

Synthesis and characterization of $[MCl_2(PAr_3)_2]$ -ethylenedioxythiophene copolymers (M = Pd, Pt), made by electropolymerisation of diphenyl(2,2',3,3'-tetrahydro-[5,5'-bithieno[3,4-*b*][1,4]dioxin]-7-yl)phosphane (Ph_2P [bis-EDOT]) complexes

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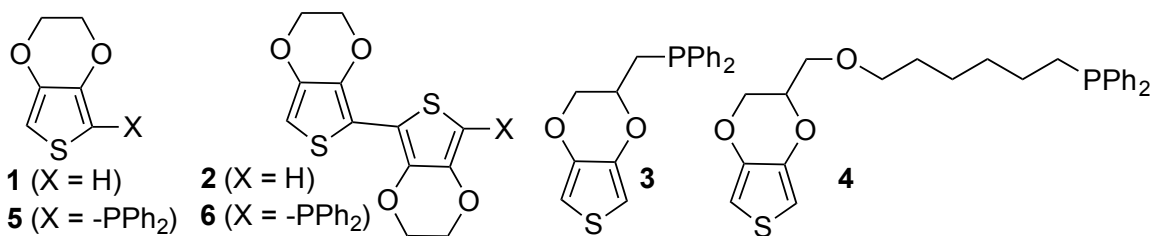
ABSTRACT

Phosphine ligands bearing 2,2',3,3'-tetrahydro-[5,5'-bithieno[3,4-*b*][1,4]dioxin]-7-yl (Bis-EDOT) groups [Ph_2P (Bis-EDOT), **6**] have been prepared, together with their complexes $[MCl_2(\mathbf{6})_2]$ [M= Pd (**7**) and Pt (**8**)]. The electrochemical co-polymerization of the complexes with EDOT was investigated, with a view to making conducting polymers incorporating covalently-bound metal-phosphine complexes. Polymer-coated electrodes were obtained in all experiments, and X-Ray fluorescence spectroscopy (XFS) and Energy Dispersive X-ray Spectroscopy (EDS) measurements established that polymers made in the presence of $[MCl_2(\mathbf{6})_2]$ were genuine co-polymers containing both EDOT units and Pd(II) or Pt(II) complexes.

1. Introduction

A well-known strategy to facilitate the electrosynthesis of conjugated polymers is to use chemically-synthesised oligomers which, being more conjugated, have a substantially lower oxidation potential than the corresponding monomer. For example, whereas 2,3-dihydrothieno[3,4-*b*][1,4]dioxine (more often known as 3,4-ethylenedioxythiophene, EDOT; **1**) is oxidised to poly-3,4-ethylenedioxythiophene (PEDOT) at $\geq +1.0$ V vs. Ag/Ag^+ in acetonitrile electrolyte, the dimer 2,2',3,3'-tetrahydro-5,5'-bithieno[3,4-*b*][1,4]dioxine (bis-EDOT; **2**) is oxidized at $\geq +0.4$ V vs. Ag/Ag^+ (and the corresponding trimer at $\geq +0.1$ V).[1] A similar strategy can be used for making copolymers of EDOT incorporating other conjugated units.[2, 3] We were interested in synthesizing hybrid

redox-active materials as potential catalysts, by incorporating covalently-bound metal-phosphine complexes into electrochemically-prepared PEDOT materials, and we found that whereas PEDOTs incorporating Pd(II) or Pt(II) complexes of ligands **3** and **4** could be made by electrochemical co-polymerisation of the complexes with EDOT, attempts to make related materials using complexes of monomer **5**, $[MCl_2(\mathbf{5})_2]$ ($M = Pd, Pt$) were unsuccessful.[4] Although polymer films were formed in electropolymerisation experiments involving mixtures of EDOT monomer and complexes of **5**, X-Ray photoelectron spectroscopy (XPS) showed that these did not contain either Cl or metal, although they did contain low levels of P. Furthermore, other workers had earlier similarly failed to electropolymerise tungsten cluster complexes of ligand **5**.[5]



The complex *trans*- $[PdCl_2(5-Ph_2P-2,2':5',2''\text{-terthiophene})_2]$ (*i.e.* in which the Ph_2P -groups occupy a terminal α -position of the terthiophenes) has previously been successfully electropolymerised.[6] Although the resulting polymer was not extensively characterised, its voltammogram suggests behaviour consistent with a structure in which $Ph_2P-(T)_6-PPh_2$ ($T = 2,5\text{-thienyl}$) units alternate with $[PdCl_2(L)_2]$ sites in the polymer. Such materials might be of interest because the reversible electroactivity of the oligothiophene unit could tune the donor/acceptor properties of the phosphine units and hence the reactivity of the complex. We reasoned that a similar ‘oligomers as monomers’ strategy might work with our EDOT-phosphines. Accordingly, we have prepared diphenyl(2,2',3,3'-tetrahydro-[5,5'-bithieno[3,4-*b*][1,4]dioxin]-7-yl)phosphane **6**, and its complexes $[MCl_2(\mathbf{6})_2]$ ($M = Pd$ (**7**) and Pt (**8**)). We have electrochemically co-polymerised these with EDOT to make co-polymer films which, as shown by X-Ray fluorescence spectroscopy (XRF) and Energy Dispersive X-ray Spectroscopy (EDS), contain Cl, P and metal, supporting their identification as genuine hybrid PEDOT-metal phosphine complex copolymer materials. These are further characterized by AC impedance spectroscopy and electrochemical methods.

2. Results and discussion

2.1 Syntheses

Bis-EDOT **2** was prepared in 48 % yield by lithiation of EDOT **1** and oxidative coupling with Cu(II) by a literature method,[1, 7] and lithiation of **2** and quenching with ClPPh₂ gave phosphine **6** in 83 % yield, again by a modification of a literature method.[5] Characterising data were in agreement with the literature values.

Treatment of **6** with [PdCl₂(CH₃CN)₂] in CH₂Cl₂ gave square planer [PdCl₂(**6**)₂], **7**, as pale yellow crystals in 68 % yield. The complex was characterized by elemental analysis, mass spectroscopy, and ¹H, ¹³C and ³¹P NMR spectroscopy. Accurate mass spectroscopy gave an experimental value of 1073.9635, compared to the theoretical value of 1073.9667 (M–HCl), and microanalytical data confirmed the bulk integrity of the sample. The ¹H NMR spectrum of **7** showed a single peak at 6.29 p.p.m. due to the terminal thienyl protons; unlike the Pd(II) and Pt(II) complexes of ligand **5** studied previously,[4] there was no resolved second-order coupling to ³¹P to assist in metal centre isomer identification. The ³¹P{¹H} NMR spectrum of **7** showed an intense singlet peak at 10.37 and a lower-intensity peak at 18.44 p.p.m. which suggests the presence of a mixture of *trans*- and *cis*-isomers. In view of the identification of the corresponding Pt(II) complex **8** (below) as exclusively the *trans* isomer, we tentatively suggest that the major isomer of **7** (δ = 10.37 p.p.m.) is also *trans*. Attempts to grow single crystals were unsuccessful, and the mixture of isomers was used in the electrochemical polymerization experiments (below).

Reaction of **6** with [PtCl₂(PhCN)₂] gave *trans*-[PtCl₂(**6**)₂], **8**, in 77 % yield after recrystallization. It was characterized by ¹H, ¹³C and ³¹P{¹H} NMR spectroscopy, elemental analysis, and mass spectroscopy. In particular, the ³¹P{¹H} NMR spectrum showed a single peak at 7.64 p.p.m. with ¹⁹⁵Pt satellite peaks (¹J_{PtP} 2669 Hz; Figure S1 in the supplementary information), characteristic of *trans* geometry. The [M–Cl]⁺ accurate mass peak was observed at 1161.0194 (calculated value 1161.0239).

2.2 Electrosynthesis and characterization of polymers incorporating **7** and **8**

For reasons that are extensively discussed in our earlier paper,[4] the metal centres in complexes **7** and **8** were not expected to be electroactive within the potential ‘window’ of the 0.1 M Bu₄NBF₄ / CH₃CN electrolyte employed in our electrochemical studies.[4] Initially, we attempted to electropolymerise complexes **7** and **8** alone, by cycling between -1.0 V and +2.0 V in 0.1 M Bu₄NBF₄ / CH₃CN electrolyte. In the case of **8**, cycling a 5 mM solution resulted in an oxidative wave at *ca.* +1.41 V vs Pt/PPy QRE, but no film formation was observed on the surface of the glassy carbon working electrode, and repetitive scans showed no increase in peak currents. A similar result was obtained for **7**.

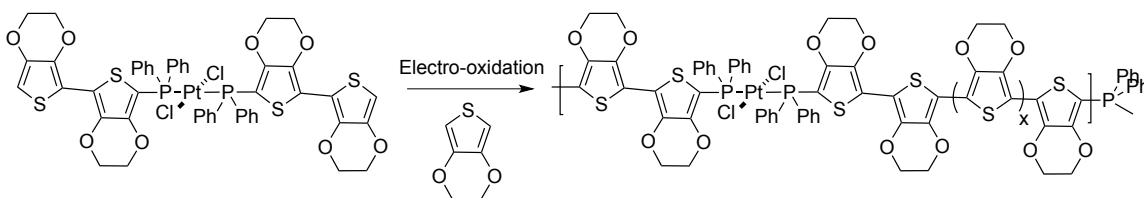


Figure 1. Synthesis of a copolymer of **8** with EDOT.

We therefore resorted to copolymerization with EDOT **1** (1:5 complex:1 mole ratio, 0.01 M total monomer concentration), again cycling between -1.0 V and +2.0 V vs. Pt/PPy. This method was successful for both **7** and **8** (Figure 1) and blue copolymers were electrodeposited on the working electrode. Figure 2 shows the first 6 cycles of the 10 used to electrodeposit films of the copolymer of EDOT with, respectively, **7** and **8**. In the first scan with **7**, there are two anodic peaks at +1.43 and +1.78 V and the peak currents increase proportionally with the scan number, as expected for an electroactive material deposited on an electrode surface. Interestingly, the form of the CV is similar to those of previous successful electro-copolymerisations of [PdCl₂(L)₂] employing ligands **3** or **4**.[4]

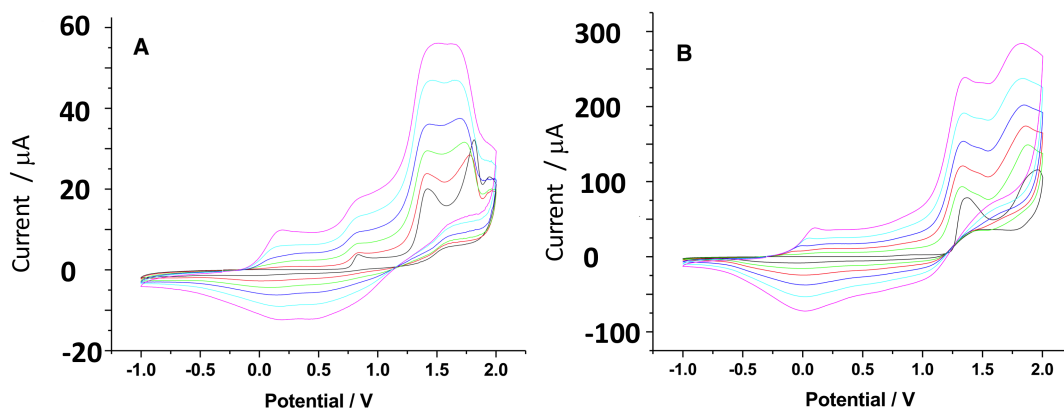


Figure 2. (A) Repetitive scan cyclic voltammetry experiment to grow copolymer **3**. Scan rate 100 mV s^{-1} , $0.1 \text{ M Bu}_4\text{NBF}_4/\text{CH}_3\text{CN}$ electrolyte; 0.01 M total monomer concentration, GC working electrode, Pt/PPy QRE, Pt gauze counter electrode. (B) Repetitive scan cyclic voltammetry experiment to grow copolymer **4**; same conditions as (A) except using monomer **4**.

With the Pt(II) complex **8**, on the first scan two anodic peaks at $+1.39 \text{ V}$ and $+1.87 \text{ V}$ were observed, together with the characteristic nucleation loop on reversing the scan direction, and successive scans displayed steadily increasing peak currents.

Once formed, the polymer-modified electrodes were removed from the growth solution, washed well with monomer-free supporting electrolyte, then electrochemically cycled in monomer-free electrolyte. The voltammograms of the copolymers of **1** and **7** and of **1** with **8** are shown in Figure 3.

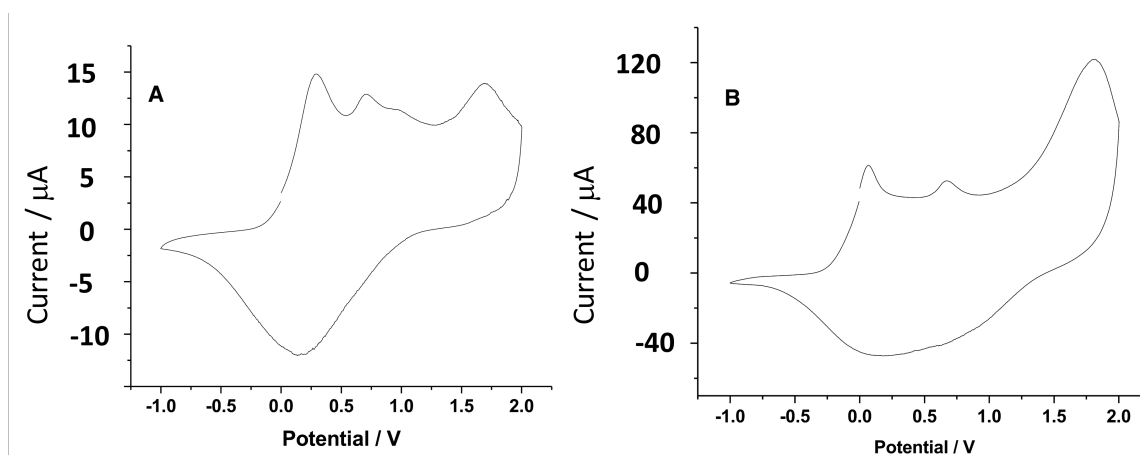


Figure 3. (A) Cyclic voltammogram of an EDOT:**7** copolymer in background electrolyte. Scan rate 100 mV s^{-1} , $0.1 \text{ M Bu}_4\text{NBF}_4/\text{CH}_3\text{CN}$, GC working electrode, Pt/PPy QRE and Pt gauze counter electrode. (B) Cyclic voltammogram of an EDOT:**8** copolymer, same conditions.

The copolymer voltammogram is notably different from that of PEDOT itself in the same electrolyte.[4] The peak potential of the first anodic wave is shifted from -0.05 V in PEDOT to +0.27 V in the cyclic voltammogram of the copolymer with **7**. This suggests that the copolymer has shorter mean conjugation lengths than PEDOT itself.[4] This is supported by the electrochemical impedance results (q.v.). For the copolymer of **1** and **8** (Figure 3(B)), the shift in the peak potential of the first anodic wave is smaller, from -0.05 V in PEDOT to +0.06 V in the copolymer, suggesting that copolymer **7** has a shorter mean conjugation than copolymer **8**.⁸

2.3 Electrochemical impedance spectroscopy of EDOT copolymers with 7 and 8.

Electrochemical impedance spectra (EIS) were acquired on copolymer films of **1** with **7** and with **8** on glassy carbon in 0.1 M Bu₄NBF₄/ CH₃CN at selected DC bias potentials, each with a 10 mV AC potential in the frequency range between 0.1 Hz and 10 MHz, in the single sine wave AC mode with 10 seconds equilibration time.⁸

The Nyquist plot of the copolymer with **7**, at 0, +0.1, and +0.4 V is given in Figure 4. This clearly shows the ideal behavior of an electronically-conducting polymer film according to the dual rail transmission line circuit proposed for the analysis of impedance behavior of conjugated polymers,[8, 9] with the distinctive high frequency semicircle and low frequency vertical line. However, the deviation of the Warburg-like region from the ideal 45° angle is probably an indication of non-uniform copolymer morphology. Decreasing the applied potential (from +0.8 to 0 V) had a complicated effect on the width of the semicircle. However it shows that the electronic resistance, R_e first increases, before showing more complicated behavior at more negative potentials. Electronic resistance is clearly also increasing drastically, as the copolymer becomes non-conducting.

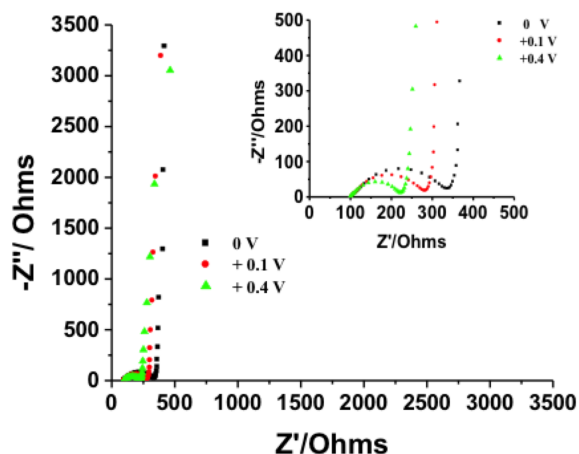


Figure 4: Nyquist plot of copolymer of **1** with **7** at positive DC potentials; inset shows expansion of the semicircle region.

The electronic, solvent and charge transfer capacitance of the copolymer **7** were determined as a function of applied potential (values in supplementary information Table S1). The ionic resistance R_i does not significantly change from +0.8 V to +0.1 V but then increases from *ca.* 90 Ω to 2700 Ω as the potential decreases from -0.1 V to -0.4 V. It is clear that the EIS data of copolymer **7** is completely different from that of PEDOT itself.[4] lending support to the proposal that the copolymer is considerably less conjugated than PEDOT itself.

Similarly, the Nyquist plot of the **1:8** copolymer at selected positive potentials is shown in Figure 5. The EIS data for copolymer **8** at positive potentials also fits the modified dual rail model.[8-10] Interestingly the electronic resistance of the copolymer with **8** did not change significantly until the most negative potentials, changing only from 514 Ω at -0.1 V to 1254 Ω at -0.3 V.

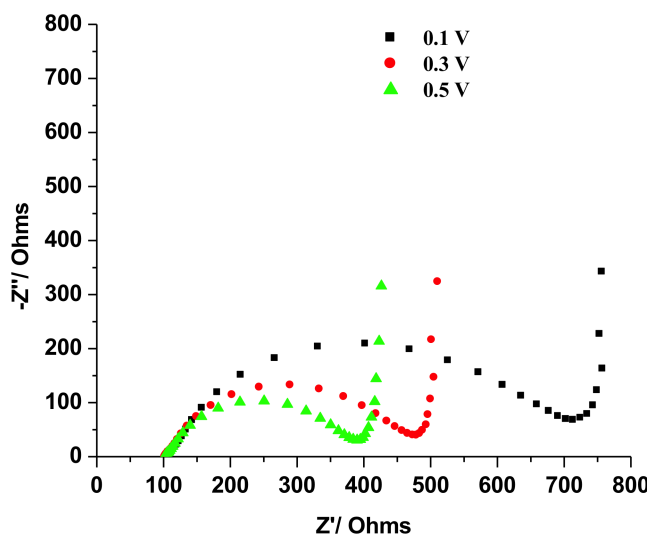


Figure 5. EIS data of the copolymer of **1** with **8** at positive DC potentials

The ionic resistance R_I , electronic resistance R_e , and the charge transfer capacitance C_e determined in 0.1 V steps from +0.8 V to 0 V are shown in the supplementary information (Table S2). For this copolymer, the fitted ionic resistance increases from 450 Ω to 725 Ω as the potential changes from +0.8 V from +0.1 V, and then increases further, up to 1366 Ω as the potential is stepped further negative. This phenomenon is consistent with the loss of anions predominating as the copolymer switches from cationic to the neutral state. Once again, the behavior is very different from that of the homopolymer PEDOT,[4] consistent with the idea that this is a less-conjugated co-polymer containing EDOT and **8**.

2.4 EDS and XRF characterization of copolymers

Owing to the fact that these $[MCl_2(PAr_3)_2]$ complexes do not show any electroactivity in this potential range, recourse was had to non-electrochemical characterization methods, in particular X-Ray fluorescence spectroscopy (XRF) and Energy Dispersive X-ray Spectroscopy (EDS), to obtain further support for the presence of the intact complexes in the copolymers.

Polymer modified electrodes for X-Ray characterisation were prepared using gold-coated glass plates as working electrodes.[4] The EDS spectrum of copolymer **7** (supplementary

information; Figure S2) showed a peak corresponding to $P_{K\alpha}$ at 1.99 keV and one due to Cl_L at 0.23 eV, although peaks expected for Pd were weak. However, the XRF spectrum of copolymer **7** showed peaks for Pd $K\alpha$, P $K\alpha$, and S $K\alpha$ at 21.15, 2.06 and 2.26 keV respectively (see supplementary information, Figure S3) and these values are in excellent agreement with the theoretical values[11] and confirm the presence of Pd and P in the copolymer matrix. This data confirms the presence of Pd, P and Cl in the polymer matrix and lends strong support to the notion that a copolymer of EDOT with **7** has been prepared.

The EDS spectrum of the copolymer (supplementary information Figure S4) of **8** showed three peaks due respectively to Pt M_r , Pt M_z and Pt M_a at 2.26, 1.60 and 2.06 keV respectively and one due to Pt L_I at 8.06 keV. Peaks due to S K_a , and S K_b were also observed at 2.26 and 2.46 keV respectively. The XRF spectrum of copolymer **8** showed peaks due respectively to Pt $K\alpha$, P $K\alpha$, and S $K\alpha$ at 9.38, 1.97 and 2.23 keV respectively (supplementary information Figure S5).[12] These values are also in excellent agreement with the theoretical values[11] and confirm the presence of Pt and P in the polymer matrix. These XRF data also support the argument that the phosphine complex **8** with bis-EDOT units is incorporated intact into the copolymer.

3. Conclusions

Although earlier attempts to make conjugated polymers incorporating covalently-bound metal-phosphine complexes using ligand **2** all failed,[4] perhaps owing to the high reactivity of the electrogenerated EDOT-based **2** radical cation, extending the degree of conjugation by employing the bis-EDOT-based ligand **6** was successful as a strategy to incorporate complexes $[MCl_2(\mathbf{6})_2]$ ($M = Pd, Pt$) into PEDOT-based crosslinked copolymers. The copolymers showed redox activity and electrochemical impedance properties consistent with a lower degree of conjugation than the corresponding PEDOT homopolymer, and the presence of the relevant elements (P, Cl, and Pd or Pt) was established using energy-dispersive X-Ray and X-Ray fluorescence spectroscopies. Future studies will be aimed at widening the coordination chemistry of this type of ligand

to more redox-active metals (e.g. Ru, Os) and examining the possibility of using these materials for catalysis.

4. Experimental

4.1 General remarks

All reactions that are air or moisture sensitive were performed in degassed and/or dry solvents in oven-dried glassware. Solvents were degassed by bubbling with nitrogen for at least 15 minutes. All reagents were used as purchased (AR grade) unless otherwise stated. Diethyl ether and THF were freshly distilled from sodium/benzophenone ketyl radical under an anhydrous nitrogen atmosphere immediately prior to use. Dichloromethane was freshly distilled from calcium hydride under an anhydrous nitrogen atmosphere. Acetonitrile was electrochemical grade, purchased from Sigma Aldrich. Triphenylphosphine was recrystallised from CH₂Cl₂/hexanes. The precursors [PdCl₂(MeCN)₂][13] and [PtCl₂(PhCN)₂][14] were prepared by literature methods.

Thin layer chromatography was performed on Merck silica gel 60 F-254 plates, compounds were visualized under UV where possible. UV-inactive compounds were stained using iodine or aqueous KMnO₄ solution. Flash column chromatography was carried out using Aldrich technical grade silica gel; an air line or bellows were used to apply pressure.

NMR spectra were recorded on a Bruker AMX 400 or Bruker DPX 400 (¹H, 400 MHz; ¹³C{¹H}, 100 MHz, ³¹P{¹H} 161.9 MHz). Mass spectra were recorded on a Fisons Trio-1000 spectrometer using electron or chemical ionization. IR spectra were acquired neat on a Bruker FTIR in the range 4000-600 cm⁻¹.

4.2 2,2-bi((2,3-dihydrothieno[3,4-b][1,4]dioxin), **2**. [1, 7] A solution of n-BuLi 1.34 M in hexane (5.37 cm³, 1.01 eq) was added to a solution of EDOT (0.995 g, 7.0 mmol) in anhydrous THF (10 cm³) at -78 °C. After 2 h, anhydrous CuCl₂ (0.941 g, 7.0 mmol) was added in one portion. Then the brown solution was allowed to warm to room temperature and it was stirred for 12 hours. To the mixture was added 10 cm³ of distilled water. The

product was extracted with CH_2Cl_2 ($2 \times 50 \text{ cm}^3$) and dried over MgSO_4 and concentrated. The green crude product was purified by column chromatography (1:1 hexane: CH_2Cl_2) to yield white solid. Yield: 0.951 g, 48 %. Calc. for $\text{C}_{12}\text{H}_{10}\text{O}_4\text{S}_2$: C, 51.06; H, 3.57 %. Found C, 51.01; H, 3.49 %. MS (ES+), m/z: calc. for $(\text{C}_{12}\text{H}_{11}\text{O}_4\text{S}_2)^+$: 283.00988. Found, 283.00978. ^1H NMR (400 MHz): δ 6.27 (s, 2H, thienyl H), 4.22 - 4.34 (m, 8H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100.6 MHz) : δ 141.63, 137.43, 100.00, 99.94, 65.41, 65.01. IR: 2944, 1465, 1170, 1056 cm^{-1} .

4.3 Diphenyl(2,2',3,3'-tetrahydro-[5,5'-bithieno[3,4-b][1,4]dioxin]-7-yl)phosphane, **6**. [5]

To a solution of **2** (1.169 g, 4.1 mmol) in anhydrous THF (10 cm^3) at $-78 \text{ }^\circ\text{C}$ was added $n\text{BuLi}$ 1.50 M in hexane (2.80 cm^3 , 4.2 mmol) dropwise over 20 minutes. The reaction mixture was stirred for two hours, whereupon ClPPh_2 (0.9249 g, 4.2 mmol) was added dropwise. The mixture was stirred at $-78 \text{ }^\circ\text{C}$ for 2 hours, then allowed to reach room temperature. Degassed distilled water (10 cm^3) was added and the mixture was extracted with degassed CH_2Cl_2 and dried over MgSO_4 . It was filtered under N_2 and the solvent was removed under reduced pressure to yield the product as a brown waxy oil. Yield 1.59 g, 83 %. The crude sample contained *ca.* 5% $\text{Ph}_2\text{PP}(\text{O})\text{PPh}_2$ identified by its characteristic ^{31}P NMR spectrum ($\delta = 37.2, -21.2, \text{d}, J_{\text{PP}} = 217 \text{ Hz}$ [15]) but was used without further purification; a small sample was recrystallized from hot Pr^iOH . Calc. for $\text{C}_{24}\text{H}_{19}\text{O}_4\text{S}_2\text{P}$: C, 61.80; H, 4.08 %. Found: C, 61.45; H, 4.40 %. MS (ES+), m/z: calc. for $(\text{C}_{24}\text{H}_{20}\text{O}_4\text{S}_2\text{P})^+$: 467.0541. Found: 467.0566. ^1H NMR: δ 7.31 - 7.46 (m, 10H), 6.28 (s, 1H, thienyl H), 4.15 - 4.35 (m, 8H, $-\text{OCH}_2\text{CH}_2\text{O}-$). $^{13}\text{C}\{^1\text{H}\}$ NMR: δ 146.75, 141.60, 137.25, 133.76, 131.20, 129.11, 107.98, 98.79, 65.38, 65.31, 65.22, 64.93. $^{31}\text{P}\{^1\text{H}\}$ NMR: δ - 28.51.

4.4 $[\text{PdCl}_2(\mathbf{6})_2]$, **7**: To a 100 cm^3 round bottom flask fitted with a magnetic stirrer bar and a reflux condenser was added degassed CH_2Cl_2 (20 cm^3) and $[\text{PdCl}_2(\text{CH}_3\text{CN})_2]$ (0.206 g, 0.8 mmol). The solution was warmed to reflux and a solution of **6** (0.744 g, 1.59 mmol) in degassed CH_2Cl_2 (30 cm^3) was added dropwise. The reaction mixture was stirred for 1 hour, after which time the solution was allowed to cool to room temperature and solvent was removed under reduced pressure. The resulting oil was washed with diethyl ether (10

cm³), whereupon it crystallized. The yellow crystals were filtered off and washed with Et₂O. Yield: 0.607 g, 68 %. Calc. for C₄₈H₃₈O₈S₄P₂PdCl₂: C, 51.92; H, 3.45 %. Found: C, 52.02; H, 3.47 %. MS (ES+, MeOH:CH₃CN 1:2, 35 V) m/z: calcd. for [C₄₈H₃₈³⁷ClO₈P₂¹⁰⁵PdS₂]⁺: 1073.9667. Found: 1073.9635. Mp 151 °C (decomp). IR: 3052, 2925, 1060, 1432 cm⁻¹. ¹H NMR: δ 7.19 - 7.79 (m, 20H), 6.29 (s, 2H, thienyl H), 4.15 - 4.37 (m, 16H). ¹³C{¹H}NMR: δ 141.64, 140.98, 135.15, 132.40, 130.86, 128.26, 97.93, 65.41, 65.11, 65.01, 64.93. ³¹P{¹H}NMR: δ 18.63, 10.37, (s, approx. 1:1 ratio).

4.5 trans-[PtCl₂(**6**)₂], **8**: A solution of [PtCl₂(PhCN)₂] (0.406 g, 0.87 mmol) in degassed CH₂Cl₂ (20 cm³) was warmed to reflux and a solution of **6** (0.801 g, 1.71 mmol) in hot degassed CH₂Cl₂ (30 cm³) was added dropwise. The reaction mixture was stirred for 4 hours, after which time the solution was allowed to cool to room temperature. The resulting oil was washed with diethyl ether (10 cm³), whereupon the oil crystallized. The off-yellow crystals were filtered off and washed with Et₂O. Yield: 0.801 g, 77 %. The sample was found to contain *ca.* 7 % of an impurity, δ(³¹P) +28.50, which we tentatively assign to phosphine oxide; the calculated analytical figures are weighted to take this into account. Calc. for C₄₈H₃₈O₈P₂S₄PtCl₂·7% C₂₄H₁₉O₅PS₂: C, 49.14; H, 3.26 %. Found C, 49.06; H, 3.13 %. MS (ES+, MeOH, 35 V) m/z: calcd for [C₄₈H₃₈³⁵ClO₈P₂¹⁹⁴PtS₄]⁺: 1161.0239. Found: 1161.0194. mp: 118 °C (decomp). IR: 3056, 2925, 1062, 1463 cm⁻¹. ¹H NMR: δ 7.35–7.89 (m, 20H), 6.29 (s, 2H, thienyl H), 4.12–4.35 (m, 16H, -OCH₂CH₂O-). ¹³C{¹H}NMR: δ 132.55, 142.23, 141.35, 133.82, 129.85, 128.66, 100.06, 99.92, 65.40, 65.07, 64.97, 64.58. ³¹P{¹H} NMR: δ 7.64 (¹J_{PtP} 2663 Hz).

4.6 Electrochemical measurements

For all electrochemistry experiments, the electrolyte used was tetrabutylammonium tetrafluoroborate (Bu₄NBF₄). This was recrystallised and dried under high vacuum for several hours prior to use. The solvent was CH₃CN (99.97 % electrochemistry grade). Solvent and the electrolyte were handled under Schlenk conditions. A three-electrode electrochemical cell having separate compartments for the working (Pt or glassy carbon, 0.1 mm), auxiliary (Pt gauze), and a quasi-reference (poly pyrrole-coated Pt wire) electrode[16] were employed for the cyclic voltammetry analysis. The potentiostat used

was an Autolab PGSTAT-12 operated by GPES software (EcoChimie, Netherlands). Potentials are quoted with respect to the Pt/PPy QRE, which has the potential +0.225 V vs saturated calomel electrode in this electrolyte.

4.7 Electrochemical copolymerization of metal complexes 7 and 8 with EDOT

Repetitive scan cyclic voltammetry at 100 mV s^{-1} was used to grow the polymer films, using a solution of the complex together with EDOT itself (1:4 mole ratio; 0.01 M total monomer) in 0.1 M $\text{Bu}_4\text{NBF}_4 / \text{CH}_3\text{CN}$. After film growth, the electrode was held at 0 V for ten minutes, then removed from the organic electrolyte, washed with CH_3CN , dried and transferred to fresh 0.1 M $\text{Bu}_4\text{NBF}_4 / \text{CH}_3\text{CN}$. Cyclic voltammetry and AC impedance characterization of the polymer films was then undertaken in the absence of monomers.

4.8 Electrochemical Impedance Spectroscopy (EIS)

The EIS data were recorded at selected DC bias potentials, each of which was superimposed with a 10 mV AC potential in the frequency range between 10 MHz to 0.1 Hz in the single sine wave mode in the 0.1 M $\text{Bu}_4\text{NBF}_4 / \text{CH}_3\text{CN}$ solution.

4.9 X-Ray fluorescence spectroscopy

For the XRF experiments, the polymer samples were electrodeposited on $1.0 \text{ cm} \times 0.5 \text{ cm}$ FTO (fluorine doped tin oxide) coated glass slides.¹⁹⁻²¹ A crocodile clip was attached to one corner of the slide to act as an electrical contact. The FTO slides were sonicated with acetone and dried in a N_2 gas stream prior to polymer electrodeposition. Subsequent to electrodeposition, the polymer-modified FTO plates were washed thoroughly with the electrolyte and their XRF spectra were acquired using a Fisherscope X-Ray XAn Spectrometer (Fischer Scientific) at an anodic current of 900 A and maximum voltage of 50 kV using a Ni primary filter.

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