Electronic Supplementary Information

A merocyanine-based conductive polymer

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Experimental

1. Synthesis

5',6-Bis(4-decyloxythien-2-yl)-1',3'-dihydro-1',3',3'-trimethyl-spiro[2H-1-benzopyran-

2,2'-[2H]indole] (TSP4)



The detailed synthesis of **1** will be described elsewhere [1]. Spiropyran 2 was prepared according to the procedure of Silvia et al. [2]. The other compounds were commercially available and used without further purification.

5',6-Dibromo-1',3'-dihydro-1',3',3'-trimethyl-spiro[2*H*-1-benzopyran-2,2'-[2*H*]indole] (**3**): We modified the method described previously [3]: **2** (5.27 g, 14.8 mmol) was dissolved in chloroform (40 mL), brought to reflux and NBS (2.63 g, 14.8 mmol, 1 eq) in chloroform (150 mL) was added dropwise in time of 60 min. The resulting mixture was refluxed for additional 30 min then cooled to room temperature. The solid was filtered off and washed with chloroform. The filtrate was washed twice with water, dried over magnesium sulphate evaporated to dryness at 50°C under vacuum. The amorphous mass was recrystallised from ethanol to give fine yellow-green crystals of **3**. Yield: 5.60 g, 87%, The spectroscopic data was identical with that reported previously [3].

5',6-Bis(4-decyloxythien-2-yl)-1',3'-dihydro-1',3',3'-trimethyl-spiro[2H-1-benzopyran-2,2'-

[2*H*]indole] (**TSP4**): **1** (1.03 g, 6 mmol) and **3** (0.87 g, 2 mmol) were dissolved in dimethoxyethane (35 mL) and degassed. The 1M solution of potassium carbonate (10 mL) was added followed by tetrakis(triphenylphosphine) palladium(0) (0.34 g, 4 mol%). The resulting mixture was stirred at 90°C overnight then cooled to room temp. The mixture was diluted with dichloromethane, washed with brine, dried over magnesium sulphate and evaporated to dryness at 50°C under vacuum. In order to remove the dithiophene impurity,

the resulting dark oil was dissolved in a minimal amount of dichloromethane and treated with warm methanol (~50 mL). The warm milky solution was decanted from the resulting yellow oil. The procedure was repeated twice to give the product **TSP4** as a yellow oil which solidified with time. Yield: 0.71 g, 47%. 1H NMR (CDCl₃, ppm) δ : 7.39 (dd, 1H, J = 8.1 and 1.9 Hz, Ar-H), 7.30 (dd, 1H, J = 8.5 and 2.3 Hz, Ar-H), 7.25-7.23 (m, 2H, Ar-H), 6.90-6.81 (m, 3H, 2 x Th-H + CH), 6.72 (d, 1H, J = 8.5 Hz, Ar-H), 6.50 (d, 1H, J = 8.1 Hz, Ar-H), 6.11 (d, 1H, J = 1.8 Hz, Th-H), 6.08 (d, 1H, J = 1.8 Hz, Th-H), 5.72 (d, 1H, J = 10.0 Hz, CH), 3.98-3.90 (m, 4H, OCH₂), 2.75 (s, 3H, NCH₃), 1.82-1.72 (m, 4H, CH₂), 1.50-1.41 (m, 4H, CH₂), 1.39-1.23 (m, 30 H, Alk-CH₂ + 2 x CH₃), 0.92-0.85 (m, 6H, Alk-CH₃); HRMS (ESI, M⁺+1) found: 754.4333, for C₄₇H₆₄NO₃S₂ requires: 754.4328. ¹³C NMR (CDCl₃, 100 MHz, ppm) δ : 157.90, 157.84, 154.22, 148.09, 143.87, 142.41, 137.40, 136.02, 129.34, 127.07, 126.94, 126.13, 125.34, 123.77, 119.76, 119.27, 118.88, 115.89, 115.42, 114.67, 113.95, 106.86, 104.58, 96.40, 95.61, 94.83, 70.17, 70.05, 69.97, 51.79, 31.92, 29.60, 29.59, 29.43, 29.41, 29.39, 29.33, 29.27, 29.24, 28.95, 26.10, 26.08, 25.92, 22.69, 20.13, 14.12.

2. Electrochemical polymerisation of TSP4.

PolyTMC4 films were electrochemically grown on either a platinum disc working electrode, with a 0.02 cm² surface area (Bioanalytical System) or on an optically transparent ITO (Indium Tin Oxide) coated glass (Delta Technologies, Limited, resistivity $R_s = 4-8 \Omega$) by cyclic voltammetry (0 – 1.2 V, scan rate 100 mV s⁻¹) or chronoamperometric deposition at constant potential (1.2 V for up to 30 mins) from an anhydrous dichloromethane:acetonitrile (1:2) solution containing 0.1 M tetrabutylammonium perchlorate (TBAP) and the monomer at a concentration of 8 mM. **PolyTMC4-Co²⁺** films were electrodeposited from the same solution containing additionally 8 mM cobalt acetate tetrahydrate (1:1, **TSP4:Co²⁺**) obtained by adding the appropriate amount of a 0.238 M methanol solution of cobalt acetate tetrahydrate. Pt mesh and Ag/Ag⁺ electrodes were used as counter electrode and quasireference electrode, respectively. For calibration of the Ag/Ag⁺ electrode, half-wave potentials were measured for 1 mM ferrocene, i.e. $E_{1/2} = 0.165$ V vs. Ag/ Ag⁺ reference electrode. Solutions were degassed prior to the measurements.

3. UV-visible spectroscopy.

a) Photoisomerisation of TSP4. A solution of $2 \cdot 10^{-5}$ M TSP4 monomer in dichloromethane:methanol (1:1) was illuminated with 254 nm UV light and spectra collected every 1 min (total exposure time to UV light was 7 min) (Fig. 2a).

- b) Acid/base catalyzed isomerisation of TSP4/TMC4. For the acid catalyzed isomerisation, 100 μ L of 1 M HCl was introduced into 50 mL of 2·10⁻⁵ M TSP4 monomer in dichloromethane:methanol (1:1) giving an excess of the acid (100:1, aq. HCl:TSP4). The spectrum of this solution was collected every 1 min for 9 min. For the base catalyzed isomerisation of the resulting TMC4, the same amount of 1 M NaOH was introduced into the acidified TMC4 solution and the spectrum was collected immediately (Fig. 2b).
- c) UV-visible spectra of TSP4 with Co²⁺. Absorbance spectra of 2·10⁻⁵M TSP4 in dichloromethane: methanol (1:1) solution were collected first, then the solution has been exposed to 254 nm UV light for 7 min. Then cobalt acetate tetra hydrate (0.238 M) dissolved in methanol was adjusted with micropipette into solution to get molar ratio with monomer (1:1).
- d) Spectroelectrochemistry of polymer films. The spectroelectrochemisty of the polymer films deposited on ITO electrode was investigated in solutions of 0.1 M TBAP in acetonitrile vs. Ag wire for the reference electrode. These applied voltages for the Ag wire were rescaled vs. Ag/Ag⁺ by using ferrocene. The controlled-potentials measurements were carried out with eDAQ system controlled by EChem software. All absorbance spectra were recorded using a Shimadzu UV-1800 spectrophotometer.

4. Conductivity measurements.

A 4 point resistivity meter (JANDEL Model RM2), with a square array 4-point probe of 0.635 mm spacing, was used in conductivity measurements. **PolyTMC4** and **polyTMC4**- Co^{2+} was electrochemically grown on optically transparent ITO-coated glass by chronoamperometric deposition at constant potential (1.2 V) during 30 min. The polymer was than peeled off the electrode and the conductivity measurement was performed on the free-standing film.

5. Elemental analysis

PolyTMC4-Co²⁺ was electrochemically grown multiple times using the conditions described in Section 2 above by chronoamperometric deposition at a constant potential of 1.2 V for 30 min to obtain a 2.2 mg sample. The analysis was carried out at the Research School of Chemistry, Australian National University in Canberra, Australia.

	Microanalysis	ICP-OES Results			
Element	Found %	Method	Element	Found %	
Ν	1.81	EA 3000	Со	0.23	
С	62.83	EA 3000			
Н	7.47	EA 3000			
S	7.79	Dionex (Sulphur only)			

Assuming that there is one perchlorate counter ion per monomer unit, the calculated analytical data is a reasonable match to the experimental data. Therefore, this was assumed in calculating the likely ratio of 1 Co^{2+} to 30 monomer units (Calc. for $\text{C}_{1410}\text{H}_{1890}\text{Cl}_{30}\text{N}_{30}\text{O}_{210}\text{S}_{60}\text{Co}$: 65.98% C, 7.42% H, 4.14% Cl, 1.64% N, 13.09% O, 7.50% S, 0.23% Co).

6. SEM imaging.

PolyTMC4 and **PolyTMC4-Co²⁺** films for SEM analyses were electrodeposited on ITO with an applied potential of 1.2 V for 10 s. A Jeol 7500 field emission scanning electron microscope (FESEM) was used for SEM analysis.

7. Fourier-transform Raman (FT-Raman) Spectroscopy

FT-Raman spectra were obtained from solid samples utilising a Bruker Equinox-55 FTinterferometer with an FRA106/5 Raman accessory and D418T liquid-nitrogen-cooled Germanium detector. 1064 nm excitation was provided by a ND:YAG laser operating at 120 mW, while the software used was the Bruker OPUS v5.5 package.

8. Computational modelling.

Computational modelling on the model bis(dithiophene)-substituted spiropyran **BDSP** and merocyanine **BDMC** was performed using Gaussian 09 software [4]. Density functional theory (DFT) calculations of the molecular geometries and vibrational modes were accomplished with the B3LYP functional and 6-31G(d) basis. Time-dependent (TD-)DFT calculations were performed using the B3LYP method and 6-31G(d) basis functions. A scale factor of 0.97 [5] was used when generating theoretical spectra using Gaussum v2.2 [6] software. Molecular orbital visualisation was accomplished with Gaussview v5.0.8 [5] and vibrational modes with Molden [7]. The optimised cartesian coordinates for the neutral and radical cation forms of BDMC are given in Table S1 and S2. Bond length alternation diagrams were obtained from density functional theory calculations by uniquely numbering

the bonds (as shown in Fig. 5a) and plotting this versus the bond length (in Å) calculated by Gaussian (Fig. 5b).

8.1 Optimised Cartesian Coordinates

Table S1: Optimised cartesian coordinates for neutral bis(dithiophene)-substituted BDMC

Row	Atom	Х	Y	Z	R	ow	Atom	Х	Y	Z
1	С	5.157195	0.808211	-0.29765		43	Н	5.581047	-1.91922	-1.11068
2	С	5.291507	2.207718	-0.3793		44	С	8.630826	-1.07327	0.077402
3	С	4.187273	3.059242	-0.42801		45	0	8.085753	-3.21501	-0.79591
4	С	2.91738	2.48628	-0.40428		46	С	7.111054	-4.08077	-1.35656
5	С	2.750773	1.097247	-0.32557		47	Н	6.734128	-3.69346	-2.31225
6	С	3.851188	0.263857	-0.26552		48	Н	7.616413	-5.03286	-1.52674
7	Ν	1.656574	3.098223	-0.4431		49	С	-6.48746	0.259055	-0.27126
8	С	0.639002	2.173899	-0.39459		50	С	-6.32418	-1.07299	-0.59487
9	С	1.263355	0.769439	-0.30476		51	S	-8.11711	0.553956	0.302363
10	С	0.887159	0.060045	1.018069		52	С	-7.49294	-1.84741	-0.38508
11	С	0.888778	-0.10158	-1.52735		53	Н	-5.40287	-1.46942	-1.0024
12	0	-2.79534	4.482199	-0.58805		54	С	-8.58254	-1.12982	0.09702
13	С	-3.58246	3.520717	-0.50708		55	0	-7.63114	-3.18372	-0.62628
14	С	-3.15055	2.099725	-0.40786		56	С	-6.5033	-3.88496	-1.12401
15	С	-1.80773	1.716345	-0.37435		57	Н	-6.18745	-3.49473	-2.10057
16	С	-0.68458	2.565538	-0.43037		58	Н	-6.81919	-4.9238	-1.23499
17	С	-5.02661	3.737153	-0.50381		59	Н	-5.65922	-3.83415	-0.42346
18	С	-5.91852	2.715924	-0.42601		60	Н	6.268997	-4.23377	-0.66873
19	С	-5.50196	1.333244	-0.33734		61	С	10.01514	-1.32934	0.384865
20	С	-4.14865	1.077266	-0.32305		62	С	10.94215	-0.45805	0.945202
21	С	1.430787	4.53177	-0.52724		63	S	10.78843	-2.88185	0.077435
22	Н	6.285665	2.642214	-0.42798		64	С	12.2402	-1.02007	1.123713
23	Н	4.335999	4.131973	-0.49546		65	С	12.30035	-2.31902	0.699552
24	Н	3.722926	-0.81083	-0.17023		66	Н	13.08364	-0.48766	1.545288
25	Н	-0.18301	-0.15843	1.068347		67	Н	13.15575	-2.98072	0.719138
26	Н	1.433298	-0.88625	1.099142		68	С	-9.90416	-1.61769	0.399242
27	Н	1.14952	0.678233	1.882032		69	С	-10.994	-0.89916	0.877444
28	Н	1.158989	0.398687	-2.46241		70	S	-10.3659	-3.30649	0.200594
29	Н	1.428984	-1.05392	-1.48304		71	С	-12.1689	-1.68094	1.079696
30	Н	-0.18253	-0.31825	-1.555	· · · · · ·	72	С	-11.9747	-2.99562	0.756004
31	Н	-1.63875	0.644158	-0.29248		73	Н	-13.1083	-1.28651	1.446818
32	Н	-0.91471	3.621029	-0.50723		74	Н	-12.6921	-3.80305	0.812435
33	Н	-5.35202	4.770441	-0.57967		75	0	10.55855	0.810461	1.268581
34	Н	-6.98377	2.9351	-0.45145		76	0	-10.864	0.439654	1.108897
35	Н	-3.80319	0.050487	-0.21762		77	С	11.53252	1.667795	1.844354
36	Н	0.835168	4.876019	0.324766		78	Н	11.90688	1.266031	2.794948
37	Н	2.389031	5.050133	-0.52221		79	Н	12.37623	1.830784	1.16104
38	Н	0.892907	4.783787	-1.44762		80	Н	11.02698	2.617408	2.027556
39	С	6.324281	-0.07253	-0.25304		81	С	-11.9971	1.137326	1.600192
40	С	6.409162	-1.38732	-0.6593		82	Н	-12.8363	1.086917	0.893739
41	S	7.859358	0.478261	0.380484		83	Н	-12.3188	0.744467	2.573868
42	С	7.700354	-1.94657	-0.47498		84	Н	-11.6842	2.176463	1.71568

Row	Atom	Х	Y	Z	Row	Atom	Х	Y	Z
1	С	5.167455	-0.73338	0.155208	43	Н	5.535373	2.097085	0.58795
2	С	5.282788	-2.14372	0.19701	44	С	8.695584	1.049096	0.015604
3	С	4.174947	-2.98303	0.203339	45	0	8.087655	3.300975	0.458705
4	С	2.912767	-2.39102	0.174175	46	С	7.075413	4.262211	0.733593
5	С	2.75774	-0.99903	0.134829	47	Н	6.346951	4.313979	-0.08548
6	С	3.863504	-0.17414	0.120652	48	Н	6.558401	4.034105	1.674208
7	Ν	1.640418	-2.98794	0.172893	49	С	-6.49907	-0.25444	-0.01333
8	С	0.647628	-2.06724	0.133754	50	С	-6.28715	1.128972	-0.04321
9	С	1.273127	-0.66511	0.10361	51	S	-8.22513	-0.61196	-0.0328
10	С	0.914435	0.088618	-1.20039	52	С	-7.46917	1.871145	-0.08064
11	С	0.879477	0.158396	1.354331	53	Н	-5.30282	1.576524	-0.03729
12	0	-2.77859	-4.40307	0.147757	54	С	-8.65257	1.088668	-0.08125
13	С	-3.57989	-3.45666	0.111218	55	0	-7.59446	3.21236	-0.11491
14	С	-3.16361	-2.02675	0.079573	56	С	-6.40538	4.00317	-0.11535
15	С	-1.80007	-1.62438	0.087302	57	Н	-5.7942	3.78515	-0.9989
16	С	-0.69718	-2.46396	0.125796	58	Н	-5.82226	3.828336	0.796307
17	С	-5.02133	-3.70002	0.096315	59	Н	-6.73895	5.04031	-0.14552
18	С	-5.92929	-2.69397	0.057119	60	Н	7.589091	5.219803	0.82453
19	С	-5.52903	-1.30487	0.027405	61	С	10.10581	1.255697	-0.12134
20	С	-4.15192	-1.03149	0.039818	62	С	11.08402	0.294415	-0.38689
21	С	1.415713	-4.43293	0.208672	63	S	10.8665	2.837772	0.034591
22	Н	6.268896	-2.59507	0.24157	64	С	12.40563	0.816234	-0.46127
23	Н	4.313691	-4.05819	0.238627	65	С	12.43185	2.169307	-0.25404
24	Н	3.741038	0.902997	0.064729	66	Н	13.28928	0.22267	-0.65748
25	Н	-0.15384	0.314719	-1.25576	67	Н	13.29921	2.815993	-0.25534
26	Н	1.465132	1.034081	-1.23845	68	С	-9.98971	1.556423	-0.11494
27	Н	1.186714	-0.49764	-2.0831	69	С	-11.1626	0.775749	-0.11506
28	Н	1.130537	-0.37679	2.274995	70	S	-10.4257	3.266577	-0.16497
29	Н	1.426749	1.106707	1.353582	71	С	-12.3607	1.534309	-0.15397
30	Н	-0.19039	0.383083	1.370183	72	С	-12.1087	2.881669	-0.18338
31	Н	-1.64242	-0.54844	0.059293	73	Н	-13.3566	1.110858	-0.16006
32	Н	-0.91877	-3.52352	0.152217	74	Н	-12.8382	3.680383	-0.21544
33	Н	-5.32636	-4.74136	0.118767	75	0	10.71429	-1.00006	-0.54605
34	Н	-6.98833	-2.93839	0.047946	76	0	-11.0527	-0.5655	-0.07994
35	Н	-3.81934	0.003436	0.017371	77	С	11.73638	-1.95909	-0.80908
36	Н	0.84317	-4.7036	1.099988	78	Н	12.25703	-1.73196	-1.74691
37	Н	0.862689	-4.75069	-0.67936	79	Н	12.45863	-2.00023	0.014834
38	Н	2.375917	-4.94429	0.232526	80	Н	11.22839	-2.91998	-0.89766
39	С	6.340696	0.121895	0.148744	81	С	-12.2526	-1.34579	-0.07986
40	С	6.40213	1.490235	0.360067	82	Н	-12.8608	-1.12141	0.803238
41	S	7.942487	-0.52566	-0.15318	83	Н	-12.8324	-1.16532	-0.99167
42	С	7.711739	2.008565	0.287835	84	Н	-11.9281	-2.38571	-0.04925

Table S2: Optimised cartesian coordinates for radical cation bis(dithiophene)-substituted **BDMC**



Figure S1. Cyclic voltammograms of $8 \cdot 10^{-3}$ M **TSP4** between 0 V and 0.8 V, inset current of peak (I) versus square root of scan rate.



Figure S2. TD-DFT calculated electronic absorption bands comparing the neutral (green) and oxidised (blue) **BDMC** forms.



Figure S3. Absorbance spectra of $2 \cdot 10^{-5}$ M **TSP4** (black line), **TMC4** (red line) and **TMC4** with Co²⁺ (1:1) (blue line). The inset shows an expansion of the 330 – 630 nm range for the three spectra.



Figure S4 SEM images of **polyTMC4** (a) and **polyTMC4-Co²⁺** on ITO glass after a constant potential deposition at 1.2 V for 10 s.



Figure S5. Spectroelectrochemistry of **polyTMC4-Co²⁺** electrodeposited on ITO glass for potential ranges of -0.5 V (red line) – 0.9 V.



Figure S6. Calculated Raman spectra of **BDSP** (top) and **BDMC** (2nd from top) compared to experimental FT-Raman spectra of **polyTMC4** (bottom) and **polyTMC4-Co²⁺** (2nd from bottom) in their oxidised forms.



Figure S7. Calculated Raman spectra of the **BDSP** (top) and **BDMC** (2^{nd} from top) compared to experimental FT-Raman spectra of **polyTMC4** (bottom) and **polyTMC4-Co²⁺** (2^{nd} from bottom) in their reduced forms.

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