Supplementary Information

Conjugated Electrochromic Polymers with Amide-containing Side Chains Enabling Aqueous Electrolyte Compatibility

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Materials

All salts used in electrolytes (tetrabutylammonium hexafluorophosphate (≥ 99.0%), ammonium hexafluorophosphate (≥99.0%), tetrabutylammonium chloride (≥ 97%) and ammonium chloride (≥99.5%)) and propylene carbonate were purchased from Sigma-Aldrich. Octadecyltrichlorosilane (95%) was purchased from Acros Organics. All chemicals were used as purchased without further purification.

Synthetic Procedures

Intermediates (**1**, **2**, and **3**) and ECP-Magenta (**P1**, M_w/M_n (GPC) =11800/9600, Figure S5) were synthesized according to reported literature.[S1-S4] NMR spectra were recorded on Mercury 300 (300 MHz). Gel permeation chromatography (GPC) was performed on an Agilent PL-GPC220 instrument at 25 °C with THF as eluent.

Synthesis of mono-substituted amide ProDOT (4): To a suspension of NaH (0.27 g, 6.7 mmol, 60% dispersion in mineral oil) in THF (50 mL) ProDOT-OH (**1)** (0.41g, 1.9 mmol) was added at 0 ° C. After stirring at 0 °C for 1 h, N-(2-ethylhexyl)-2-chloroacetamide (**2**) (1.0 g, 5.0 mmol) was added and the mixture was stirred at room temperature for 12 h. Then the reaction solution was poured into saturated aqueous NH_4Cl and extracted with ethyl acetate. The combined organic phase was dried over $MgSO_4$, concentrated in vacuo, and finally purified by flash column chromatography on silica gel (EtOAc) to afford a colorless oil (0.85 g, 81 %). ^1H NMR (300 MHz, $CDCl_3$, δ ppm): 6.49 (s, 2H), 6.49 (b, 2H), 4.04 (s, 4H), 3.96 (s, 4H), 3.61 (s, 4H), 3.23 (t, 4H), 1.43 (m, 2H), 1.24-1.31 (m, 16H), 0.88 (m, 12H). ^{13}C NMR (300 MHz, $CDCl_3$, δ): 168.70, 148.89, 106.06, 73.16, 71.06, 70.85, 47.71, 41.90, 39.33, 31.05, 28.90, 24.32, 23.10, 14.19, 10.96.

Synthesis of di-substituted amide ProDOT (5): The synthetic procedure is similar to compound **4** using N,N-dibutyl-2-chloroacetamide (**3**) in place of **2**. (87%). ^1H NMR (300 MHz, $CDCl_3$, δ ppm): 6.44 (d, 2H), 4.15 (s, 4H), 4.10 (s, 4H), 3.69 (s, 4H), 3.26 (t, 4H), 3.12 (t, 4H), 1.46 (m, 8H), 1.26 (m, 8H), 0.88 (m, 12H). ^{13}C NMR (300 MHz, $CDCl_3$, δ): 168.18, 149.55, 105.29, 73.57, 70.71, 70.08, 47.79, 46.53, 45.50, 31.05, 29.73, 20.31, 20.17, 13.96, 13.91.

Synthesis of P2: A 1 mol/L solution of anhydrous $FeCl_3$ (453 mg, 2.79 mmol) in nitromethane was added dropwise to compound **4** (310 mg, 0.559 mmol) in chloroform (0.1 mol/L). The mixture was stirred overnight at room temperature and subsequently poured into 200 mL of methanol. The precipitated solid was dissolved in 200 mL of chloroform and stirred for 1 h with 3 mL of hydrazine monohydrate. The solution was washed with 1 mol/L HCl and concentrated by evaporation, and then dropped into methanol. The precipitated solid was subsequently purified via Soxhlet extraction with methanol, hexanes, and chloroform. The chloroform fraction was collected, concentrated by evaporation, and precipitated from methanol to afford a dark-purple solid in a yield of 63%. ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm): 7.41 (bs), 4.03 (bs), 3.72 (bs), 3.19 (bs), 1.75 (bs), 1.46 (bs), 1.22 (bs), 0.84 (bs). Elemental Analysis Calc. for C29H48N2O6S: Calc. C 63.01, H 8.75, N 5.07; Found C 62.60, H 9.01, N 5.22. M_w/M_n (GPC) =12400/9400.

Synthesis of P3: The synthetic procedure is similar to **P2** (71%).^{1}H NMR (300 MHz, CD_2Cl_2, δ ppm): 4.25 (bs), 3.85 (bs), 3.31 (bs), 3.21 (bs), 1.66 (bs), 1.54 (bs), 1.33 (bs), 0.94 (bs). Elemental Analysis Calc. for C29H48N2O6S: Calc. C 63.01, H 8.75, N 5.07; Found C 62.68, H 9.25, N 5.38. M_w/M_n (GPC) =10100/8000.

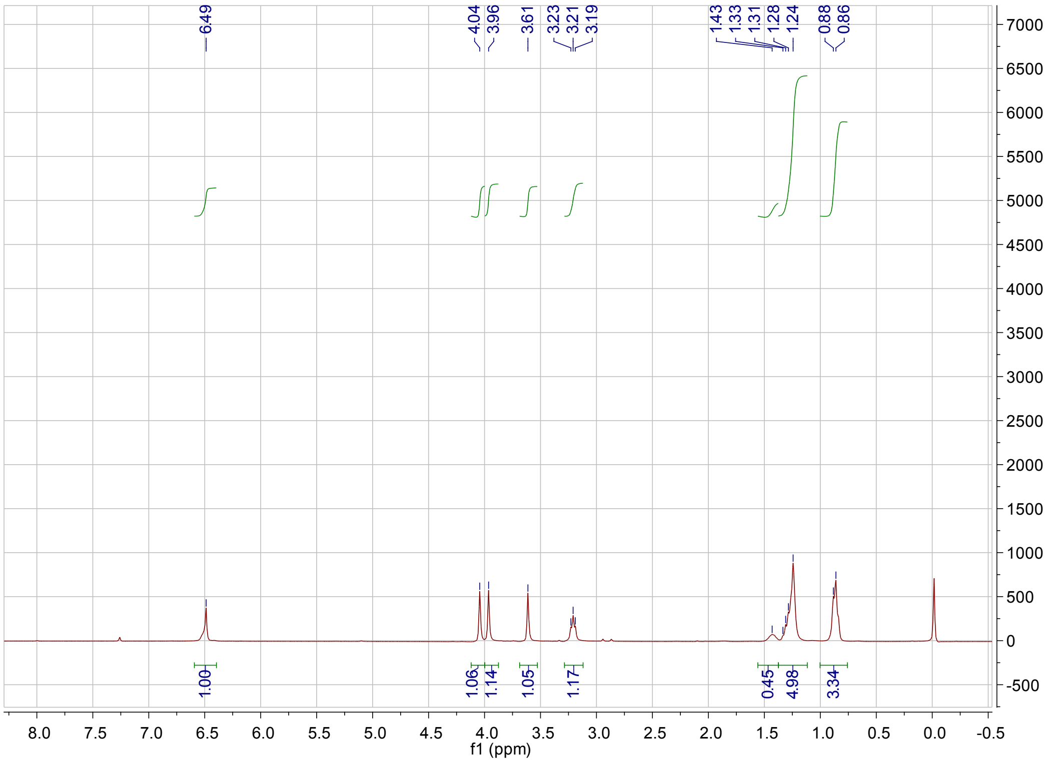


Figure S1. ^{1}H NMR spectrum of **compound 4**.

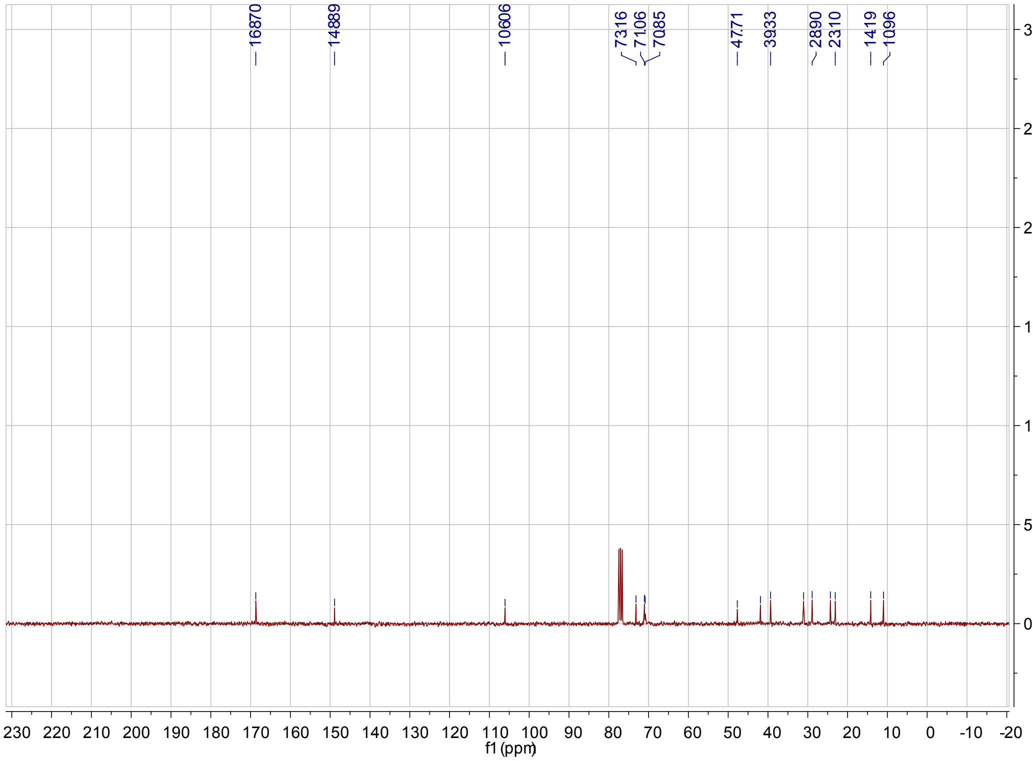


Figure S2. ^{13}C NMR spectrum of **compound 4**.

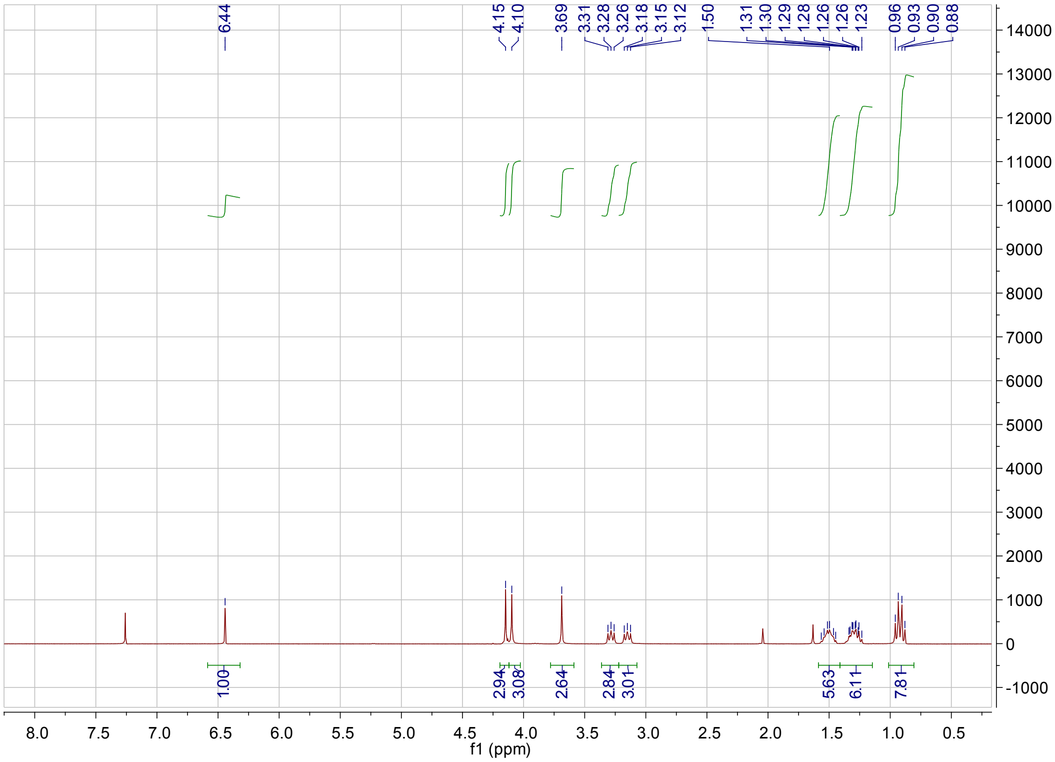


Figure S3. ^{1}H NMR spectrum of **compound 5**.

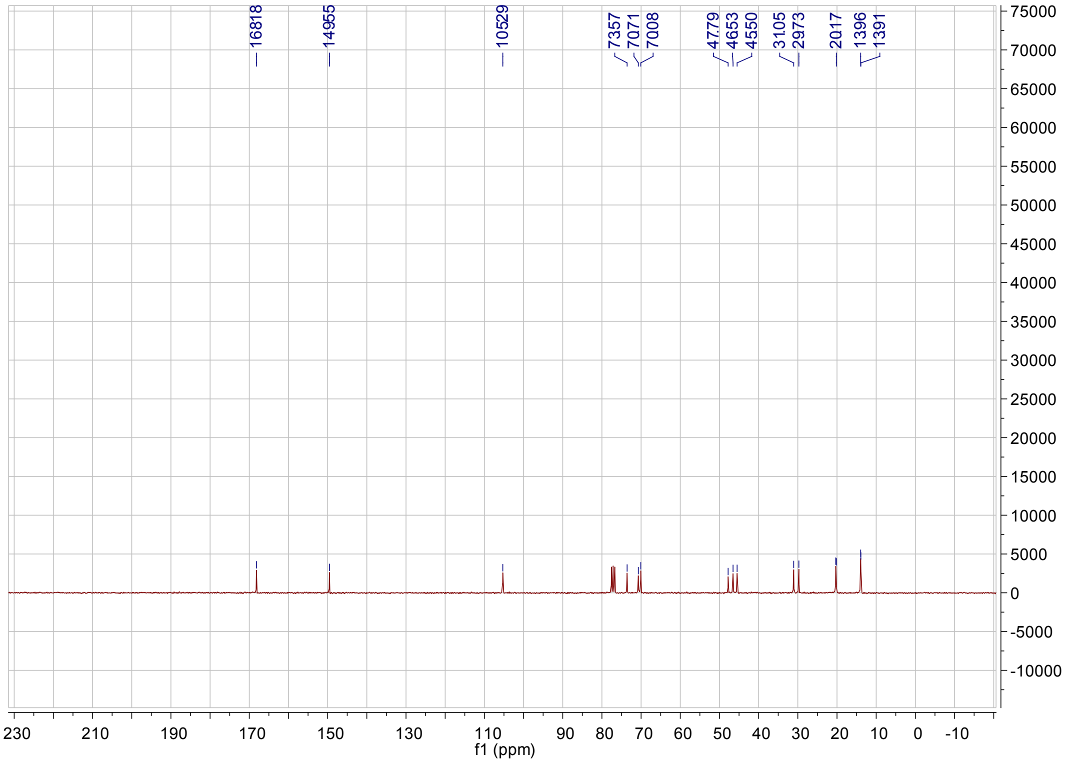


Figure S4. ^{13}C NMR spectrum of **compound 5**.

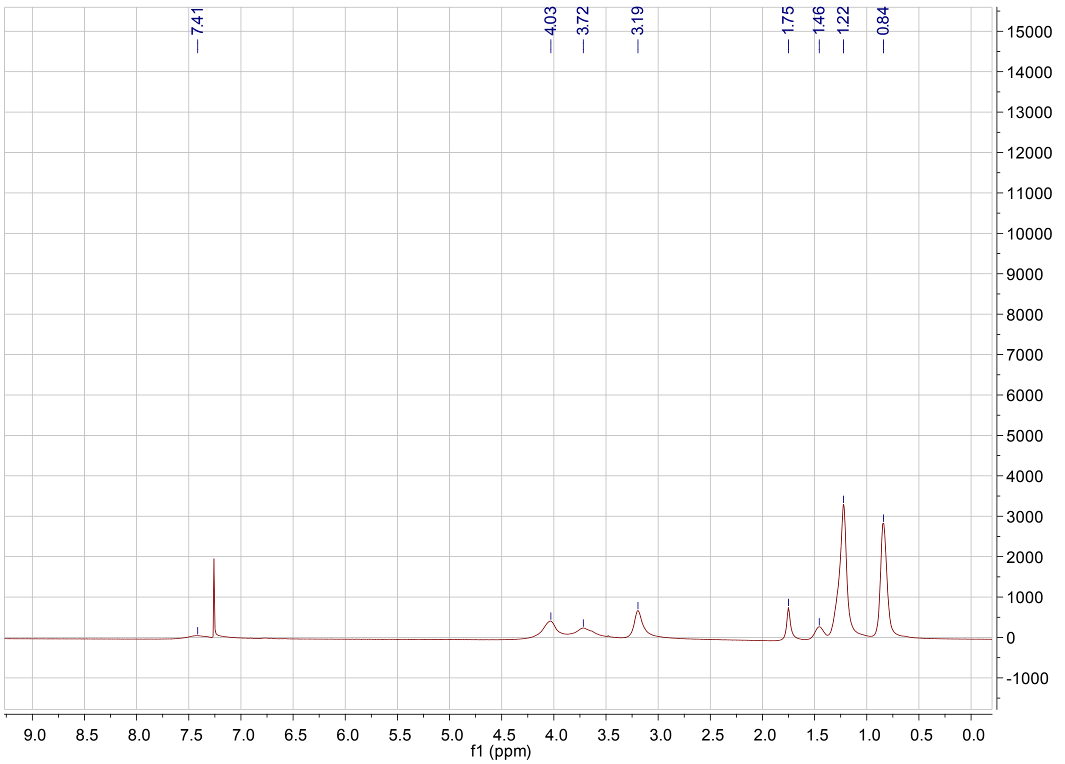


Figure S5. ^{1}H NMR spectrum of **P2**.

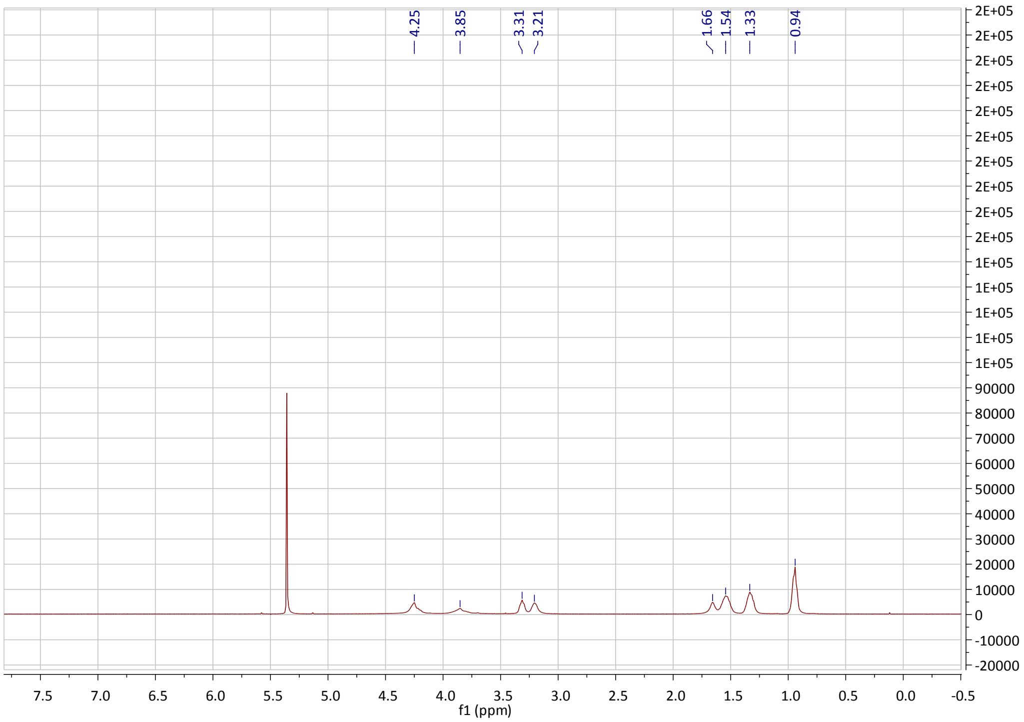
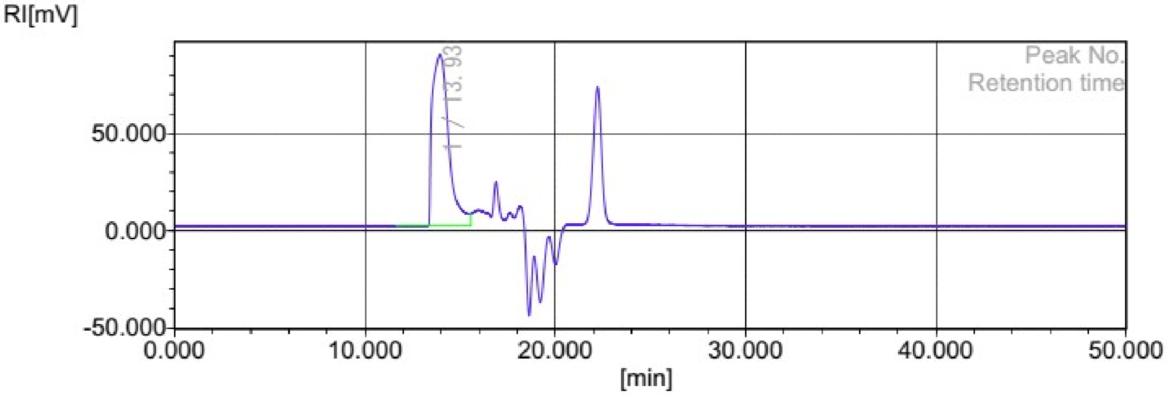


Figure S6. ^{1}H NMR spectrum of **P3**.

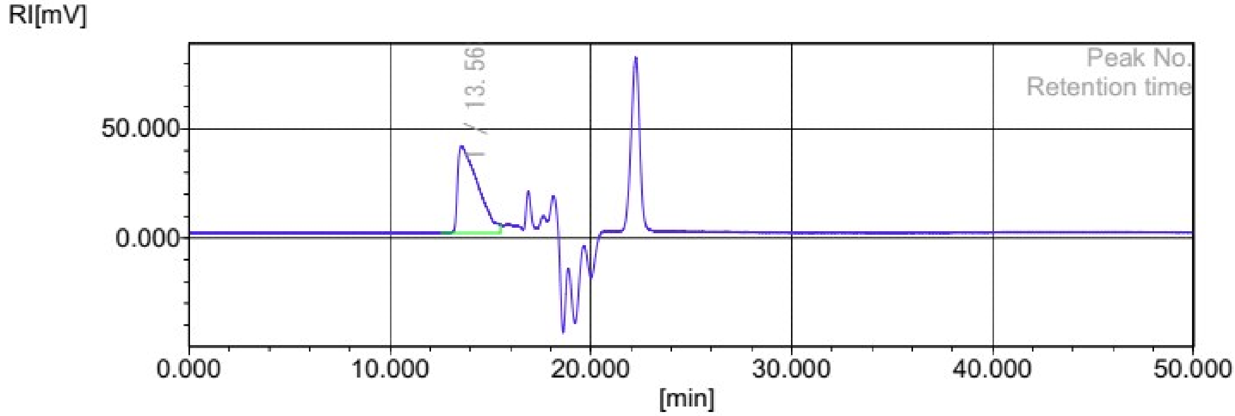


Result of molecular weight calculation (RI)

Peak 1 Base Peak

	[min]	[mV]	[mol]		
				Mn	9,604
Peak start	11.647	2.457	128,681	Mw	11,807
Peak top	13.938	90.332	12,139	Mz	13,964
Peak end	15.548	8.702	2,311	Mz+1	18,544
				Mv	11,807
Height [mV]			87.859	Mp	12,140
Area [mV*sec]			5295.193	Mz/Mw	1.183
Area% [%]			100.000	Mw/Mn	1.229
[eta]			11807.45491	Mz+1/Mw	1.571

Figure S7. GPC chromatograms of **P1** using THF as an eluent.



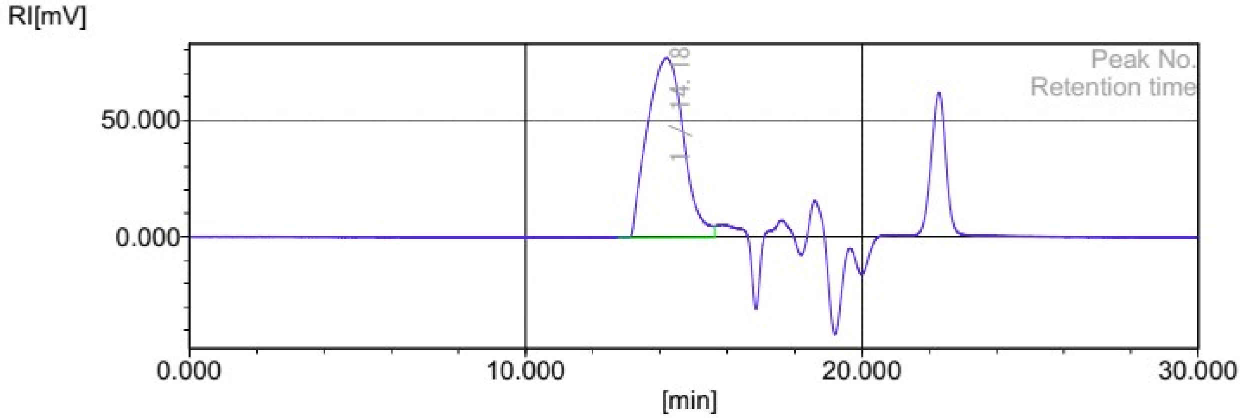
Result of molecular weight calculation (RI)

Peak 1 Base Peak

	[min]	[mV]	[mol]
Peak start	12.562	2.218	50,134
Peak top	13.563	42.183	17,864
Peak end	15.488	6.127	2,458
Height [mV]			39.947
Area [mV*sec]			2797.537
Area% [%]			100.000
[eta]			12407.74013

Mn	9,429
Mw	12,408
Mz	14,976
Mz+1	17,005
Mv	12,408
Mp	17,864
Mz/Mw	1.207
Mw/Mn	1.316
Mz+1/Mw	1.371

Figure S8. GPC chromatograms of **P2** using THF as an eluent.



Result of molecular weight calculation (RI)

Peak 1 Base Peak

	[min]	[mV]	[mol]
Peak start	12.768	-0.562	38,280
Peak top	14.183	76.596	9,064
Peak end	15.622	4.408	2,096
Height [mV]			77.056
Area [mV*sec]			5770.148
Area% [%]			100.000
[eta]			10111.13703

Mn	8,017
Mw	10,111
Mz	12,287
Mz+1	14,355
Mv	10,111
Mp	9,065
Mz/Mw	1.215
Mw/Mn	1.261
Mz+1/Mw	1.420

Figure S9. GPC chromatograms of **P3** using THF as an eluent.

FT-IR spectra of polymer thin films

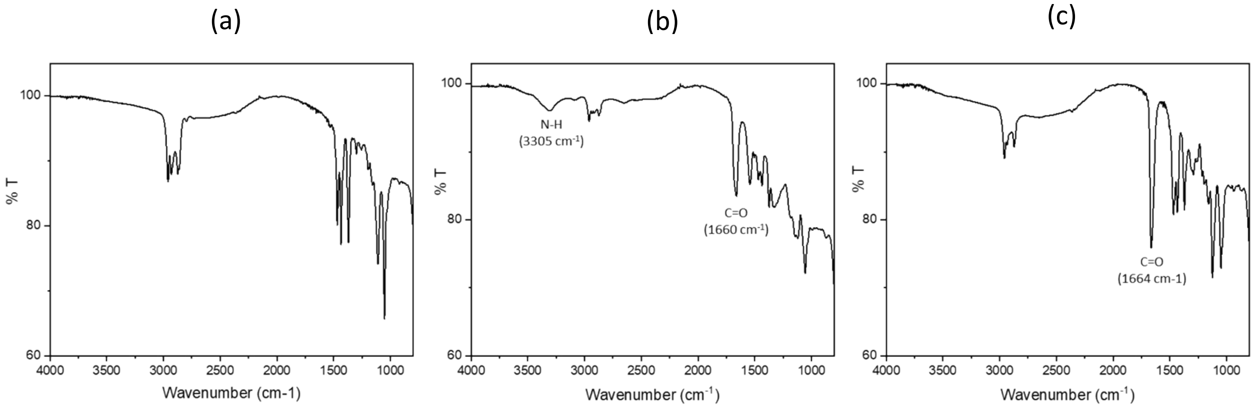


Figure S10 – FT-IR spectra of thin films (a) P1 (b) P2 and (c) P3 coated on ITO/glass substrates. Figured (b) and (c) clearly show the presence of the carbonyl peak and (b) indicated the presence of the N-H bond.

Thin Film topology

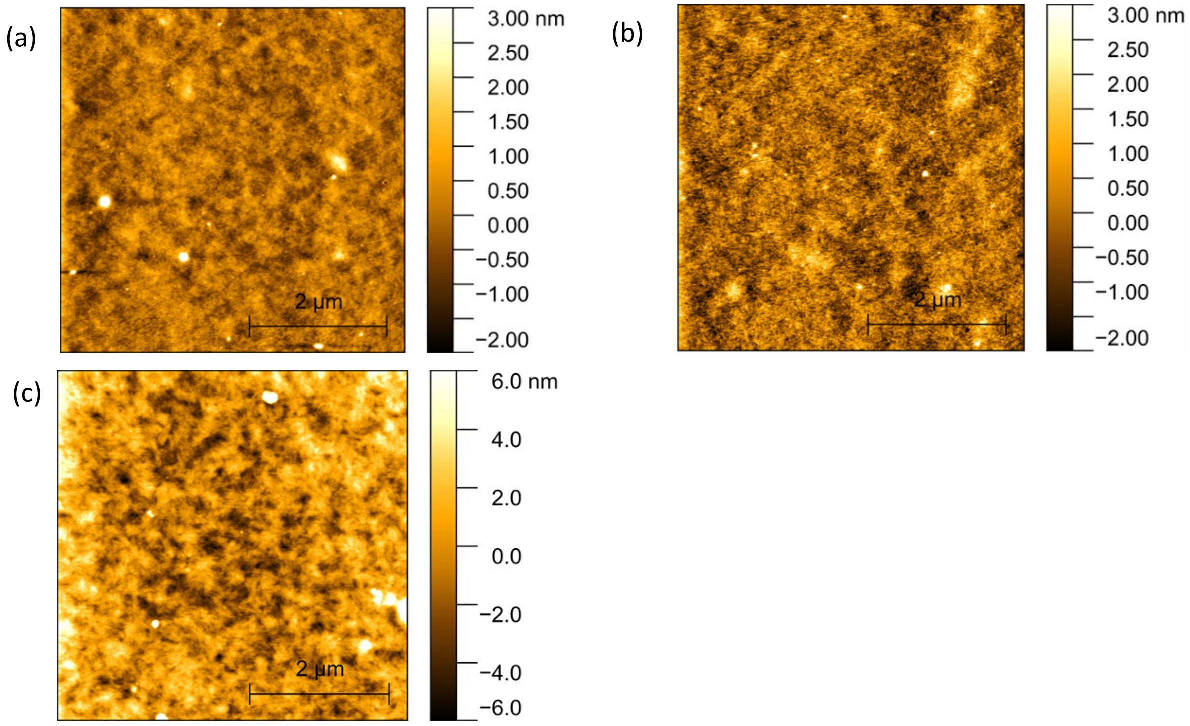
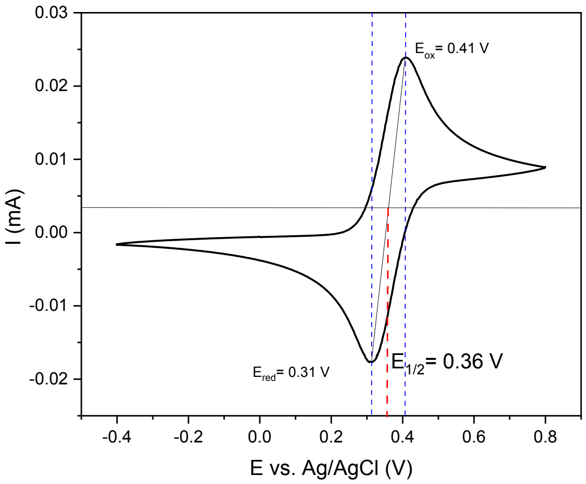


Figure S11 - AFM images of (a) P1, (b) P2 and (c) P3 revealing the rough topology of P3 thin films compared to P1 and P2.



Calibration of Ag/AgCl reference electrode in 0.2 M $TBAPF_6$/PC

Figure S12 – Cyclic voltammetry curve for 5 mM ferrocene dissolved in 0.2 M $TBAPF_6$/PC using a Pt button as the working electrode, a leak-free Ag/AgCl reference electrode and a Pt wire as the counter electrode.

Electrochemistry of P1, P2 and P3 in organic and aqueous electrolytes

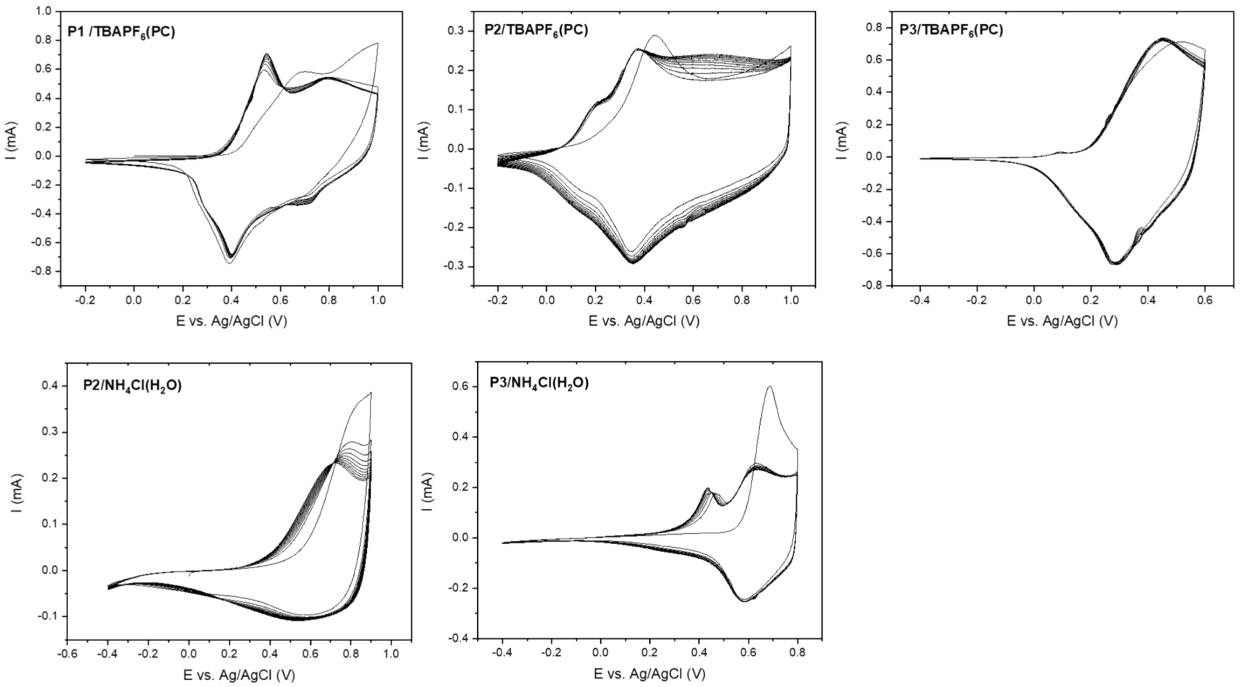


Figure S13 – First 10 CV cycles of the polymers in the respective electrolytes; the first cycle is a clear outlier in each case.

Spectroelectrochemistry of P1, P2 and P3

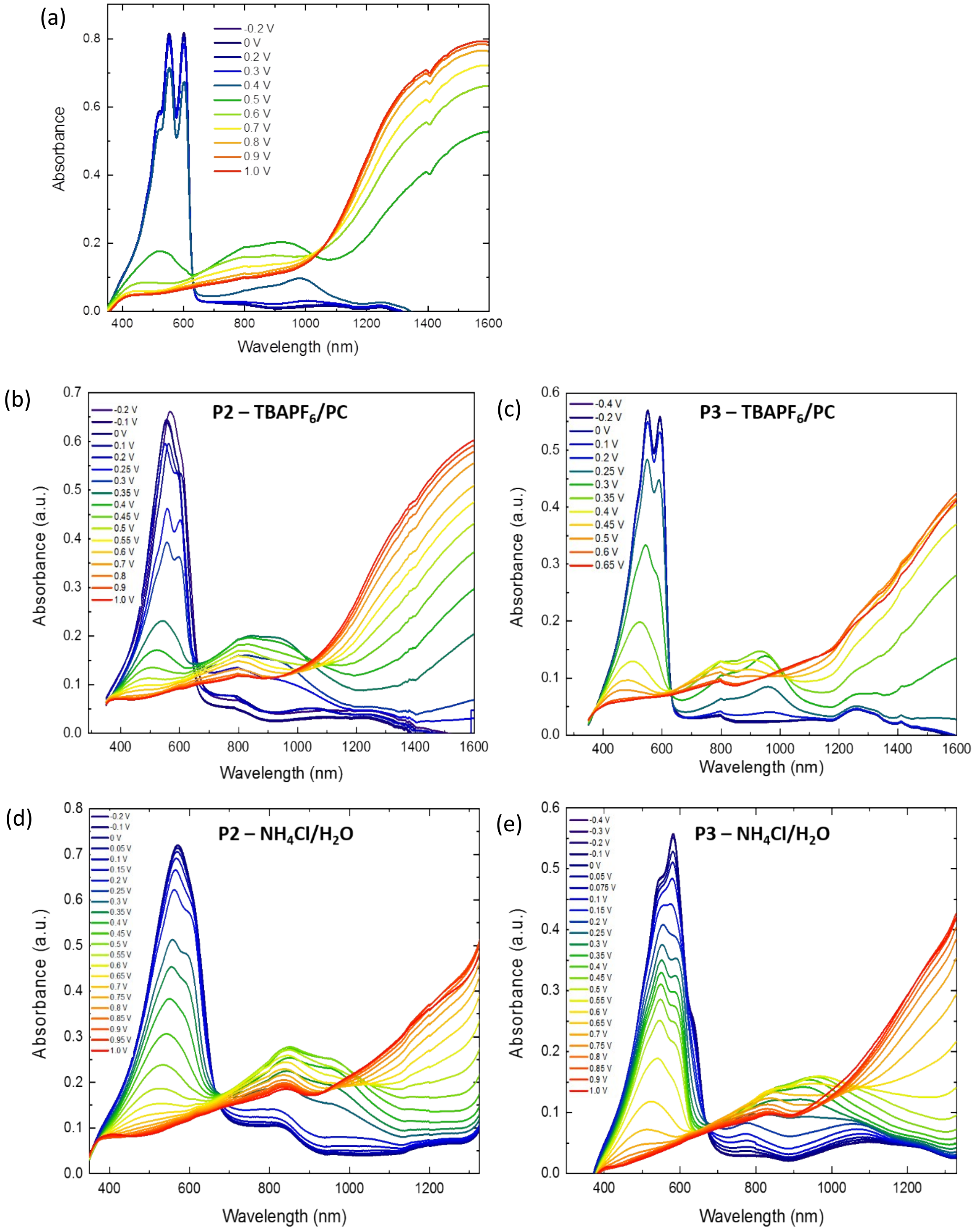


Figure S14 Variation of absorbance spectra with applied potential for P1, P2 and P3 in TBAPF$_6$/PC (a,b,c) and P2 and P3 in 0.2 M NH$_4$Cl (d, e)

OTS modification of ITO/glass substrates

ITO/glass substrates were modified with OTS to prevent delamination of the P1 films during electrochemical testing in 0.2 M TBAPF$_6$ in propylene carbonate. The ITO/glass substrates were cleaned by sonicating for 10 minutes in ethanol followed by acetone. The washed substrates were dried in an oven and blow-dryed with N$_2$ to remove any dust particles. Then the substrates were UV-ozone treated (HELIOS-500 UV-ozone cleaning system) for 20 minutes to remove any organic residues remaining on the substrates. The glass substrates were then dipped in DI water, blow-dryed so that only a thin film of water remains on the surface and immersed in an OTS-solution (80 mL of hexane + 80 μL of OTS) for 10 seconds. The substrates were then immediately washed with hexane. The treated substrates were stored in a glovebox.

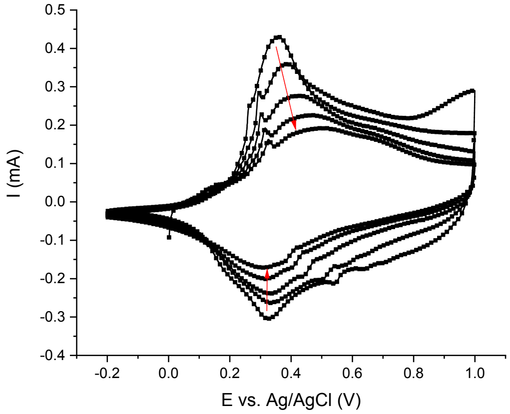


Figure S15 – Cyclic voltammetry of P3 in 0.2 M TBAPF$_6$/PC in the potential range +1.0 V to -0.2 V. The charge density decreases with each cycle indicating instability.

Long term electrochemical cycling

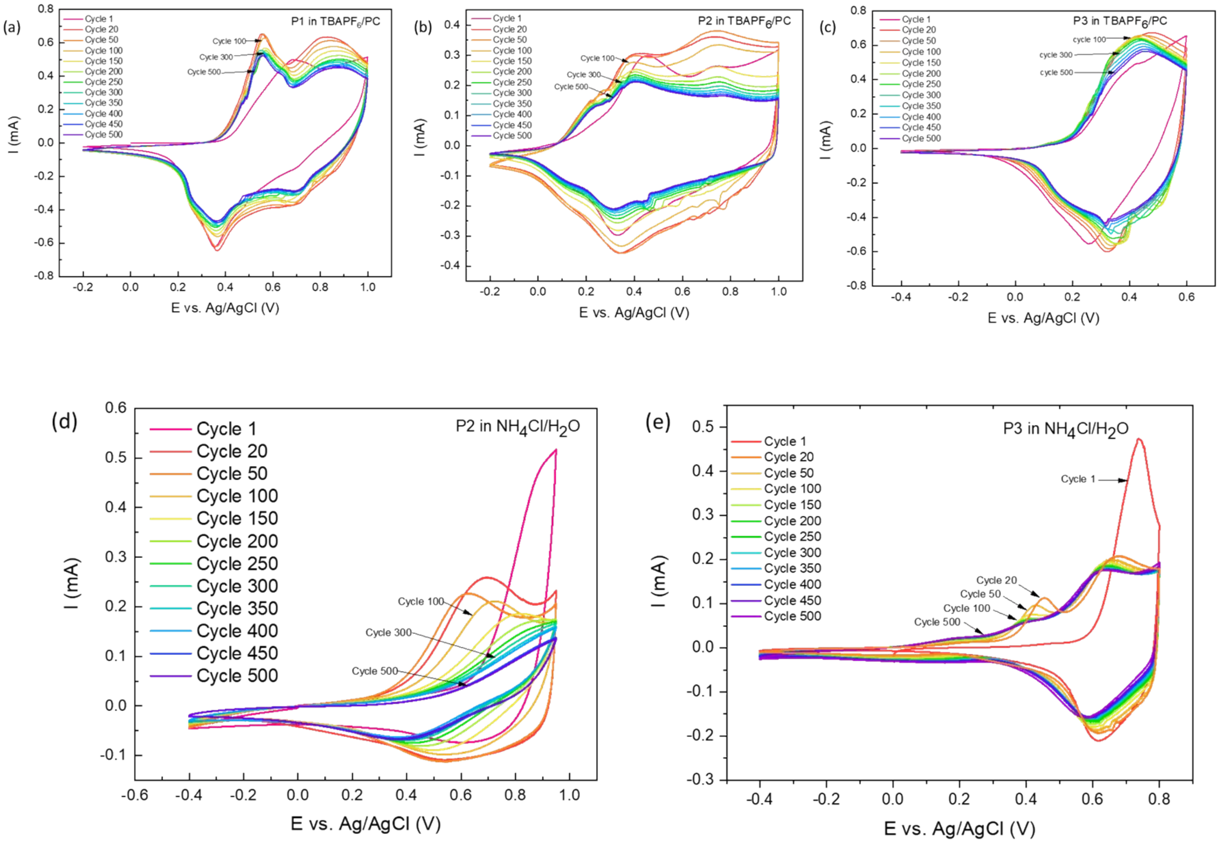


Figure S16 – Variation of current for 500 consecutive cycles for P1, P2 and P3 in TBAPF$_6$/PC (a, b, c) and P2 and P3 in NH$_4$Cl/H$_2$O

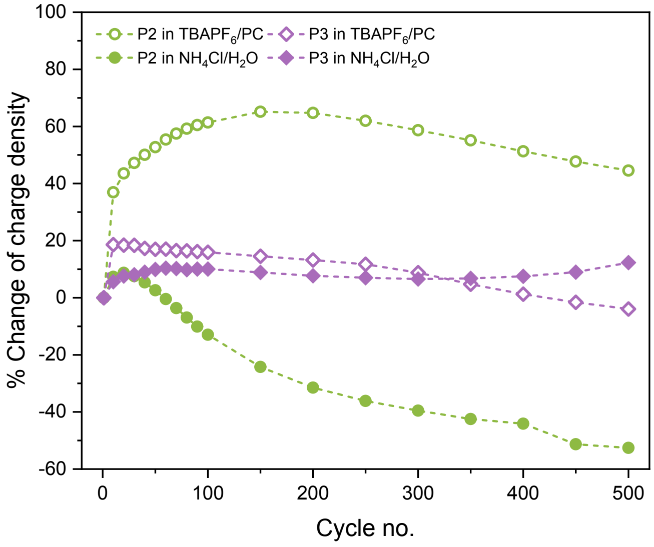


Figure S17 - Percent charge density variation over 500 repetitive CV cycles for P2 and P3

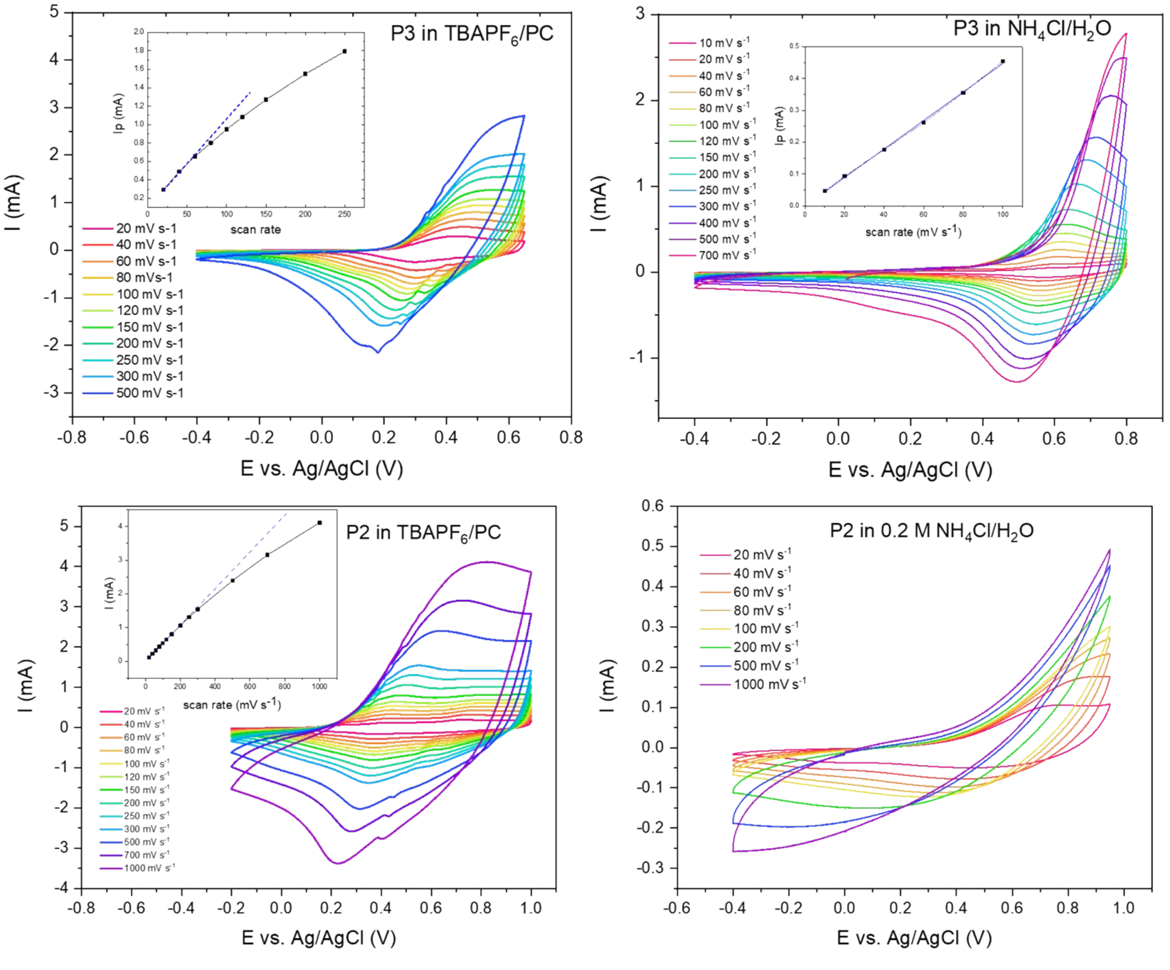


Figure S18 – Scan rate dependence of peak current for P2 and P3 aqueous and non-aqueous electrolytes

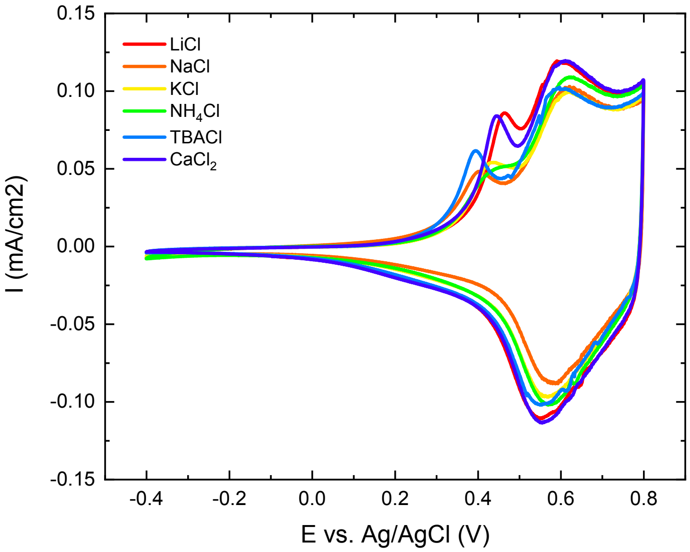


Figure S19 – Cyclic voltammograms of P3 in different aqueous chloride salts

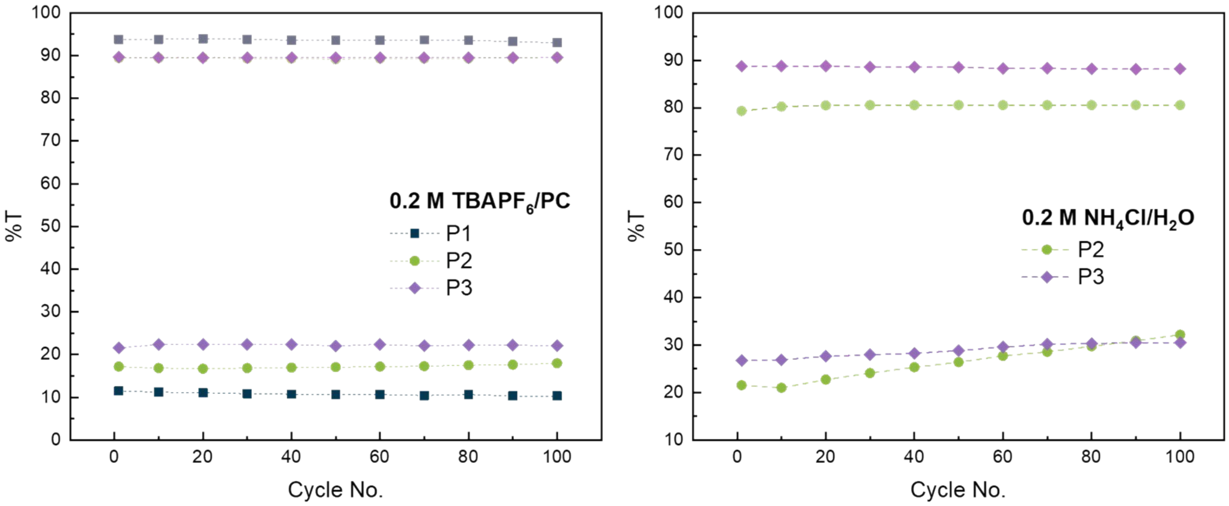


Figure S20 - Transmittance of ProDOT polymers measured in the coloured and bleached states at the respective λ_{max} values in (a) 0.2 M $TBAPF_6$/PC and (b) 0.2 M NH_4Cl/H_2O

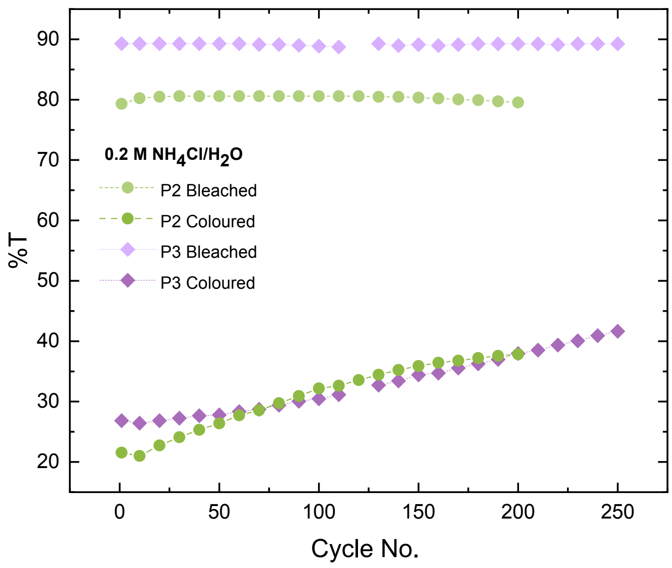


Figure S21 Transmittance measurements of P2 and P3 in the coloured and bleached states in 0.2 M NH_4Cl/H_2O electrolyte.

Table 1 Contrast, coloration efficiency, coloration time and bleaching time for P2 and P3 for organic and aqueous electrolytes

Electrochromic Property	**P2**		**P3**	
	0.2 M $TBAPF_6/PC$	**0.2 M NH_4Cl/H_2O**	**0.2 M $TBAPF_6/PC$**	**0.2 M NH_4Cl/H_2O**
Contrast	72% (569 nm)	66% (570 nm)	69% (550 nm)	63% (582 nm)
Bleaching				
Efficiency (cm^2 C^{-1})	425	571	698	764
Time (s)	0.7	5.7	0.6	2.0
Coloration				
Efficiency (cm^2 C^{-1})	439	492	370	536
Time (s)	2.0	21.5	0.5 s	13.2 s

The wavelength at which the transmittance measurements were recorded is indicated in parenthesis for each instance.

Coloration efficiency (CE) calculations and switching times were calculated using transmittance values and times corresponding to 95% of the maximum contrast.

Equation for CE calculation: $\mathrm{CE} = \log\left(\frac{T_{0.95\Delta\%T}}{T_{initial}}\right)/\mathrm{Q}$

Where T_{initial} = initial transmittance, $T_{0.95\Delta\%\mathrm{T}}$ = transmittance at 95% of the complete transmittance change, Q = charge density required for the transmittance change.

*The main reason for the higher colouration efficiencies in aqueous electrolytes, is due to the smaller charge density that brings about the transmittance change. However the slower switching times, reflect the slow charging/discharging in aqueous systems compared to non-aqueous electrolytes.

References

[S1] B. D. Reeves, E. Unur, N. Ananthakrishnan, J. R. Reynolds. Macromolecules 2007, 40, 5344–5352.

[S2] K. M. Kem, N. V. Nguyen, D. J. Cross. J. Org. Chem. 1981, 46, 5188–5192.

[S3] J. D. Sivey, A. L. Roberts. Environ. Sci. Technol. 2012, 46, 2187–2195.

[S4] L. A. Estrada, J. J. Deininger, G. D. Kamenov, J. R. Reynolds, ACS Macro Lett. 2013, 2, 869−873.