$  a peak at  $3.2$  eV and a peak at  $3.7$  eV are seen to decrease and increase, respectively.

## FTIR

In the fingerprint region several peaks are increasing, most of which are connected to the pendant group, suggesting that larger dipole shifts come from the oxidized form.

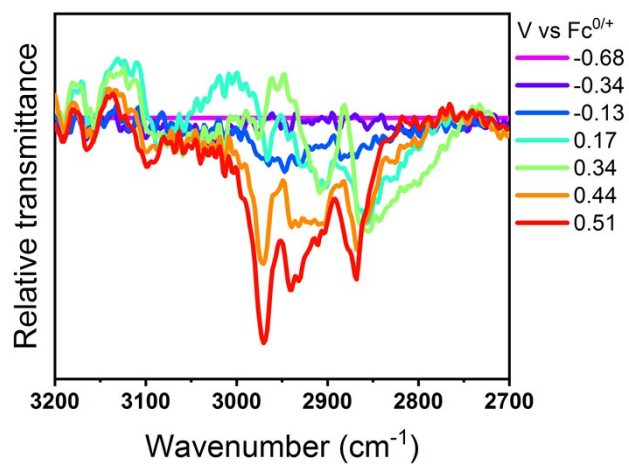


Fig. S 13 Difference spectra (vs the reduced spectra at  $-0.51$  V vs  $Fc^{0/+}$ ) of the higher region of the spectra.

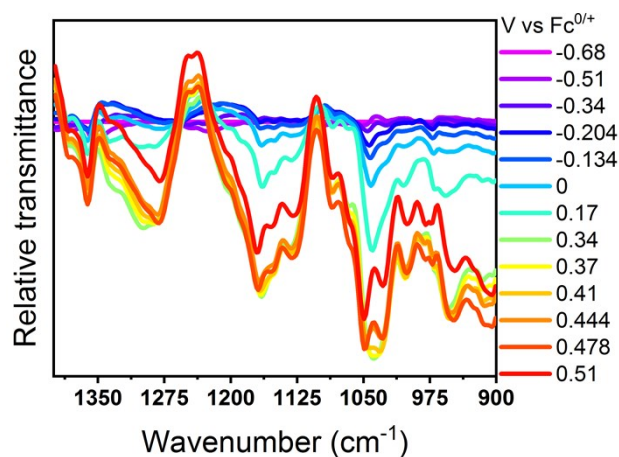


Fig. S 14 Difference spectra (vs the reduced spectra at  $-0.51$  V vs  $\text{Fc}^{0/+}$ ) of the fingerprint region during an oxidation scan of p(EPE-trap-EPE).

## Batteries

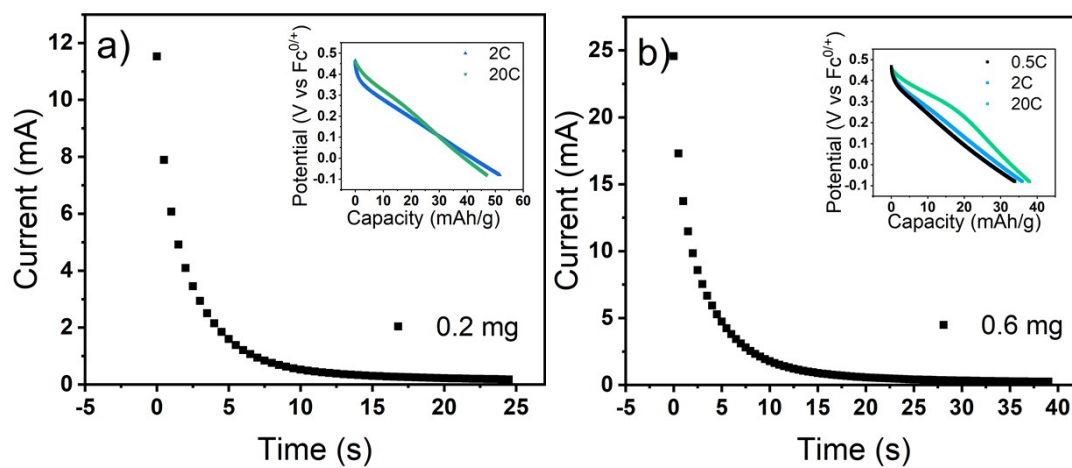
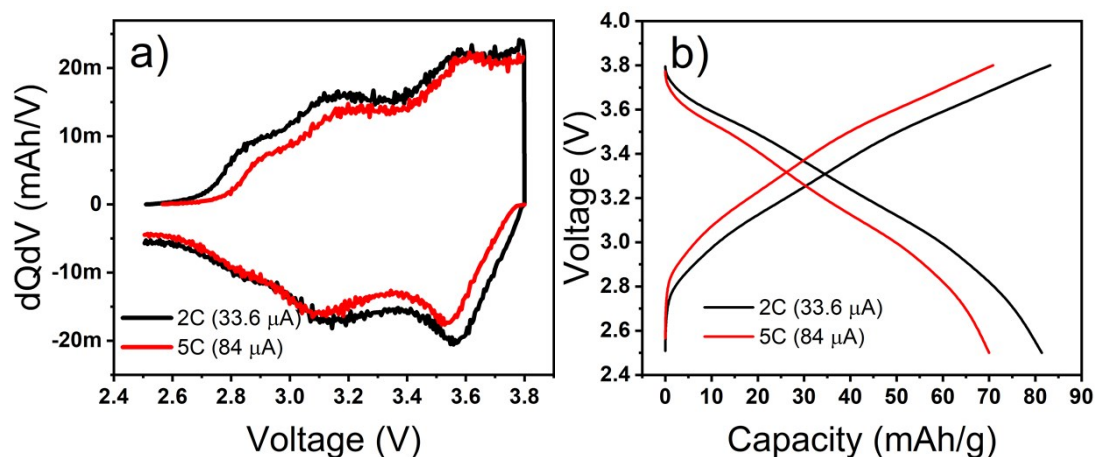
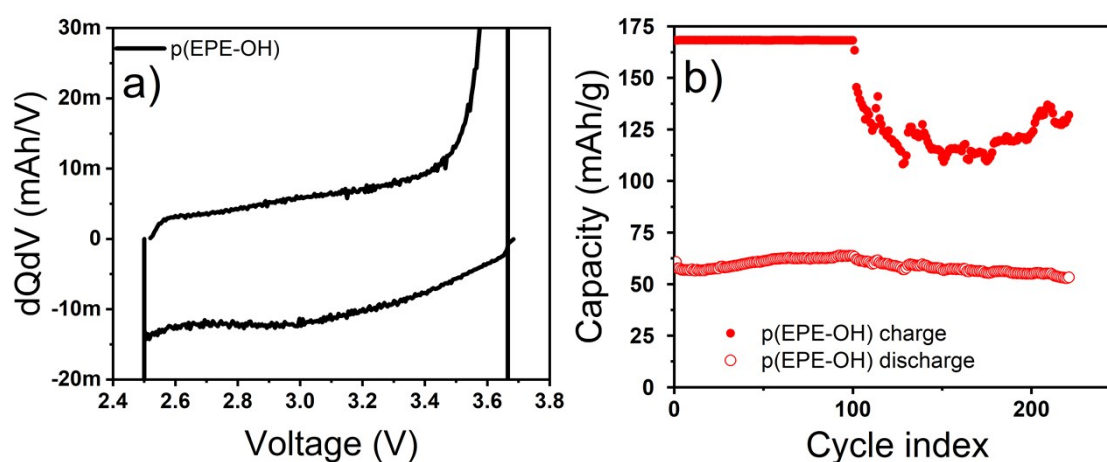


Fig. S 15 Charging curves at constant potential ( $0.48$  V vs  $\text{Fc}^{0/+}$ ) for a)  $0.2$  mg and b)  $0.6$  mg electrodes. Discharge curves are shown as insets.



**Fig. S 16** Comparison of different current rates (2C and 5C) for a coin cell battery with 0.2 mg **p(EPE-trap-EPE)** as cathode material. **a)** Differential capacity plots, and **b)** plot of galvanostatic charge/discharge, the 15<sup>th</sup> cycle.

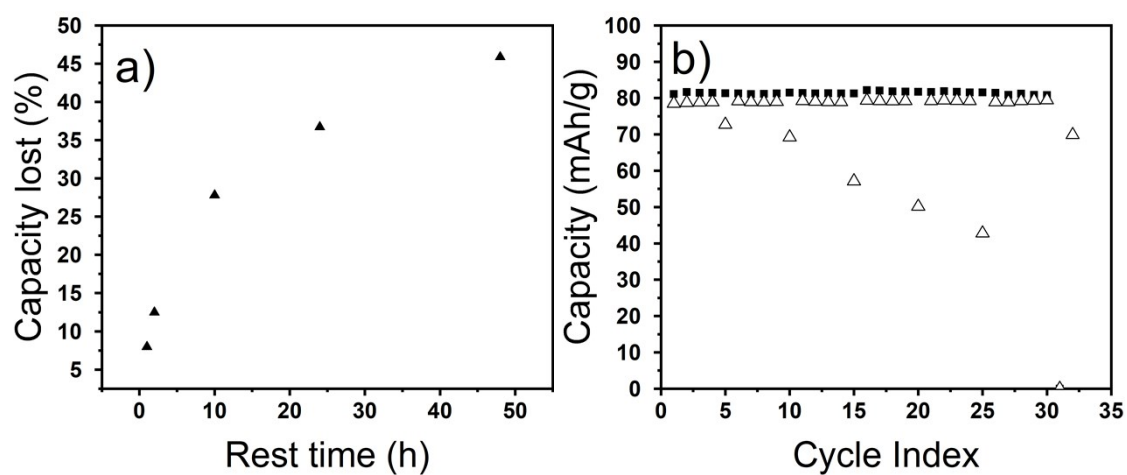


**Fig. S 17** Galvanostatic charge and discharge at 33.6  $\mu\text{A}$  of a coin cell battery containing 0.2 mg **p(EPE-OH)**. **a)** Differential capacity plot, and **b)** capacity during charge and discharge.

**Table S1.** Discharge capacity retention of coin cell batteries containing 0.2 mg active material cycled at 33.6  $\mu\text{A}$ .

<b>p(EPE-OH)</b> mAh/g (cap. retention from 1 <sup>st</sup> cycle)	61	64 (104%)	55 (90%)	56
<b>p(EPE-OH)</b> (% of theor)	108	110	98	100

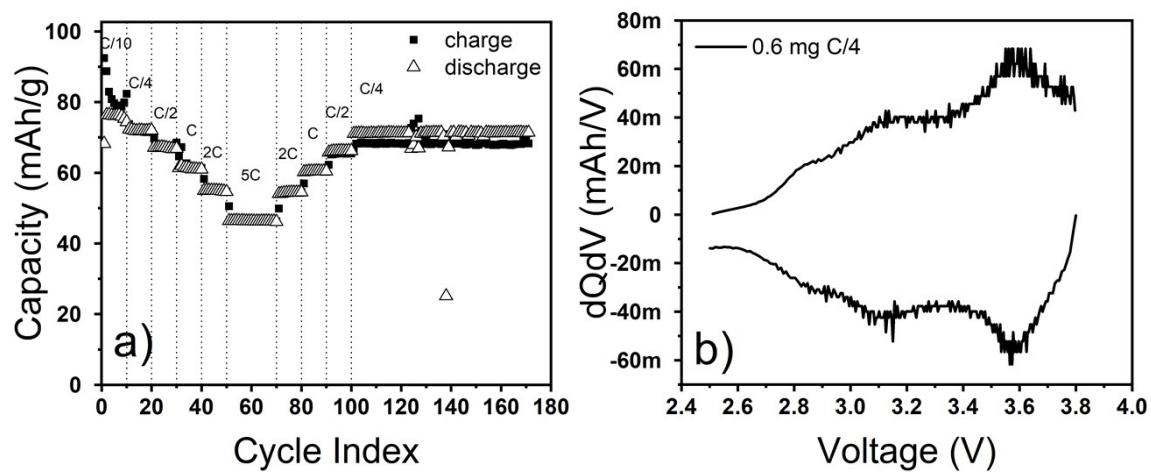




**Fig. S 18 a)** Self-discharge measurements with intermittent resting time of 1-48 (648) h. **b)** Galvanostatic charge discharge measurements post a self discharge test always regained the initial capacity, except for when applying the longest waiting time (648 h).

**Table S 2.** Rest time vs capacity loss.

Rest time (h)	Capacity lost (%)
1	8.0
2	12.5
10	27.8
24	36.7
48	45.9
648	100



**Fig. S 19** Evaluation of a battery with 0.6 mg **p(EPE-trap-EPE)** as cathode vs Lithium metal. **a)** C-rate study and **b)** differential capacity plot at C/4.

## References

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