Electronic Supplementary Material (ESI) for Energy & Environmental Science.

Supplementary Information for

Ultra-high cycling stability of poly(vinylphenothiazine) as battery cathode material resulting from π-π interactions

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1 Synthesis and characterization data of PVMPT

1.1 Materials and methods

Commercially available chemicals were purchased from ACROS, FISHER CHEMICAL, MERCK, and SIGMA-ALDRICH and used without further purification. Cyclohexane, dichloromethane and ethyl acetate were purchased from JULIUS HOESCH in technical grade and distilled prior to use. Anhydrous solvents were obtained from a solvent purification system (M. BRAUN) and stored over molecular sieves (3 Å) for a minimum duration of 72 h. All other solvents were used in analytical grade. Air- and moisture-sensitive reactions were carried out under an argon atmosphere in glassware dried by heating under vacuum using standard Schlenk techniques.

NMR spectra of non-polymeric compounds were recorded on BRUKER *Avance dmx 500* (^{1}H = 500 MHz, ^{13}C = 125 MHz) and BRUKER *Avance dpx 400* (^{1}H = 400 MHz) spectrometers, spectra of polymers on a BRUKER *Avance III HD* (^{1}H = 300 MHz) spectrometer in deuterated solvent solution at 298 K.

HR-MS spectra were measured on a THERMO FISHER SCIENTIFIC *Orbitrap XL* spectrometer (ESI) or on a *MAT 95 XL* sector field device from THERMO FINNIGAN.

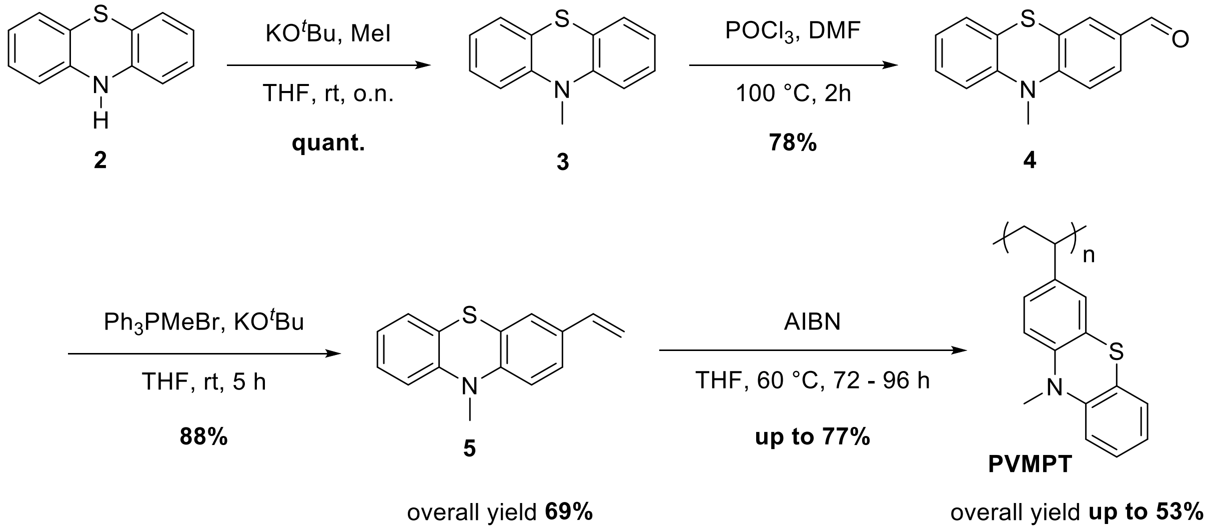
Polymer molecular weights were determined by **MALDI-TOF** spectrometry on a BRUKER DALTONIK *autoflex II*.

GPC was performed on a *SECcurity GPC System* from PSS POLYMER STANDARDS SERVICE using components of the *1260 Infinity* series from AGILENT TECHNOLOGIES. Measurements in THF were performed at 35 °C with a flow rate of 1 mL min^{-1} and a set of three columns (PSS SDV, 8 mm × 50 mm pre-column, 8 mm × 300 mm columns with a porosity of 1.000 Å and 100.000 Å). Measurements in $CHCl_3$ were performed at 22 °C with a flow rate of 1 mL min^{-1} and a set of five columns (PSS SDV, 8 mm × 50 mm pre-column, 8 mm × 300 mm columns with a porosity of 1.000 Å, 10.000 Å, 100.000 Å and 100.000 Å). For calibration, polystyrene standards by PSS were used.

UV/Vis absorption spectra were measured against the specific solvent reference (Quartz glass cuvettes, HELLMA ANALYTICS 115-QS, 10 mm path length) on a SHIMADZU *UV-2450*.

Optical light microscopy images were recorded with 50x magnification on a KEYENCE VK-X260 microscope. The electrodes from cycled cells were disassembled from the cells and pasted on a microscope slide.

1.2 Synthesis of PVMPT



1.2.1 Synthesis of *N*-methylphenothiazine (2)

2 was prepared following a literature procedure.[1] Phenothiazine (**3**, 20.0 g, 100 mmol) and potassium *tert*-butoxide (16.9 g, 150 mmol) were dissolved in dry THF (200 mL) at 0 °C. After stirring for 20 min, methyl iodide (12.6 mL, 201 mmol) was added to the solution. The mixture was stirred at room temperature overnight. The reaction was quenched with water (100 mL), and the resulting mixture was extracted with CH_2Cl_2 (3 × 200 mL). The combined organic layers were washed with brine, dried ($MgSO_4$), filtered and evaporated to dryness under vacuum. Column chromatography (silica gel, cyclohexane/CH_2Cl_2: 2/1) afforded *N*-methylphenothiazine (**2**, 21.3 g, 100 mmol, quant.) as a white crystalline solid. R_f 0.56 (cyclohexane/CH_2Cl_2: 2/1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.19 – 7.14 (m, 4H), 6.94 (dd, *J* = 7.5, 7.5 Hz, 2H), 6.82 (d, *J* = 8.1 Hz, 2H), 3.38 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 146.0, 127.5, 127.3, 123.5, 122.6, 114.2, 35.4; HR-MS (ESI+): *m/z* calcd. for $C_{13}H_{11}NS$ 213.0607 $[M]^+$, found 213.0598.

1.2.2 Synthesis of *N*-methylphenothiazinyl-3-carbaldehyde (4)

4 was prepared following a literature procedure.[2] Phosphoryl chloride ($POCl_3$, 4.7 mL, 50 mmol) was added dropwise to dry DMF (14.0 mL, 182 mmol) at 0 °C. *N*-Methylphenothiazine (**2**, 10.0 g, 46.9 mmol) was added, and the dark brown solution was stirred at 100 °C for 2 h. Crushed ice was added, and saturated aq. NaOAc solution was added until the pH was 6. The aqueous layer was extracted with CH_2Cl_2 (3 × 50 mL). The combined organic layers were washed with brine, dried ($MgSO_4$), filtered and evaporated to dryness under vacuum. Column chromatography (silica gel, cyclohexane/ethyl acetate: 20/1 to 10/1 to 5/1) afforded *N*-methylphenothiazinyl-3-carbaldehyde (**4**, 8.83 g, 36.6 mmol, 78%) as a yellow solid. R_f 0.15 (cyclohexane/ethyl acetate: 10/1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.80 (s, 1H), 7.65 (d, *J* = 8.3 Hz, 1H), 7.60 (s, 1H), 7.19 (dd, *J* = 7.7, 7.7 Hz, 1H), 7.12 (d, J = 7.5 Hz, 1H), 6.99 (dd, J = 7.4, 7.4 Hz, 1H), 6.86 – 6.83 (m, 2H), 3.42 (s, 3H); ^{13}C NMR (125 MHz, CDCl$_3$): δ 190.2, 151.2, 144.2, 131.3, 130.6, 128.1, 127.9, 127.4, 124.1, 123.8, 122.6, 114.9, 113.8, 36.0; HR-MS (ESI+): *m/z* calcd. for $C_{14}H_{11}NOSNa$ 264.0454 [M+Na]$^+$, found 264.0459 [M+Na]$^+$.

1.2.3 Synthesis of 3-vinyl-*N*-methylphenothiazine (5)

5 was prepared following a literature procedure.[3] Methyltriphenylphosphonium bromide (8.70 g, 24.3 mmol) was added to a solution of potassium *tert*-butoxide (3.00 g, 26.6 mmol) in dry THF (30 mL), and the solution was stirred at room temperature for 15 min. *N*-Methylphenothiazinyl-3-carbaldehyde (**4**, 3.92 g, 16.2 mmol) was added to the solution, and the reaction mixture was stirred at room temperature for 5 h. The reaction was quenched with water (50 mL) and was extracted with ethyl acetate (3 × 100 mL). The combined organic extracts were washed with water (3 × 50 mL), brine (50 mL), dried (MgSO$_4$), filtered and the solvent was removed under vacuum. Column chromatography (silica gel, cyclohexane/CH$_2$Cl$_2$: 2/1 to 0/1) yielded 3-vinyl-*N*-methylphenothiazine (**5**, 3.39 g, 14.2 mmol, 88%) as a yellow solid. R_f 0.9 (CH$_2$Cl$_2$); ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.22 – 7.13 (m, 4H), 6.93 (ddd, J = 7.5, 7.5, 1.2 Hz, 1H), 6.81 (dd, J = 8.1, 0.9 Hz, 1H), 6.75 (d, J = 8.3 Hz, 1H), 6.60 (dd, J = 17.6, 10.9 Hz, 1H), 5.61 (dd, J = 17.6, 0.8 Hz, 1H), 5.14 (dd, J = 10.9, 0.7 Hz, 1H), 3.37 (s, 3H); ^{13}C NMR (125 MHz, CDCl$_3$): δ 145.6, 145.5, 135.7, 132.4, 127.6, 127.3, 125.8, 124.7, 123.6, 123.1, 122.6, 114.2, 114.0, 112.4, 35.5; HR-MS (EI+): *m/z* calcd. for $C_{15}H_{13}NS$ 239.0769 [M]$^+$, found 239.0768 [M]$^+$.

1.2.4 Synthesis of poly(3-vinyl-*N*-methylphenothiazine) (PVMPT)

General procedure (exact conditions see **Table S1**): Azobisisobutyronitrile was added to a stirred solution of 3-vinyl-*N*-methylphenothiazine (**5**) in degassed THF, and the solution was stirred at 60 °C in a preheated oil bath for three days. The reaction was stopped by cooling to room temperature, and the solvent was removed under vacuum. The residue was dissolved in CHCl$_3$, and the polymer was precipitated from methanol and acetone to afford **1** as an off-white solid. ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.18 – 5.84 (m, 7H), 3.34 – 2.79 (m, 3H), 1.75 (br, 1H), 1.45 – 0.79 (m, 2H); TGA (10 °C min^{-1}, air): onset 383 °C, T_d10% (temperature for 10% weight loss) 387 °C; DSC (10 °C min^{-1}, air): T_g 179 °C.

Table S1. Conditions for the polymerization of **5** to **PVMPT**.

Entry	n_{Monomer} [mmol]	m_{Monomer} [g]	n_{AIBN} [µmol]	m_{AIBN} [mg]	V_{THF} [mL]	t [h]	yield [%]	M_n [g mol^{-1}]	PDI
Batch 1	10.5	2.50	79.4	13.0	6.8	72	56	$2.4 \cdot 10^4$	1.98
Batch 2	8.36	2.00	63.5	10.4	8.0	96	77	$4.3 \cdot 10^4$	2.96

1.3 Characterization data

1.3.1 ^{1}H NMR spectra

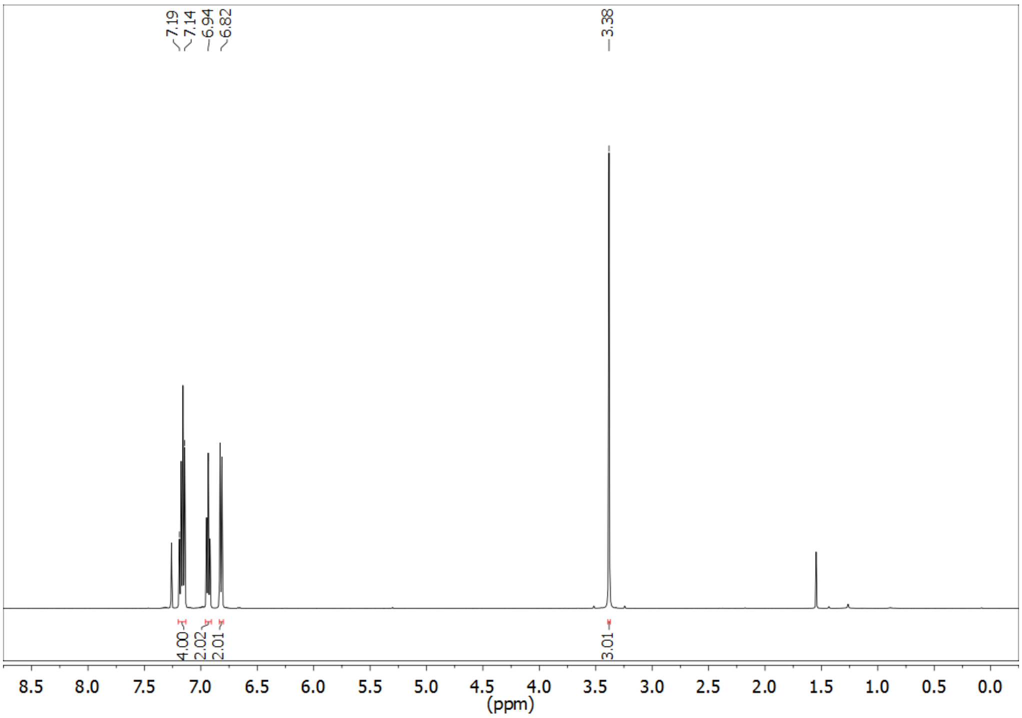


Figure S1. 500 MHz ^{1}H NMR spectrum of *N*-methylphenothiazine (**2**) in $CDCl_3$.

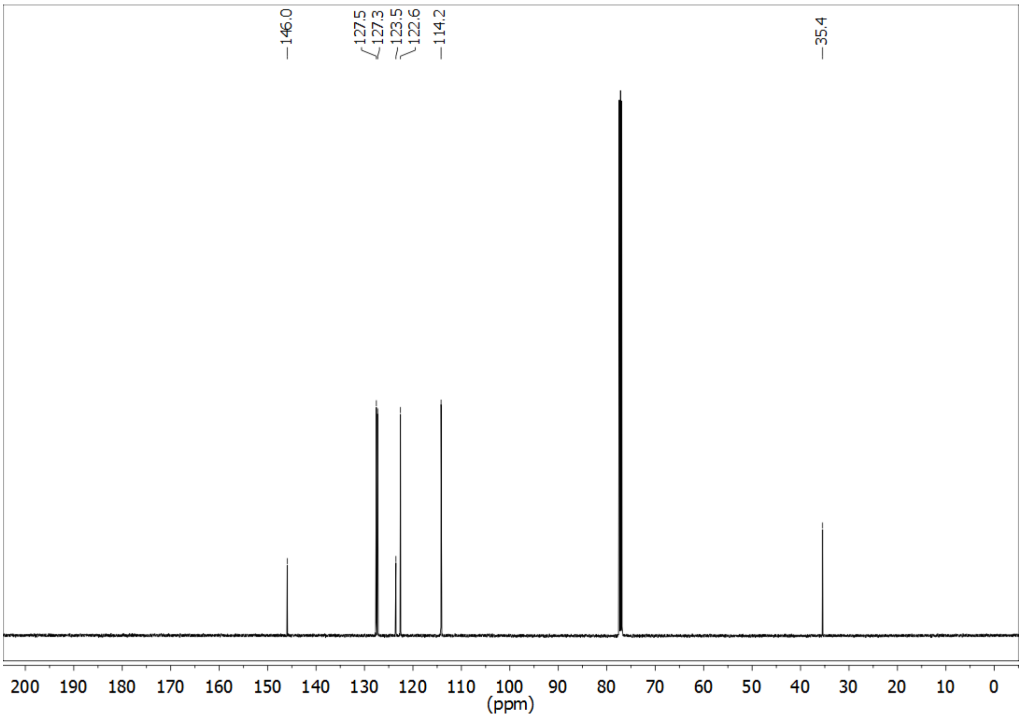


Figure S2. 125 MHz ^{13}C NMR spectrum of *N*-methylphenothiazine (**2**) in $CDCl_3$.

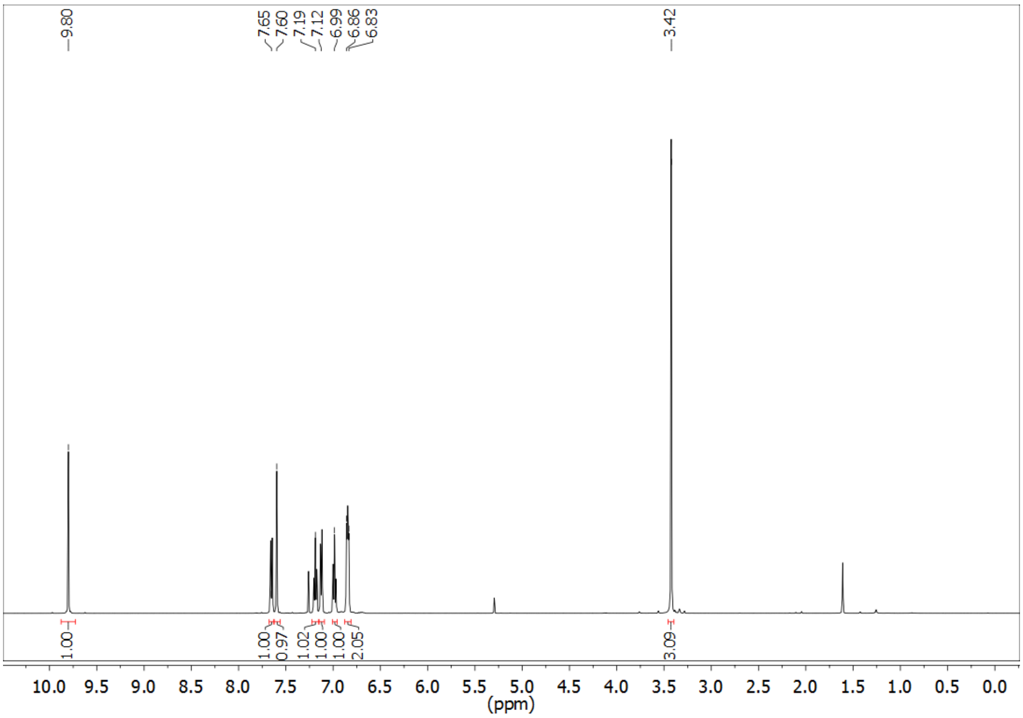


Figure S3. 500 MHz ^{1}H NMR spectrum of *N*-methylphenothiazinyl-3-carbaldehyde (**4**) in $CDCl_3$.

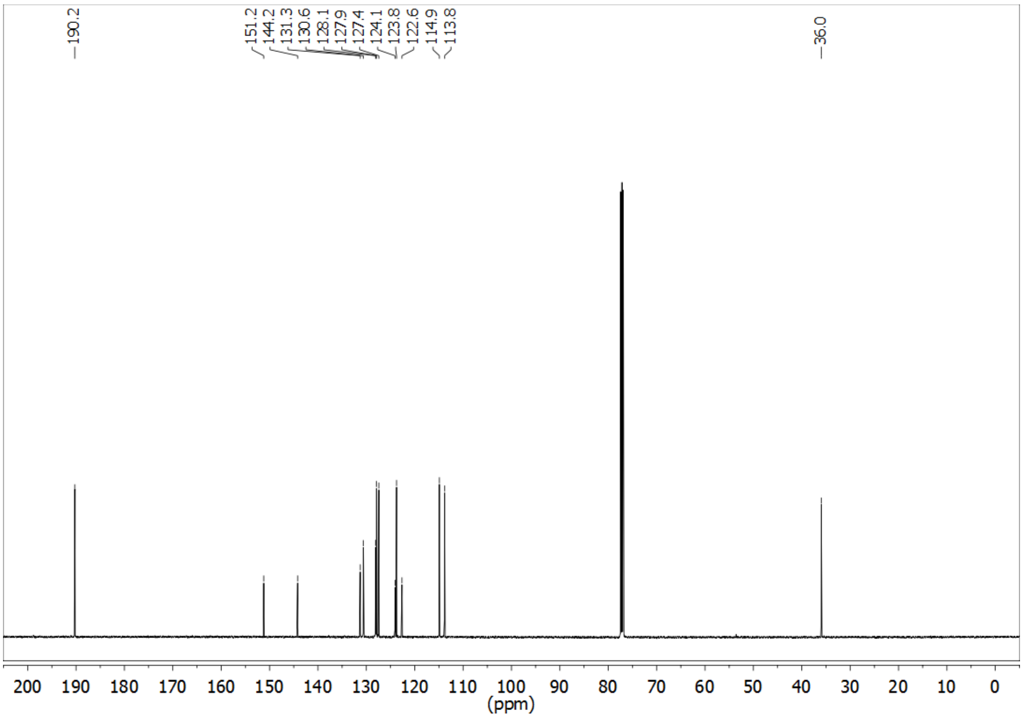


Figure S4. 125 MHz ^{13}C NMR spectrum of *N*-methylphenothiazinyl-3-carbaldehyde (**4**) in $CDCl_3$.

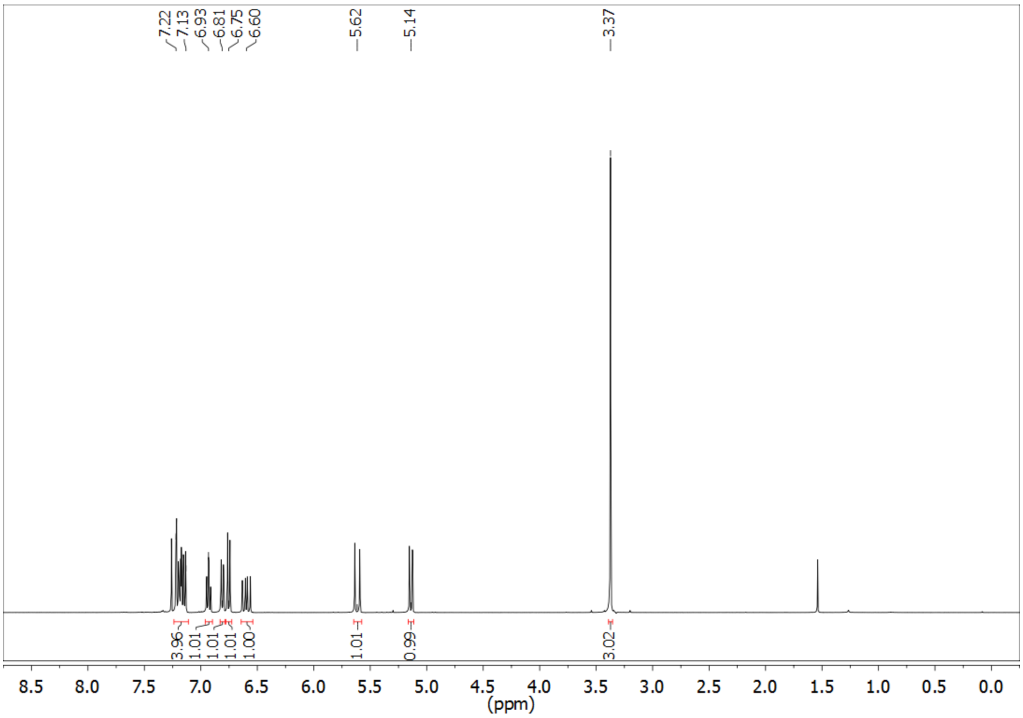


Figure S5. 400 MHz ^{1}H NMR spectrum of 3-vinyl-*N*-methylphenothiazine (**5**) in $CDCl_3$.

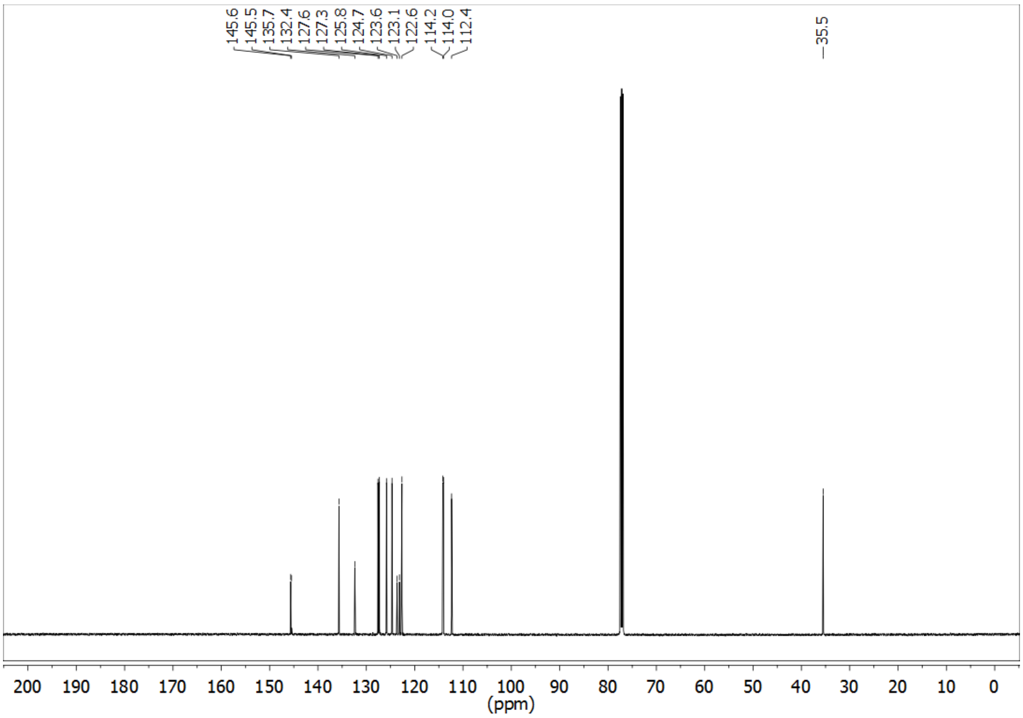


Figure S6. 125 MHz ^{13}C NMR spectrum of 3-vinyl-*N*-methylphenothiazine (**5**) in $CDCl_3$.

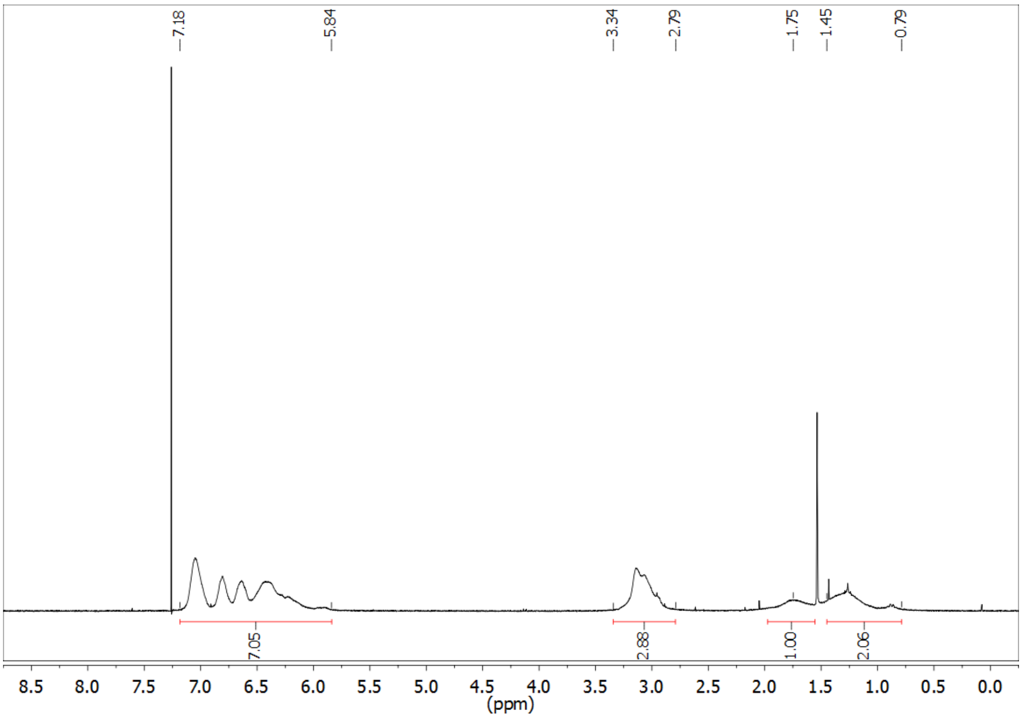


Figure S7. 300 MHz ^{1}H NMR spectrum of poly(3-vinyl-*N*-methylphenothiazine) (**PVMPT**), **batch 1** in CDCl$_3$.

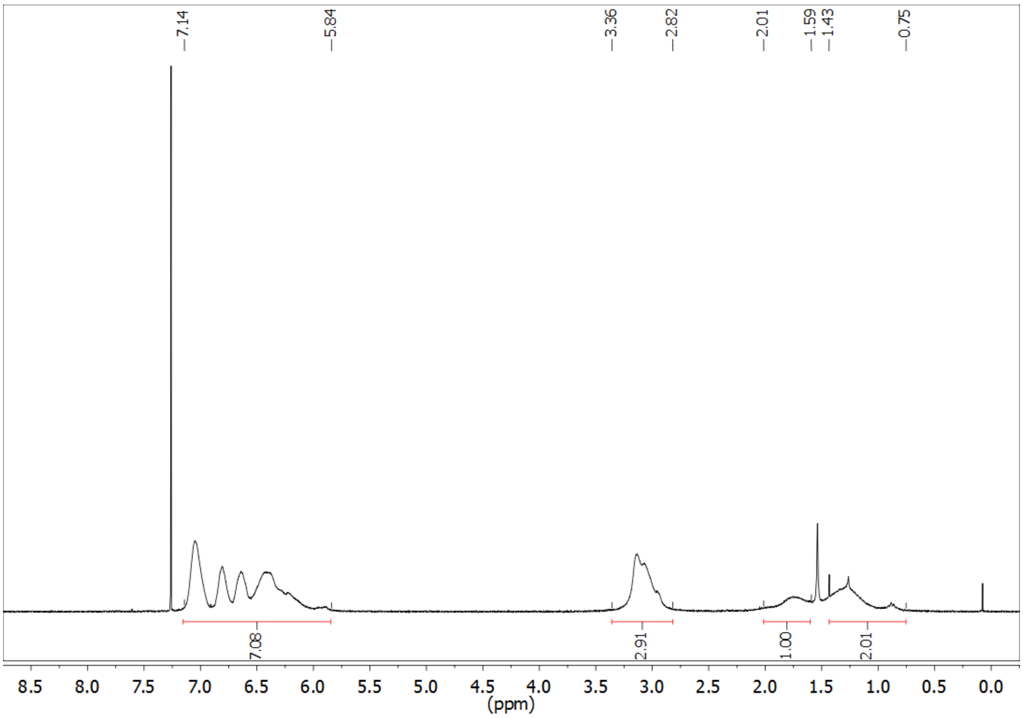


Figure S8. 300 MHz ^{1}H NMR spectrum of poly(3-vinyl-*N*-methylphenothiazine) (**PVMPT**), **batch 2** in CDCl$_3$.

1.3.2 MALDI-TOF measurements of PVMPT

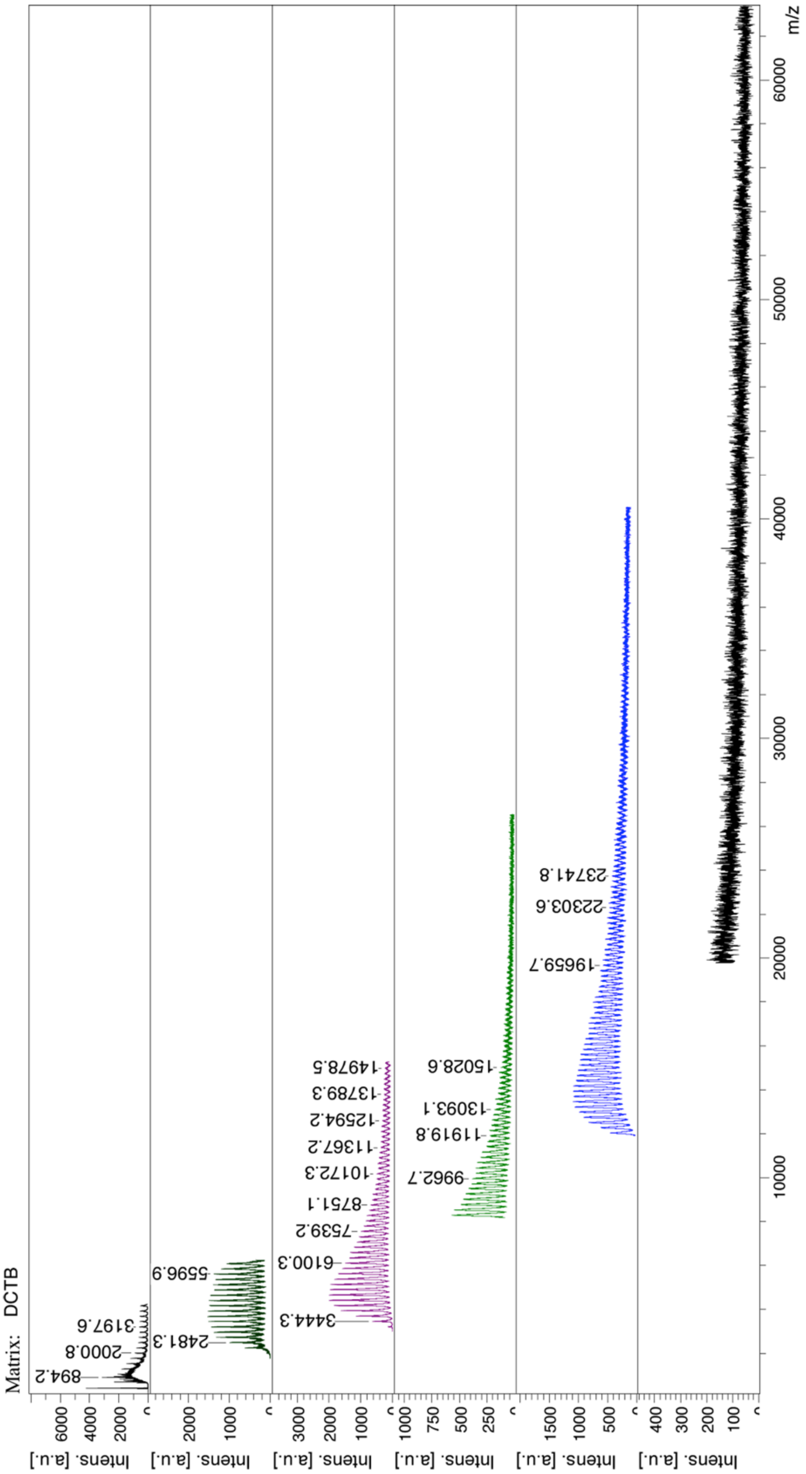


Figure S9. MALDI-TOF spectrum of **PVMPT**, **batch 1**.

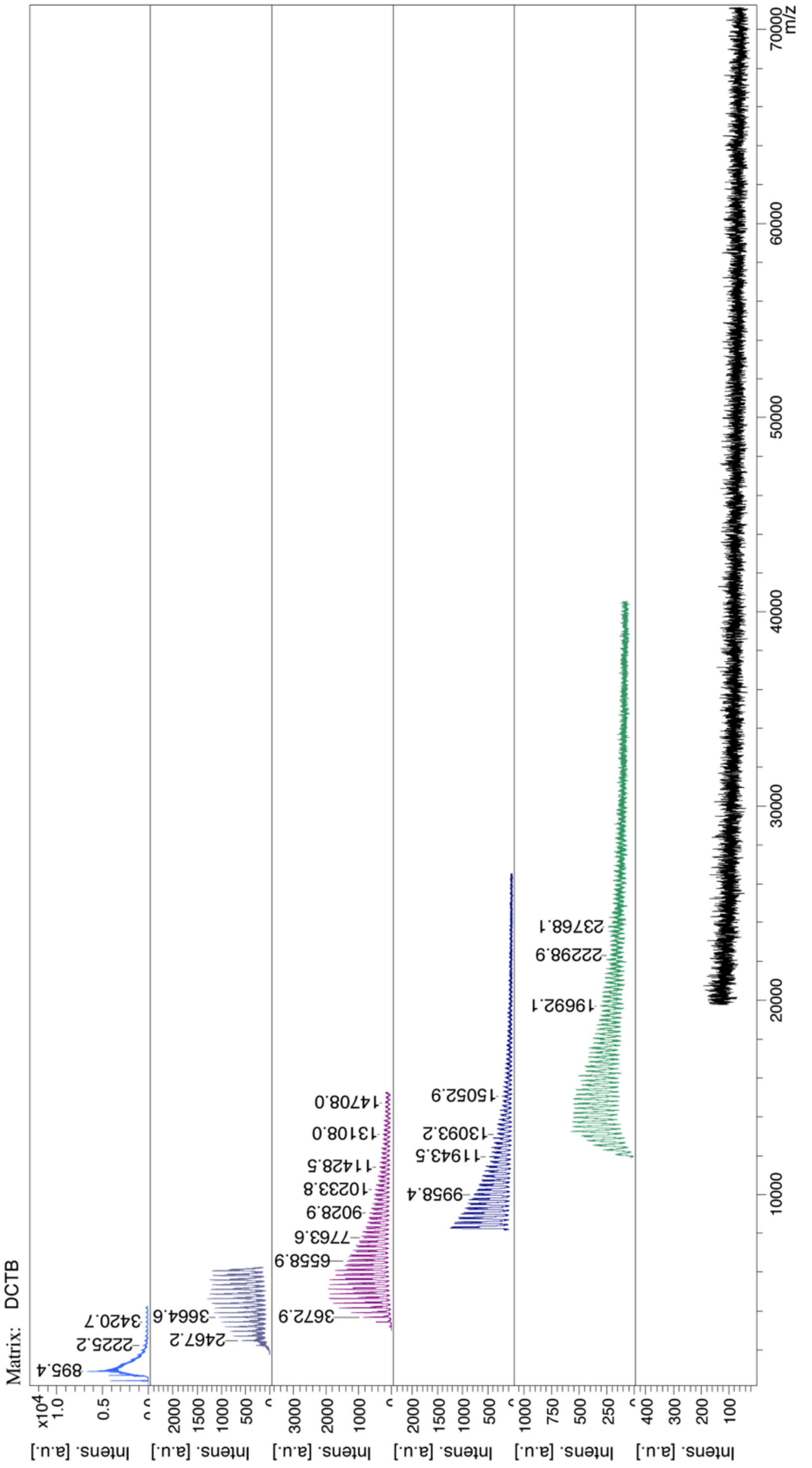


Figure S10. MALDI-TOF spectrum of **PVMPT**, **batch 2**.

1.3.3 Thermal gravimetric analyses (TGA) of PVMPT

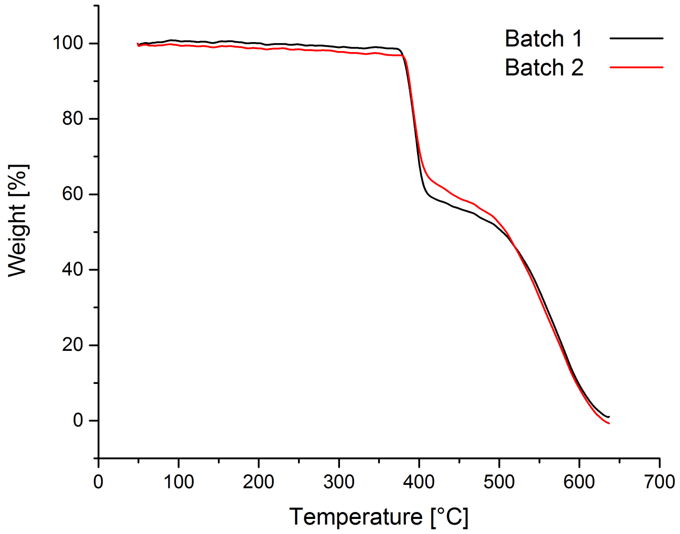


Figure S11. TGA curves of **PVMPT**, **batch 1** and **batch 2**, in ambient air atmosphere at a heating rate of 10 °C min^{-1}.

1.3.4 Differential scanning calorimetry (DSC) measurements of PVMPT

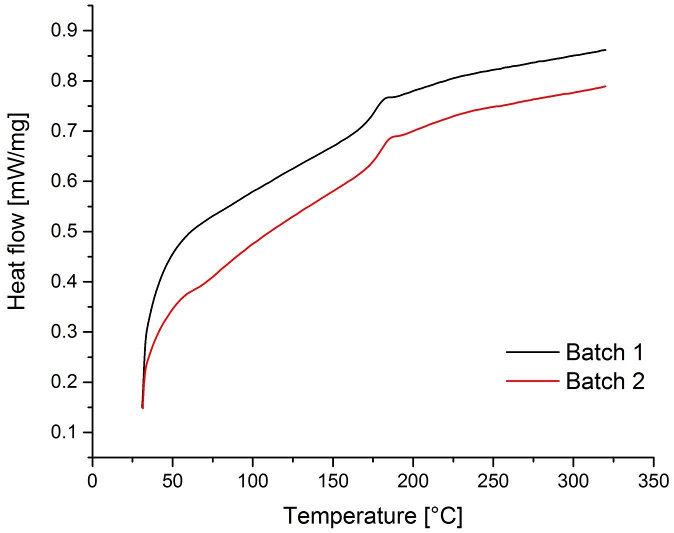


Figure S12. DSC measurements of **PVMPT**, **batch 1** and **batch 2**, in ambient air atmosphere at a heating rate of 10 °C min^{-1}.

1.3.5 Gel permeation chromatography of PVMPT

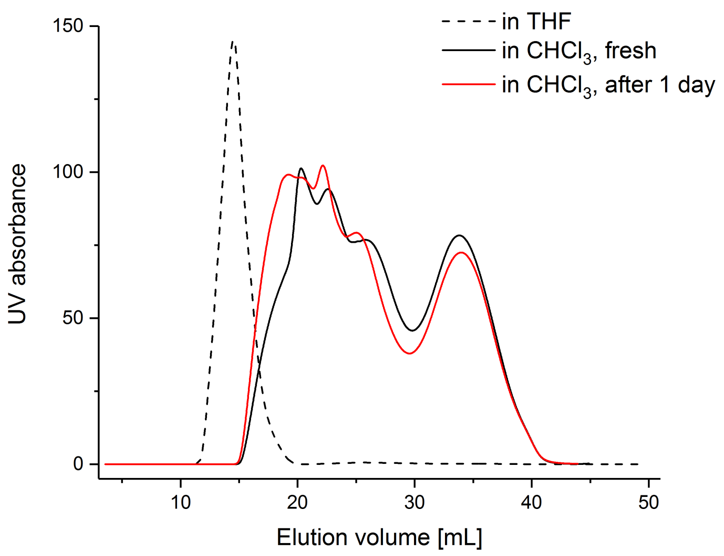


Figure S13. GPC elugrams of **PVMPT**, **batch 2**. Eluent: THF respective $CHCl_3$, polystyrene standard, UV detector.

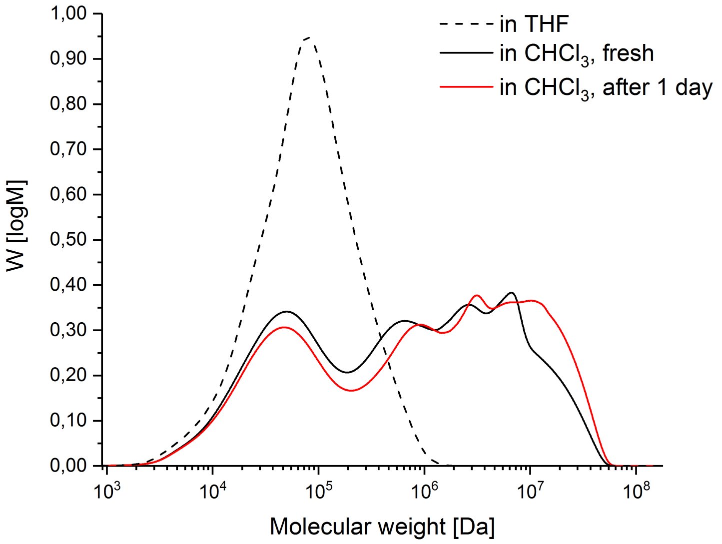


Figure S14. Molecular weight distribution of **PVMPT**, **batch 2**. Eluent: THF respective $CHCl_3$, polystyrene standard, UV detector.

2 DFT calculations on model system 1

2.1 Energies

Table S2. Energies obtained for all structures after geometry optimization and calculation of the harmonic vibrational frequencies (TPSS-D3/def2-TZVP+COSMO). Single point energy calculations with PWPB95-D3/def2-TZVP+COSMO.[a]

Oxidation state of **1**	*E*(TPSS-D3) (E_h)	ZPE (kcal/mol)	*G*(298) (kcal/mol)	*E*(PWPB95-D3)[b] (E_h)
A	-2106.192027	329.953	295.196	-2104.891067
B	-2106.033616	331.220	296.671	-2104.716506
C	-2105.858913	332.781	298.686	-2104.537303

[a] In all calculations, the def2-TZVP basis set and the COSMO solvation model (ε = 37.5, acetonitrile) were used.

[b] PWPB95-D3 single point calculations with the structures optimized with TPSS-D3.

Table S3. Free energies of oxidation $\Delta G_{ox}(298)$ and oxidation potentials calculated from Energies Table S2 (PWPB95-D3//TPSS-D3/def2-TZVP+COSMO).

Oxidation process of **1**	ΔG_{red} (kcal/mol)	$E^{[a]}$ (V)
A → **B** + e^-	111.0	–4.82
B → **C** + e^-	114.5	–4.97

[a] $E = \Delta G_{ox}(298)/F$

2.2 Cartesian coordinates

2.2.1 Cartesian coordinates of 1 in oxidation State A

E(TPSS-D3/def2-TZVP) = –2106.192027340 (conv)
Lowest Freq. = 15.48 cm^{-1}
65
2-A (009/c1/tpss-d3.def2-TZVP_COSMO_37.5)

C	-1.9400504	-4.6628775	2.3218148
C	-1.0268916	-3.4277905	2.3993792
C	0.4539255	-3.8709897	2.4726267
C	1.4746220	-2.7864976	2.8779875
C	2.8219937	-3.4533981	3.2266671
C	-2.5531934	2.2163550	-2.9379955
C	-3.2049392	3.4473675	-2.8319171
C	-3.3670405	4.0581824	-1.5903859
C	-2.8640393	3.4276440	-0.4507386
C	-2.1739852	2.2207015	-0.5548428
C	-2.0091191	1.5907751	-1.8053365
S	-1.3884427	1.5532132	0.8783273
N	-1.2969911	0.3805877	-1.9032316
C	-1.3694104	-0.5741255	-0.8668699
C	-1.4375790	-0.1629216	0.4762014
C	-1.3363324	-1.9523910	-1.1252724
C	-1.4111424	-1.0965766	1.5093754
C	-1.2601353	-2.8749107	-0.0807073
C	-1.2649127	-2.4630529	1.2545587
C	-0.9302899	-0.0911619	-3.2347851
C	1.1394092	3.3447035	-1.8675342
C	0.4834097	4.5602843	-1.6683856
C	0.3437654	5.0873061	-0.3862007
C	0.8623651	4.3846855	0.7034407
C	1.5451184	3.1852780	0.5053498
C	1.6951665	2.6460772	-0.7860186
S	2.2668996	2.3338437	1.8806173
N	2.3925776	1.4309436	-0.9620884
C	2.1688494	0.3812709	-0.0415975
C	2.0307237	0.6653861	1.3280332
C	2.0822379	-0.9575443	-0.4438653
C	1.7746533	-0.3522134	2.2466151
C	1.8783945	-1.9730138	0.4901613
C	1.6991756	-1.6925481	1.8465516
C	2.7877438	1.0671738	-2.3203545
H	-2.9937909	-4.3677444	2.2782089
H	-1.7176348	-5.2622519	1.4317902
H	-1.7935247	-5.3010716	3.2002664
H	-1.2564195	-2.8933318	3.3312514
H	0.5225253	-4.6745515	3.2179874
H	0.7422170	-4.3171678	1.5112788
H	1.0972265	-2.3006597	3.7883125
H	3.2296693	-3.9695399	2.3494322
H	2.6940324	-4.1883819	4.0297049
H	3.5536438	-2.7058623	3.5508043
H	-2.4642467	1.7476554	-3.9113234
H	-3.5964665	3.9168545	-3.7299795
H	-3.8766086	5.0129363	-1.5026251
H	-2.9732509	3.8890723	0.5267461
H	-1.3304743	-2.3125818	-2.1479270
H	-1.4340579	-0.7411088	2.5369121
H	-1.1707297	-3.9296714	-0.3267362
H	-0.5644476	0.7560091	-3.8177461
H	-0.1263419	-0.8221872	-3.1341708
H	-1.7680919	-0.5573620	-3.7728836
H	1.2060473	2.9345006	-2.8687495
H	0.0568180	5.0775969	-2.5223945
H	-0.1811723	6.0240898	-0.2268577
H	0.7429847	4.7664474	1.7135658
H	2.1616136	-1.2156710	-1.4937430
H	1.6366787	-0.0936236	3.2940896
H	1.8191138	-2.9970803	0.1341033
H	3.1978304	1.9513294	-2.8117540
H	1.9548661	0.6803983	-2.9235543
H	3.5654548	0.3031931	-2.2635890

2.2.2 Cartesian coordinates of 1 in oxidation state B

E(TPSS-D3/def2-TZVP) = –2106.033616181 (conv)
Lowest Freq. = 25.05 cm^{-1}
65
2-B (010/c1/tpss-d3.def2-TZVP_COSMO_37.5)

C	-1.7346219	-4.9561822	1.9967021
C	-0.9742489	-3.6530867	2.3039878
C	0.5362395	-3.9433149	2.4632610
C	1.3928842	-2.7509390	2.9451498
C	2.7533482	-3.2593446	3.4641394
C	-2.3293877	2.5318019	-2.5988867
C	-3.0119961	3.7349087	-2.4744662
C	-3.5176183	4.1442668	-1.2368879
C	-3.3387656	3.3276820	-0.1288233
C	-2.6370481	2.1203698	-0.2397222
C	-2.1046404	1.7044792	-1.4830494
S	-2.4095435	1.2157734	1.2362876
N	-1.3738957	0.5198564	-1.6179949
C	-1.4049199	-0.5165628	-0.6862885
C	-1.8552699	-0.3282034	0.6427422
C	-0.9564848	-1.8051504	-1.0367393
C	-1.7752428	-1.3652195	1.5786000
C	-0.8535529	-2.8092973	-0.0891598
C	-1.2230733	-2.5984566	1.2495896
C	-0.6166194	0.3135813	-2.8580066
C	1.4562864	3.2507155	-2.3050287
C	0.7415326	4.4416772	-2.3825952
C	0.0485829	4.9307205	-1.2738198
C	0.0746056	4.2091489	-0.0860073
C	0.8061690	3.0204933	0.0094329
C	1.5189818	2.5190028	-1.1035085
S	0.8641523	2.2447470	1.5779950
N	2.2685536	1.3392027	-1.0279646
C	2.0350383	0.3477976	-0.0713267
C	1.3896440	0.6308626	1.1548216
C	2.4477201	-0.9803398	-0.2906303
C	1.1933453	-0.3717904	2.1079108
C	2.2408613	-1.9641010	0.6667254
C	1.6055825	-1.6840780	1.8874668
C	3.2252388	1.0541530	-2.1041132
H	-2.8098997	-4.7689564	1.9130044
H	-1.3895956	-5.3976708	1.0550213
H	-1.5690891	-5.6876898	2.7947439
H	-1.3401604	-3.2582399	3.2602782
H	0.6416014	-4.7522344	3.1967883
H	0.9372504	-4.3267358	1.5155946
H	0.8659544	-2.2777271	3.7837330
H	3.3050571	-3.7715474	2.6678111
H	2.6042194	-3.9672376	4.2862814
H	3.3678011	-2.4284042	3.8251443
H	-1.9747847	2.2301605	-3.5758011
H	-3.1568374	4.3521508	-3.3553897
H	-4.0513795	5.0837557	-1.1390001
H	-3.7304706	3.6195624	0.8413961
H	-0.6711313	-2.0201388	-2.0582539
H	-2.0943876	-1.1711699	2.5997686
H	-0.4595500	-3.7730474	-0.3977718
H	-0.2379060	1.2769468	-3.1980268
H	0.2302102	-0.3371116	-2.6448768
H	-1.2318570	-0.1368895	-3.6440332
H	1.9593449	2.8813175	-3.1898893
H	0.7137447	4.9780357	-3.3258032
H	-0.5180904	5.8532331	-1.3358621
H	-0.4669868	4.5632187	0.7859113
H	2.9096685	-1.2546627	-1.2308735
H	0.6882585	-0.1150737	3.0355654
H	2.5648586	-2.9764926	0.4436995
H	3.6641012	1.9939185	-2.4376942
H	2.7501964	0.5516171	-2.9550061
H	4.0180221	0.4219386	-1.7062525

2.2.3 Cartesian coordinates of 1 in oxidation state C

E(TPSS-D3/def2-TZVP) = –2105.858912845 (conv)

Lowest Freq. = 35.57 cm^{-1}

65

2-C (011/c1/tpss-d3.def2-TZVP_COSMO_37.5)

C	-1.7889392	-4.8166887	2.2272582
C	-0.9343068	-3.5526296	2.4417070
C	0.5646808	-3.9308762	2.5082000
C	1.5193260	-2.7837383	2.9128213
C	2.9064104	-3.3559853	3.2710322
C	-2.2186128	2.5760460	-2.5609733
C	-2.7736644	3.8336253	-2.3985685
C	-3.1690059	4.2950414	-1.1327331
C	-2.9975511	3.4796087	-0.0313284
C	-2.4172056	2.2080126	-0.1789101
C	-2.0104596	1.7283455	-1.4539297
S	-2.1843654	1.3144262	1.2771132
N	-1.4408562	0.4689358	-1.6255897
C	-1.4260424	-0.5183460	-0.6541050
C	-1.7595922	-0.2558367	0.7065288
C	-1.0697514	-1.8459561	-0.9758993
C	-1.6625705	-1.2567663	1.6836100
C	-0.9406224	-2.8043937	0.0085378
C	-1.1954659	-2.5224619	1.3693038
C	-0.8488504	0.1627678	-2.9416510
C	1.3299488	3.2579012	-2.3398050
C	0.7681599	4.5236444	-2.3098681
C	0.2284990	5.0471913	-1.1269191
C	0.2413936	4.2763861	0.0219252
C	0.7981841	2.9876786	0.0069526
C	1.3788229	2.4587570	-1.1779514
S	0.7656014	2.1334929	1.5103588
N	1.9789627	1.2048473	-1.2129372
C	1.8613803	0.2542482	-0.2125104
C	1.3464859	0.5661156	1.0786261
C	2.2597202	-1.0811039	-0.4370169
C	1.2850185	-0.4086426	2.0841630
C	2.1445461	-2.0350259	0.5549733
C	1.6505524	-1.7241017	1.8410952
C	2.8095726	0.8728117	-2.3896988
H	-2.8537351	-4.5661857	2.2021288
H	-1.5285920	-5.3117750	1.2854553
H	-1.6153426	-5.5252353	3.0431430
H	-1.2114225	-3.1061752	3.4042185
H	0.6705242	-4.7309540	3.2497575
H	0.8805354	-4.3532847	1.5451063
H	1.1068954	-2.2992890	3.8061405
H	3.3459207	-3.8788666	2.4145872
H	2.8120456	-4.0692822	4.0955932
H	3.5900146	-2.5574422	3.5747050
H	-1.9672617	2.2431358	-3.5583085
H	-2.9185831	4.4596552	-3.2725913
H	-3.6108362	5.2786425	-1.0183289
H	-3.2974864	3.8082815	0.9588555
H	-0.8892058	-2.1296161	-2.0034447
H	-1.8997000	-1.0027395	2.7132229
H	-0.6311619	-3.8025905	-0.2850509
H	-0.4000833	1.0715250	-3.3398233
H	-0.0692634	-0.5838630	-2.8124103
H	-1.6046018	-0.2106233	-3.6370525
H	1.7154535	2.8802907	-3.2770378
H	0.7396294	5.1064353	-3.2243293
H	-0.2026551	6.0416492	-1.1090988
H	-0.1802486	4.6548768	0.9478186
H	2.6166483	-1.3859396	-1.4112401
H	0.8928035	-0.1257516	3.0572727
H	2.4329401	-3.0551157	0.3213371
H	3.2785846	1.7855400	-2.7493941
H	2.2076929	0.4234465	-3.1849714
H	3.5910880	0.1839199	-2.0800709

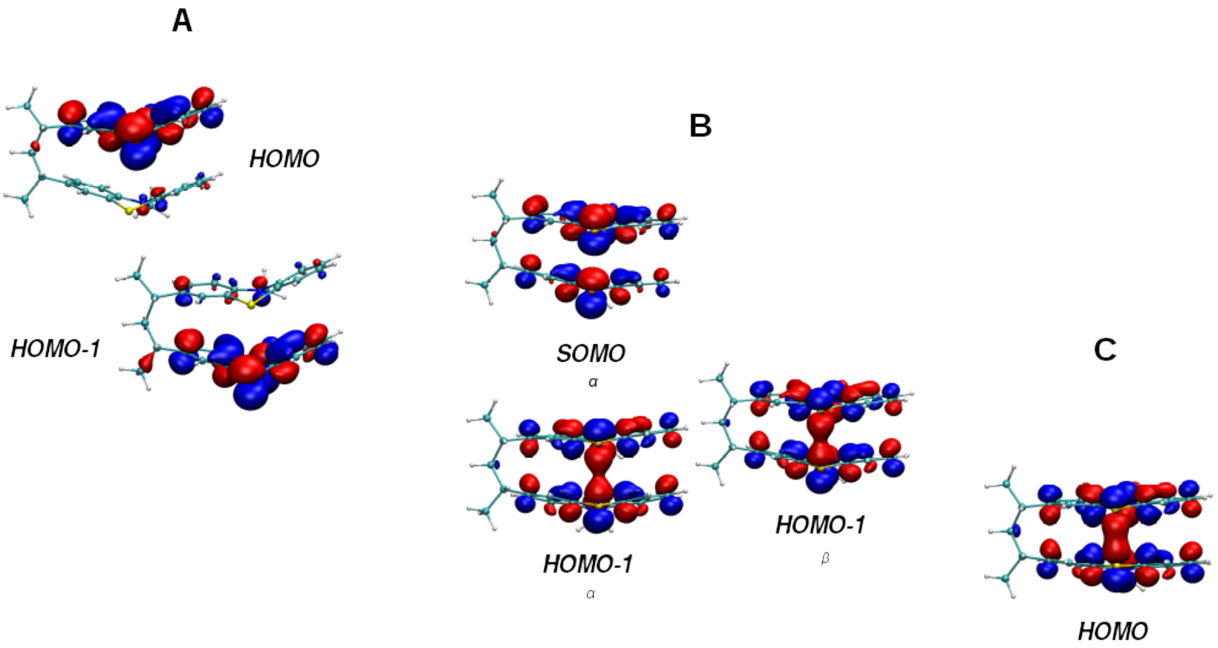


Figure S15. Highest occupied molecular orbitals (TPSS-D3/def2-TZVP+COSMO) of **1** in oxidation state **A** (uncharged), **B** (radical cation), and **C** (dication).

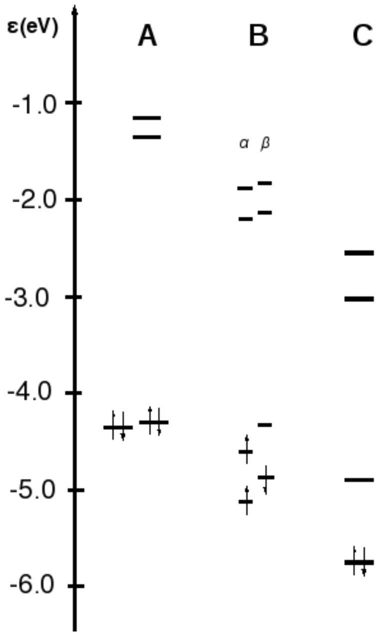


Figure S16. Frontier molecular orbital energies (TPSS-D3/def2-TZVP+COSMO) of **1** in oxidation state **A** (uncharged), **B** (radical cation), and **C** (dication).

3 Investigation of PVMPT-based composite electrodes

All composite electrodes had the composition described in the Methods section of the manuscript.

3.1 SEM micrographs

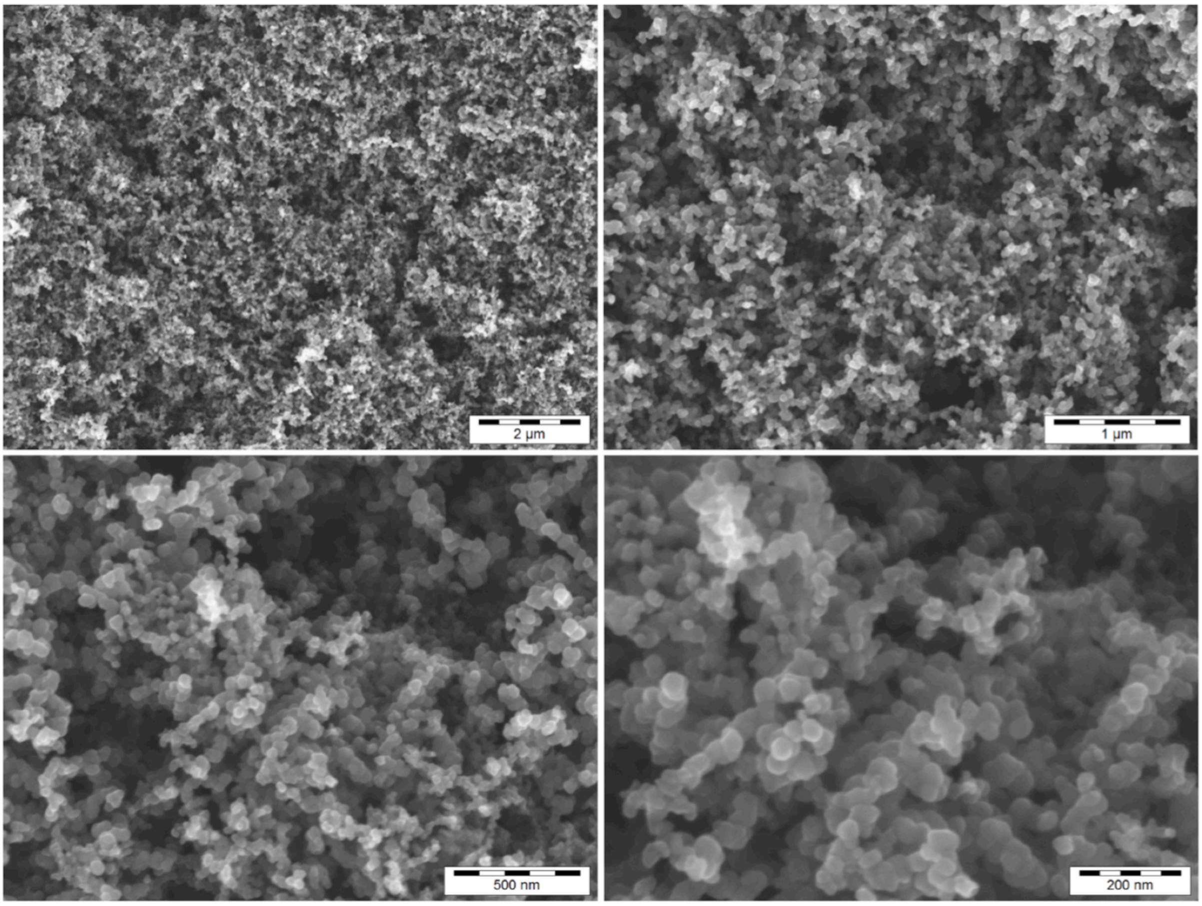


Figure S17. SEM micrographs of the carbon black (Super C65).

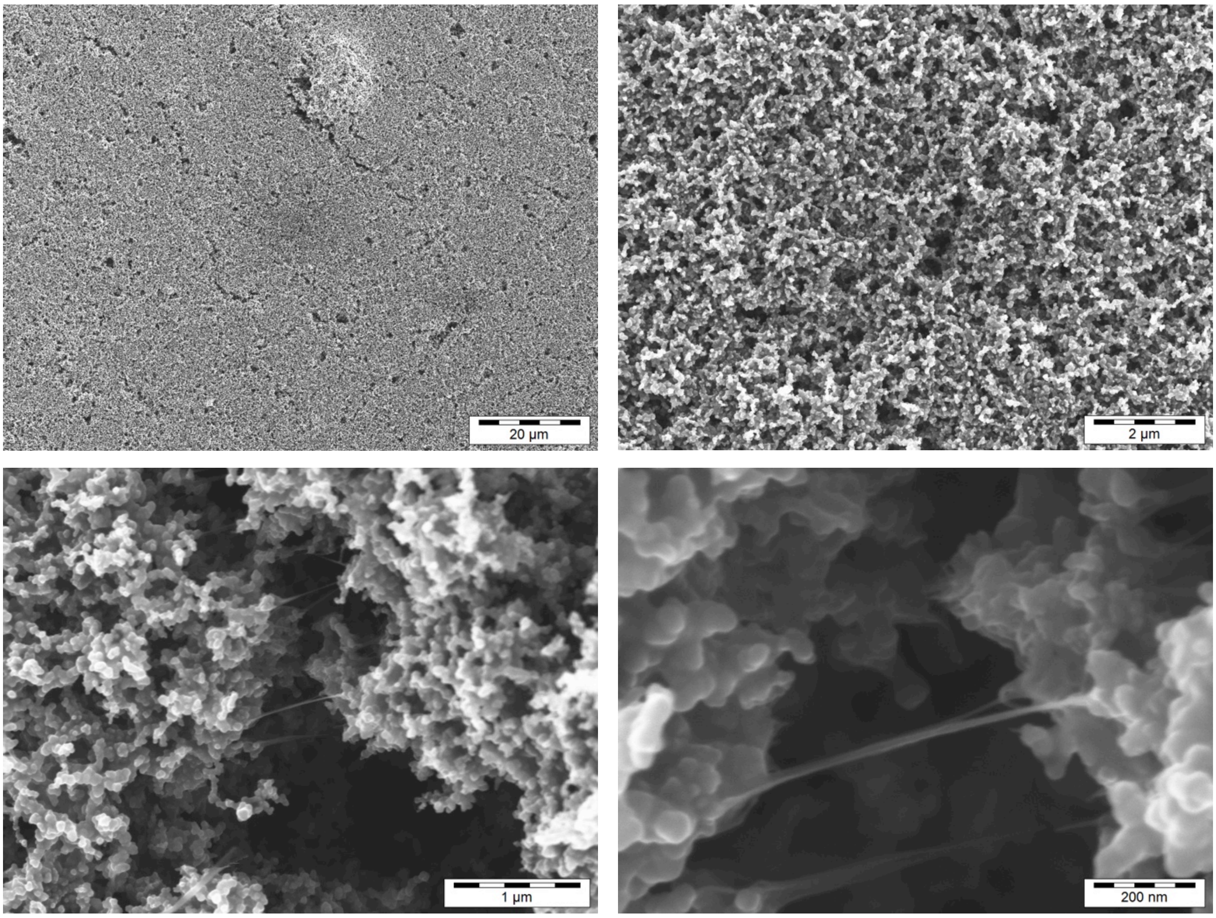


Figure S18. SEM micrographs of a pristine **PVMPT**-based composite electrode.

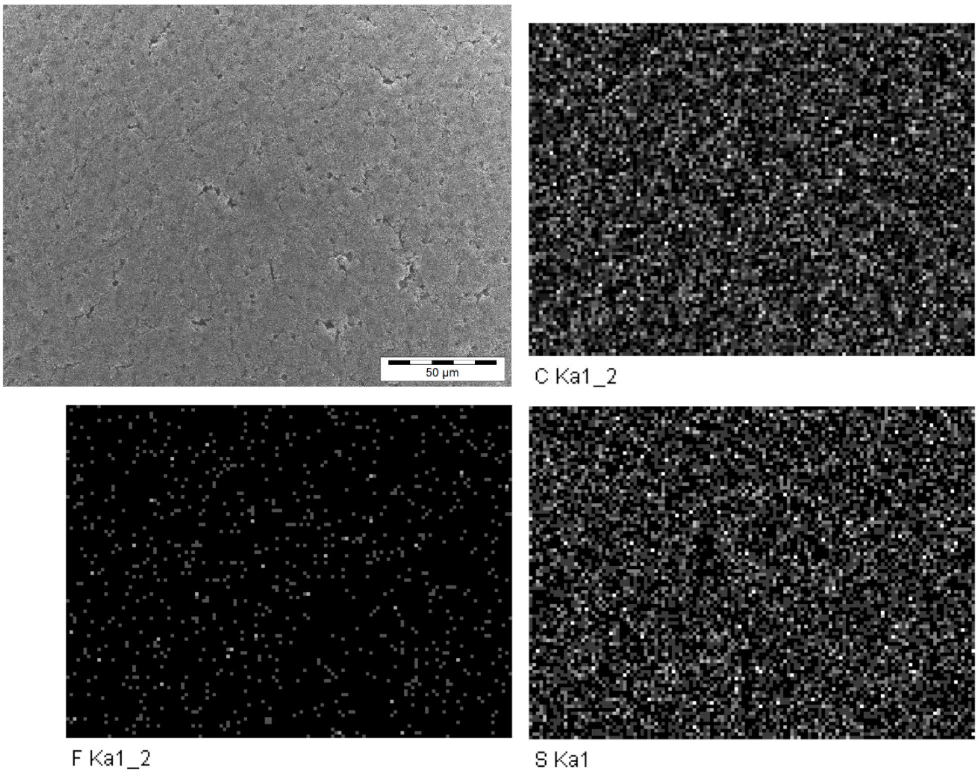


Figure S19. EDS mappings of a pristine **PVMPT**-based composite electrode (50 µm scale bar).

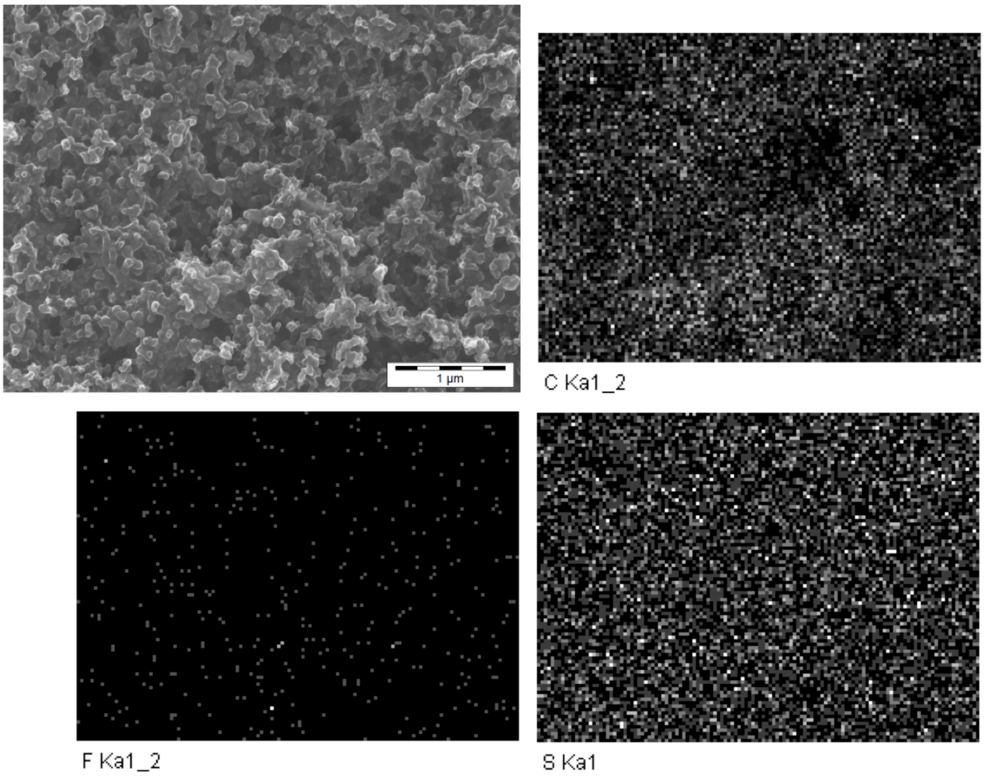


Figure S20. EDS mappings of a pristine **PVMPT**-based composite electrode (1 µm scale bar).

3.2 Electrochemistry of PVMPT-based composite electrodes up to 4.5 V

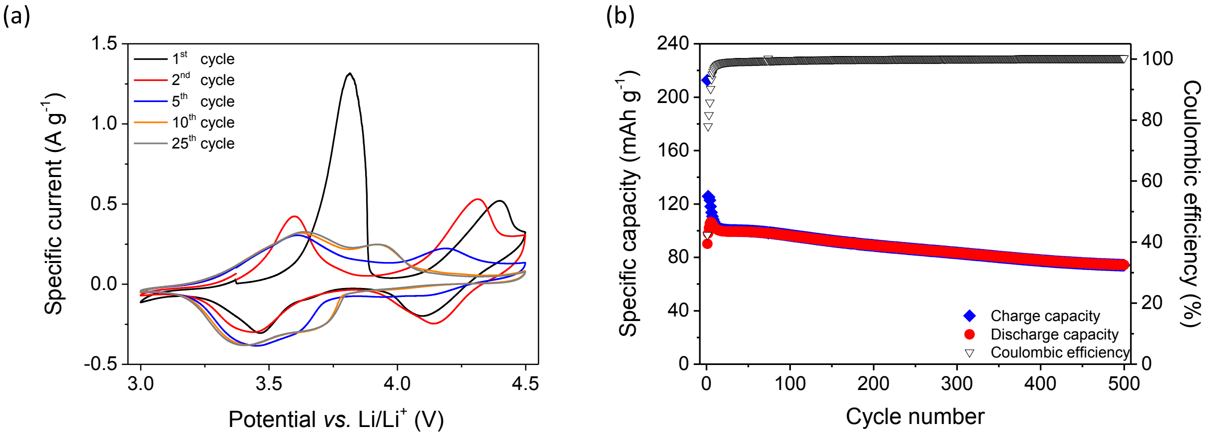


Figure S21. Electrochemistry of a **PVMPT**-based composite electrode (0.23 mg cm^{-2}) between 3 and 4.5 V *vs.* Li/Li$^+$. (a) Cyclic voltammograms, scan rate 0.5 mV s^{-1}. (b) Constant current cycling measurement at 1C rate.

3.4 Rate capability of a PVMPT-based composite electrode

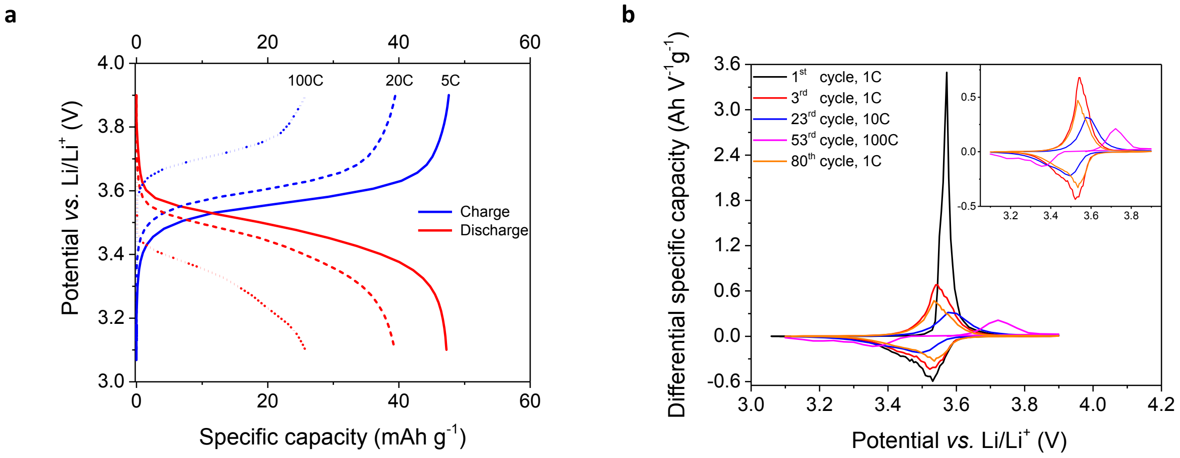


Figure S22. C-rate test of a **PVMPT**-based composite electrode (0.16 mg cm^{-2}). **a.** Selected charge/discharge curves **b.** Differential capacity plots.

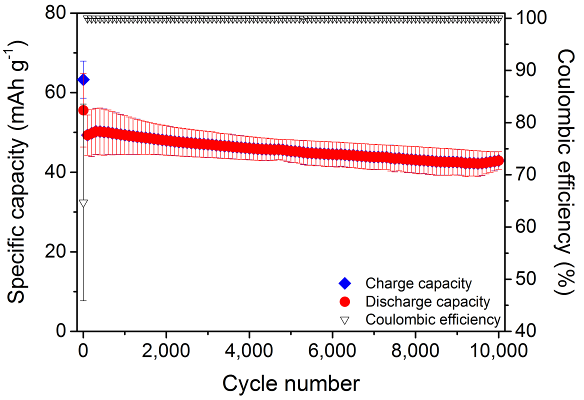


Figure S23. Average of three long-term cycling measurements (constant current cycling measurement at a 10C rate) of **PVMPT**-based composite electrodes with error bars (three cells with mass loadings of 0.07, 0.11 and 0.15 mg cm^{-2}).

3.5 Self-discharge of a PVMPT-based composite electrode

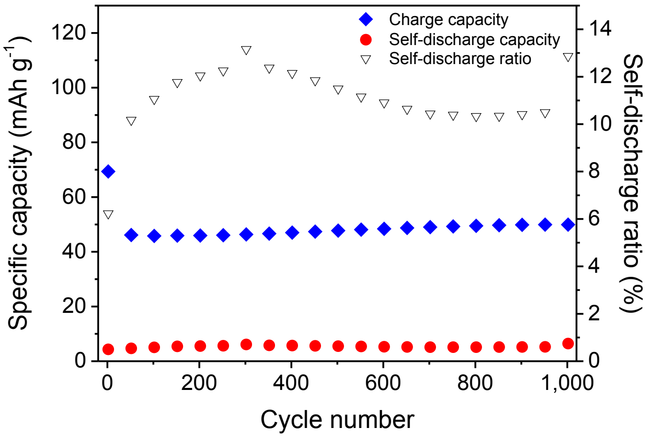


Figure S24. Self-discharge analysis of a **PVMPT**-based composite electrode (0.36 mg cm^{-2}) during constant current cycling at 1C rate. The analysis was performed every 50th cycle. Plotted is the inital charge capacity of each cycle as well as the "recharge capacity" after a 72 h rest step required to achieve full charge again (named self-discharge capacity). The ratio of self-discharge capacity to charge capacity is plotted as the self-discharge ratio.

3.7 Investigation of cycled electrodes

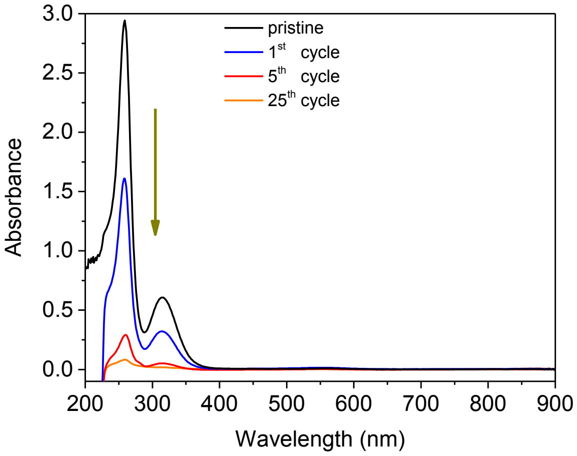


Figure S25. UV/Vis absorption spectra of solutions, obtained by immersion of pristine or cycled **PVMPT**-based composite electrodes in the discharged state in CH_2Cl_2 for two days.

4 References

1. Yang, C.-J., Chang, Y. J., Watanabe, M., Hon, Y.-S. & Chow, T. J. Phenothiazine derivatives as organic sensitizers for highly efficient dye-sensitized solar cells. *J. Mater. Chem.* **22,** 4040 (2012).
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