Synthesis and characterization of monomeric and polymeric Pd(II) and Pt(II) complexes of 3,4-ethylenedioxythiophene-functionalized phosphine ligands†

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Phosphine ligands bearing 3,4-ethylenedioxythiophene (EDOT) groups, in which a Ph_2P group is either connected directly to the thiophene ring [Ph_2P(5–EDOT), **1**] or to the EDOT ethylene bridge *via* a methylene (**4**) or longer (**7**) 'spacer', have been prepared, together with their complexes *cis*-[$MCl_2(L)_2$] (M = Pd and Pt). The electrochemical co-polymerization of the complexes with EDOT was investigated, with a view to making conducting polymers incorporating covalently-bound metal–phosphine complexes. Although polymer-coated electrodes were obtained in all experiments, XPS measurements established that polymers made in the presence of *cis*-[MCl_2(**1**)$_2$] consisted only of poly(3,4-ethylenedioxythiophene) (PEDOT), whereas polymers made in the presence of *cis*-[$MCl_2(L)_2$] (L = **4**, **7**) were genuine co-polymers containing Pd(II) or Pt(II) complexes.

Introduction

Interest in polymer-supported catalysts and reagents has revived in recent years, stimulated by the growth of research into combinatorial and automated organic synthesis.[1–4] At the same time, there has been continuing activity in the study of conjugated polymers containing covalently-bound metal complexes.[5–11] The latter have usually been redox-active (*e.g.* 2,2′-bipyridine derivatives or azamacrocycle complexes), because the applications aimed at in such work have included sensing, electrocatalysis and electrochromism, all of which would require that the metal complex has reversible redox activity. Depending upon the application aimed at, the metal complex can either be directly coordinated to the conjugated chain (for instance, by the use of 2,2′-bipyridine or bithiazole monomer units),[8,10,11] or it can be attached as a pendant group *via* a 'spacer'.[5,6,10]

We were intrigued by the possibility of incorporating catalytically-active metal–phosphine complexes into conducting polymer supports, with the long-term goal of building new (electro)catalytic systems. Some time ago, we described a polypyrrole incorporating a pendant redox-active Ru(II)–diphosphine complex,[12] and other workers prepared polypyrroles bearing pendant diphosphine ligands and their Pd(II) complexes, which are not reversibly redox-active.[13] Later, the latter materials were tested in polymer-supported catalysis.[14] More recently, complexes of oligothiophenes bearing $-PPh_2$ groups in terminal (α) or internal (β) positions have been examined.[15–21] It has been found that oligothiophenes are interesting substituents for phosphines in several respects. In principle, oligothiophene–(metal phosphine complex) dimers, copolymers or metallocycles could be made directly from $Ph_2P–(T)_n–PPh_2$ (T = thiophene; n = 1,2,3) using simple metal complexation reactions,[19,22] while the electrochemical polymerization of complexes containing ligands $Ph_2P–(T)_n$ could also result in dimeric, polymeric or network materials in which the metal centres are connected by dimers, $Ph_2P–(T)_{2n}–PPh_2$.[15,23] Secondly, oligothiophenes themselves can participate in the coordination shell of the metal centre in an unusual and interesting manner. For example, Wolf and co-workers found that, depending upon the mole ratios used, 3′-(Ph_2P)-2,2′:5′,2″-terthiophene reacted with $PdCl_2$ to give either a conventional *trans*-[$PdCl_2$(phosphine)$_2$], or a chloro-bridged palladium dimer in which each Pd unit was coordinated to a phosphine donor and a neighboring cyclometallated thiophene ring β-position.[15] Moreover, when the *trans*-[$PdCl_2$(phosphine)$_2$] was treated with two equiv. of $AgBF_4$, this also induced cyclometallation of one ligand, while the second ligand coordinated in hemilabile fashion *via* the phosphine and a neighboring thiophene S atom. Interestingly, all of the Pd(II) complexes of this ligand, in which the oligothiophene units have both terminal α-positions free, could be electrochemically polymerized to give polymer films. The redox activity of these was consistent with polyterthiophenes containing intact metal complexes.[15]

The complex *trans*-[$PdCl_2$(5-Ph_2P-2,2′:5′,2″-terthiophene)$_2$] (*i.e.* in which the Ph_2P– groups occupy a terminal α-position of the terthiophenes) has also been electropolymerized.[15] Although little data on the polymer was reported in the latter case, examination of the voltammogram suggests behaviour consistent with a structure in which $Ph_2P(T)_6–PPh_2$ units alternate with Pd(II) sites in the polymer. However, other attempts to polymerize similar complexes with oligothiophenes terminally substituted with phosphines have been notably less successful. For instance, a series of octahedral phosphine–capped clusters [$W_6S_8\{R_2P–(T)_n\}_6$] (R = Ph, Et; n = 1, 2, 3) has been prepared. Attempts to

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electropolymerize these complexes failed to yield any redox-active polymer films.[24]

Poly(3,4–ethylenedioxythiophene) (PEDOT) is a particularly stable polythiophene derivative.[25,26] The electron rich EDOT unit greatly lowers the redox potential of both monomer and polymer compared with thiophenes. For the (co)polymerization of metal complexes with pendant thiophene units, the main advantage is that the likelihood of oxidative degradation of the complex is lessened.[27] Secondly, the blocking of potentially reactive thiophene β-positions in EDOT prevents the formation of conjugation-limiting α,β′ links in the polymer during electrodeposition, and avoids complications due to cyclometallation *etc*. Thirdly, PEDOT is extremely chemically robust. For example, it has even been used as a catalyst support material in the aggressive environment of the direct methanol fuel cell anode.[28] We were interested in the possibility of using phosphine-substituted 3,4-ethylenedioxythiophenes to achieve the goal of preparing robust conducting materials incorporating covalently-attached metal–phosphine complexes. This could afford a route to electropolymerized, catalytically-active polymer films for organic synthesis in automated systems. While complexes of many different ligands bearing pendant EDOTs (*e.g.* pyridines, 2,2′-bipyridyl derivatives, tetraazamacrocycles) have been made and successfully electropolymerized,[27,29] there are only two reports of EDOT-containing phosphines. Ligands Ph_2P(5–EDOT) and (R_2P)(5-biEDOT) (R = Ph, Et) were prepared by Perruchas *et al*, and used in their unsuccessful attempts to polymerize [W_6S_8(phosphine)$_6$],[24] and ligands $Ph_{3-n}P$(5–EDOT)$_n$ were prepared by Chahma *et al*, along with their complexes [$Mo(CO)_4(L)_2$].[30] Attempts to electropolymerize the free ligands and their Mo(0) complexes were all unsuccessful.

In this paper, we describe the syntheses of two new phosphine ligands bearing pendant EDOT groups in which both EDOT α-positions are free for polymerization, with little chance that any part of the EDOT unit will participate in coordination to the metal. We describe their complexes [$MCl_2(L)_2$] (M = Pd, Pt), and the successful electrochemical copolymerization of these complexes with EDOT. For comparison, we have also prepared related complexes with Ph_2P(5-EDOT), and we describe attempts to copolymerize these complexes with EDOT.

Experimental section

Syntheses and structures of ligands and complexes

General methods and instrumentation used were as recently described in other papers from this laboratory.[31] Reagents and solvents were reagent grade from Aldrich Chemical Company, unless otherwise specified. Reactions involving free phosphines were routinely carried out using Schlenk techniques under Ar. 2-(Chloromethyl)-2,3-dihydrothieno[3,4-*b*][1,4]dioxine (EDOTCH$_2$Cl, **3**) was prepared by a literature route.[32] 2-[(6-Bromohexyloxy)methyl]-2,3-dihydrothieno[3,4-*b*][1,4]dioxine (EDOTCH$_2$O(CH$_2$)$_6$Br, **6**) was prepared as described previously for the bromopentyl analog;[33] full details are in the ESI.†

Polymer preparation and characterization

For all electrochemistry experiments, the electrolyte was Bu_4NBF_4. This was recrystallised and dried under high vacuum for several hours prior to use. The solvent was CH_3CN (99.97% electrochemistry grade). Solvent and electrolyte were handled under Schlenk conditions. A three-electrode electrochemical cell having separate compartments for the working (Pt or glassy carbon, 0.1 mm diameter except for XPS samples; see below), auxiliary (Pt gauze), and quasi-reference (polypyrrole-coated Pt wire)[34] electrodes was employed. The potentiostat was an Autolab PG-30, running GPES software (EcoChimie, Netherlands). For electrochemical impedance spectra, polymers were deposited on glassy carbon working electrodes. Potentials are quoted with respect to the Pt/PPy QRE, which was +0.225 V *vs.* standard calomel electrode with this electrolyte.

X-Ray photoelectron spectroscopy

For XPS experiments, polymer samples were electrodeposited upon 1.1 × 1.1 cm gold on Cr-primed glass slides. A gold wire was attached to one corner of the slide to act as a contact. The gold slides were annealed in a butane flame prior to polymer electrodeposition. Spectra were acquired using a Scienta ESCA 300 spectrometer (NCESS, Daresbury Laboratory, UK) at 90° take-off angle. The spectra were referenced to the main C–H 1s peak at 285.0 eV. In all cases, a survey scan (0–1300 eV) was run, followed by high-resolution scans at characteristic peak positions for the metal, Cl and P. In one case, data for S and O were also obtained at high resolution, but time limitations prevented this being done for all samples.

Syntheses

(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)diphenylphosphine, Ph_2P(5–EDOT), 1. To a solution of 3,4-ethylenedioxythiophene (0.682 g, 4.8 mmol) in anhydrous THF (10 cm^3) was added lithium diisopropylamide (0.524 g, 4.9 mmol) dropwise over a period of 1 h at 0 °C. The reaction mixture was stirred for 2 h. The mixture was then cooled to −78 °C and chlorodiphenylphosphine (1.10 g, 5.0 mmol) was added dropwise. The mixture was stirred for 2 h and gradually brought to room temperature. Degassed distilled water (10 cm^3) was added and the product was extracted with degassed CH_2Cl_2. The organic layer was dried over $MgSO_4$, filtered, and the solvent was removed under reduced pressure to yield an off-white solid. This was pure enough to be used for complex formation. Yield 1.23 g, 78%. Anal. Calcd for $C_{18}H_{15}O_2PS$: C, 66.25; H, 4.63%. Found: C, 67.01; H, 4.96%. MS (CI+, NH_3): *m*/*z* calcd for $(M + H)^+$: 327.06086. Found: 327.06008. ^1H NMR (400 MHz, $CDCl_3$): δ 4.19 (m, 4H, –OCH_2CH_2O–), 7.31–7.46 (m, 10H, Ph), 6.57 (d, 1H, J_{PH} 0.9 Hz, thienyl H). $^{13}C\{^1H\}$ NMR (100 MHz): δ 65.07, 65.33, 99.90, 106.59, 128.61, 129.23, 132.13, 137.10, 142.17, 146.93. $^{31}P\{^1H\}$ NMR (162 MHz): δ −28.0.

***trans*-[$PdCl_2(1)_2$], 2a.** 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 [$PdCl_2(CH_3CN)_2$] (0.492 g, 1.9 mmol). The solution was brought to reflux and **1** (1.226 g, 3.8 mmol) in hot degassed CH_2Cl_2 (30 cm^3) was added dropwise. The reaction mixture was left stirring for 1 h, after which time the solution was allowed to cool to room temperature and the solvent was removed *in vacuo*. The resulting oil was washed with diethyl ether (10 cm^3), whereupon it crystallized. The yellow crystals were filtered off and washed with Et_2O. Yield 1.16 g, 74.2%. Anal. Calcd for $C_{36}H_{30}Cl_2O_4P_2PdS_2$: C, 52.09; H, 3.64%. Found: C, 52.29; H, 3.84%. MS (ES+, MeOH, 30 V) m/z: 795 [M–Cl]$^+$. IR: 3056, 2937, 1058, 1475 cm^{-1}. ^{1}H NMR (400 MHz): δ 4.20 (m, 8H, –OCH_2CH_2O–), 6.69 (t, 2H, $|J_{PH} + J_{P'H}|$ 3.8 Hz, thienyl H), 7.36 (m, 16H, Ph), 7.81 (m, 4H, Ph). ^{13}C{^{1}H} NMR (162 MHz): δ 63.0, 63.5, 101.4, 106.5, 126.9, 128.2, 132.6, 135.0, 140.8, 145.0. ^{31}P{^{1}H} NMR (162 MHz): δ 11.62.

***trans*-[PtCl$_2$(1)$_2$], 2b.** A solution of [$PtCl_2(PhCN)_2$] (0.8456 g, 1.79 mmol) in degassed CH_2Cl_2 (20 cm^3) was refluxed for 15 min. A solution of **1** (1.173 g, 3.6 mmol) in hot degassed CH_2Cl_2 (30 cm^3) was added dropwise. The reaction mixture was stirred for 4 h, then the solution was allowed to cool to room temperature, and the solvent was removed in *vacuo*. The resulting oil was washed with diethyl ether (10 cm^3), whereupon the oil crystallized. The greenish yellow crystals were filtered off and washed with diethyl ether. Yield 1.176 g, 71.2%. Anal. Calcd for $C_{36}H_{30}Cl_2O_4P_2PtS_2$: C, 47.07; H, 3.29%. Found: C, 46.69; H, 3.42%. MS (ES+, MeOH, 0.5% HCOOH, 40 V) m/z: 883 [M–Cl]$^+$. IR: 3073, 2940, 1062, 1467 cm^{-1}. ^{1}H NMR (400 MHz): δ 4.23 (m, 8H, –OCH_2CH_2O–), 6.67 (t, 2H, $|J_{PH} + J_{P'H}|$ 4.2 Hz, thienyl H), 7.40 (m, 16H, Ph), 7.83 (m, 4H, Ph). ^{13}C NMR (400 MHz): δ 63.0, 63.5, 101.4, 106.5, 126.6, 128.3, 129.3, 133.4, 140.9, 145.8. ^{31}P{^{1}H} NMR (162 MHz): δ 9.79 ($^1J_{PtP}$ 2670 Hz).

[(2,3-dihydrothieno[3,4-*b*][1,4]dioxin-2-yl)methyl]diphenylphosphine, EDOTCH$_2$PPh$_2$, 4. To a solution of **3** (0.40 g, 2.1 mmol) in anhydrous THF (20 cm^3) at −30 °C was added $LiPPh_2$ (0.422 g, 2.2 mmol) in THF (10 cm^3) dropwise over a period of 30 min. The reaction was stirred for 2 h and allowed to warm to room temperature. Degassed distilled water (10 cm^3) was added, the solution was extracted with CH_2Cl_2 and the organic layer was dried over $MgSO_4$, filtered, and evaporated to dryness yielding a yellow air sensitive oil, 0.584 g, 82%. Anal. Calcd for $C_{19}H_{17}O_2PS$: C, 67.25; H, 5.05%. Found: C, 67.04; H, 5.03%. MS (CI+, NH_3) m/z: calcd for [M + H]$^+$: 341.07691. Found: 341.07626. ^{1}H NMR (400MHz): δ 2.32, 2.56 (m's, –CH_2P), 3.70 (m, –$CHCH_2P$), 3.96, 4.20 (m's, –OCH_2CH), 6.29 (m, thienyl H), 7.35, 7.45 (m's, Ph), 7.70 (m, Ph). ^{13}C{^{1}H} NMR (162 MHz): δ 32.75, 65.98, 69.27, 100.06, 106.59, 129.10, 130.94, 132.44, 133.00, 140.90, 141.50. ^{31}P{^{1}H} NMR (162 MHz): δ −22.58.

[PdCl$_2$(4)$_2$], 5a. This was prepared as for **2a** using [$PdCl_2(CH_3CN)_2$] (0.22 g, 0.85 mmol) and **4** (0.58 g, 1.70 mmol) in CH_2Cl_2 (30 cm^3). Workup was as for **2a**. The resulting oil was washed with diethyl ether (10 cm^3), whereupon it crystallized. The yellow crystals were filtered off and with washed with Et_2O. Yield 0.516 g, 70.8%. Anal. Calcd for $C_{38}H_{34}Cl_2O_4P_2PdS_2$: C, 53.19; H, 3.99%. Found: C, 52.80; H, 3.93%. MS (ES+, MeOH, 35V) m/z: calcd for $C_{38}H_{34}{}^{35}ClO_4P_2{}^{105}PdS_2{}^+$: 820.0113. Found: 820.0152. IR: 2902, 1058, 1479 cm^{-1}. ^{1}H NMR (400 MHz): δ 2.67, 2.96 (m's, –CH_2P), 3.92, 4.11, 4.67 (m's –$CHCH_2P$ and –OCH_2CH), 5.91, 6.25 (m, thienyl H), 7.35, 7.45, 7.72 (m, Ph). ^{13}C{^{1}H} NMR (101 MHz): δ 53.8, 68.8, 70.9, 128.6, 131.2, 133.6, 134.99, 99.99, 100.5, 141.0, 141.6. ^{31}P{^{1}H} δ 15.4, 18.3 (s, 3:1 ratio).

[PtCl$_2$(4)$_2$], 5b. This was prepared as for **2b** from [$PtCl_2(PhCN)_2$] (0.495 g, 1.05 mmol) and **7** (0.714 g, 2.10 mmol) in refluxing CH_2Cl_2 (50 cm^3). After 4 h the reaction was worked up as for **2b**. The resulting oil was washed with diethyl ether (10 cm^3), whereupon it crystallized. The greenish yellow crystals were filtered off and washed with Et_2O. Yield 0.736 g, 74.1%. Anal. Calcd for $C_{38}H_{34}Cl_2O_4P_2PtS_2\cdot 0.5CH_2Cl_2$: C, 46.75; H, 3.57%. Found: C, 46.69; H, 3.42%. MS (ES+, MeOH:CH_2Cl_2 2:1, 0.1% HCOOH, 35 V) m/z: calcd for $C_{38}H_{34}{}^{35}ClO_4P_2{}^{195}PtS_2{}^+$: 910.0752. Found: 911.0744. IR: 3060, 1430, 1097 cm^{-1}. ^{1}H NMR (400 MHz): δ 2.30, 3.10 (complex m), 3.90, 4.25 (complex m), 5.10 (m), 5.98, 6.29 (m's, thienyl H), 6.95, 7.20, 7.45, 7.50, 7.65, 7.80 (m's, Ph). ^{13}C{^{1}H} NMR (101 MHz): δ 53.85, 65.05, 65.39, 99.29, 129.101, 130.94, 132.44, 133.00, 135.17, 138.30, 142.0. ^{31}P{^{1}H} NMR (162 MHz): δ 9.13 ($^1J_{PtP}$ 3664 Hz), 10.76 ($^1J_{PtP}$ 3669 Hz).

{6-[(2,3-Dihydrothieno[3,4-*b*][1,4]dioxin-2-yl)methoxy]hexyl}-diphenylphosphine, 7. To a solution of **6** (1.05 g, 3.1 mmol) in anhydrous THF (20 cm^3) at −30 °C was added $LiPPh_2$ (0.61 g, 3.2mmol) in THF (10 cm^3) dropwise over a period of 30 min. The reaction was stirred for 2 h and gradually warmed to room temperature. Degassed distilled water (10 cm^3) was added and the product was extracted with CH_2Cl_2. The organic layer was dried over $MgSO_4$, filtered, and the solvent was removed *in vacuo* to yield yellow, air sensitive oil. This was used without further purification. Yield 1.286 g, 91.4%. Anal. Calcd for $C_{25}H_{29}O_3PS$: C, 68.16; H, 6.64 %. Found: C, 69.16; H, 6.33 %. MS (ES+, MeOH/10 % HCOOH) m/z: calcd for [M + H]$^+$: 441.1653. Found: 441.1661. ^{1}H NMR (400 MHz): δ 1.36 (m, 2H), 1.46 (m, 4H), 1.57 (m, 2H, *J* 7.1 Hz), 2.07 (t, 2H, PCH_2), 3.48 (t, 2H, –$OCH_2(CH_2)_5Br$), 3.59 (m, 2H, –CH(O-thienyl)CH_2OCH_2–, J_{AB} 10.4, J_{HH} 5.0), 4.06, 4.25 (m's, 2H, –$OCH_2CH(R)O$–, J_{AB} 11.6 Hz), 4.18–4.25 (m, 1H, –OCH_2-CH(R)O–), 6.34 (s, thienyl H), 7.25–7.6, 7.7–7.8 (m's, 10H, Ph). ^{13}C{^{1}H} NMR (101 MHz): δ 26.01, 26.10, 29.67, 29.76, 32.16, 66.61, 69.91, 72.20, 73.03, 99.94, 100.06, 128.74, 129.38, 132.10, 133.187, 142.00. ^{31}P{^{1}H} NMR (162 MHz): δ −14.98.

[PdCl$_2$(7)$_2$], 8a. This was prepared as for **2b** using [$PdCl_2(CH_3CN)_2$] (0.464 g, 1.8 mmol) and **7** (1.58 g, 3.6 mmol) in hot CH_2Cl_2 (50 cm^3). The reaction mixture was stirred for 1 h, and worked up as for **2b**. The yellow crystals were filtered off and washed with Et_2O. Yield 1.254 g, 65.9 %. Anal. Calcd for $C_{50}H_{58}O_6S_2P_2PdCl_2$: C, 56.74; H, 5.52 %. Found: C, 56.49; H, 5.35 %. MS (ES+, MeOH, 45 V) m/z: calcd for $C_{50}H_{58}O_6P_2S_2{}^{35}Cl^{106}Pd^+$: 1021.1873. Found: 1021.1881. ^{1}H NMR (400 MHz): δ 1.30, 1.38 (m's, 8H total) 1.48 (m, 4H), 1.65 (br m, 4H), 2.45 (br m, 4H, –PCH_2), 3.42 (t, 4H, –$OCH_2(CH_2)_5P$), 3.55, 3.63 (m's, 4H, –CH(O-thienyl)CH_2OCH_2–, J_{AB} 10.4, J_{HH} 5.0), 4.01, 4.20 (m's, 4H, –$OCH_2CH(R)O$–, J_{AB} 11.6 Hz), 4.25 m, 2H, –$OCH_2CH(R)O$–), 6.31 (s, thienyl H), 7.26–7.42 (m's, 20H). ^{31}P{^{1}H} NMR (162 MHz): δ 17.60.

***cis*-[PtCl$_2$(7)$_2$], 8b.** This was prepared as for **2b** using [$PtCl_2(PhCN)_2$] (0.5664 g, 1.20 mmol) and **7** (1.056 g, 2.4 mmol) in hot CH_2Cl_2 (50 cm^3). The reaction mixture was stirred for 4 h, and worked up as for **2b**. The off-white crystals were filtered off and washed with Et_2O. Yield 1.26 g, 91.6 %. Anal. Calcd for $C_{50}H_{58}Cl_2O_6P_2PtS_2$: C, 52.35; H, 5.10 %. Found: C, 51.72; H, 5.15 %. MS (ES+, 1:1 MeOH:CH_3CN, 0.1 % HCOOH) m/z: calc for $C_{50}H_{58}{}^{35}ClO_6P_2{}^{194}PtS_2{}^+$: 1109.2465. Found 1109.2458. ^{1}H NMR (400 MHz): δ 1.22, 1.46, 1.55 (m′s, 16 H), 2.25, 2.45 (br m′s, 4H, –PCH_2), 3.41 [t, 4H, –$OCH_2(CH_2)_5P$], 3.55, 3.62 (m′s, 4H, –CH(O-thienyl)CH_2OCH_2–, J_{AB} 10.4, J_{HH} 5.0), 4.02, 4.21 (m′s, 4H, –OCH_2CH(R)O–, J_{AB} 11.6 Hz), 4.18–4.29 [m, 2H, –OCH_2CH(R)O–], 6.31 (s, thienyl H), 7.24–7.46 (m′s, 20H). ^{13}C{^{1}H} NMR (101 MHz): δ 22.90, 23.07, 25.45, 25.79, 29.67, 32.01, 66.59, 69.51, 72.19, 73.03, 99.92, 100.06, 128.66, 129.85, 132.55, 133.82, 141.67, 142.00. ^{31}P{^{1}H} NMR (162 MHz): δ 8.67 ($^1J_{PtP}$ 3657 Hz).

Electrochemical (co)polymerization

Repetitive scan cyclic voltammetry at 100 mV s^{-1} was used to grow the polymer films, using a solution of EDOT (0.01 M) or of the complex together with EDOT itself (1:5 mole ratio; 0.01 M total monomer) in 0.1 M Bu_4NBF_4–CH_3CN. Ten cycles between −0.1 and +2.0 V were used to grow all polymer films. 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 Bu_4NBF_4–CH_3CN. Cyclic voltammetry and EIS characterization of the polymer films was then undertaken in the absence of monomers.

Electrochemical impedance spectroscopy

EIS spectra were collected in background electrolyte 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 s equilibration time.

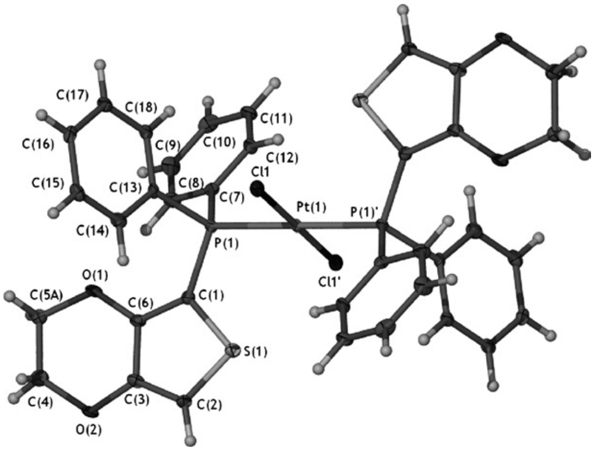

Fig. 1 Thermal ellipsoid plot (50% probability ellipsoids) of the molecular structure of complex **2b**. There are two independent half molecules in the asymmetric unit, and in each case the Pt atom lies on an inversion centre. One of these two molecules is shown. The inversion related P1′ and Cl1′ atoms are labelled in this figure. Significant bond distances and angles are as follows. Pt(1)–P(1) 2.3126(15), Pt(1)–Cl(1) 2.354(2), P(1)–C(1) 1.787(6), P(1)–C(13) 1.810(6), P(1)–C(7) 1.832(6) Å; P(1)–Pt(1)–P(1′) 180.0°, P(1)–Pt(1)–Cl(1) 92.32(5), P(1)–Pt(1)–Cl(1′) 87.68(5), Cl(1)–Pt(1)–Cl(1) 180.0°.

Results and discussion

Synthesis and characterization of EDOT-functionalized ligands and complexes

To test the possibility of using phosphine-substituted 3,4-ethylenedioxythiophenes to achieve the goal of preparing robust polythiophene materials incorporating covalently-attached metal–phosphine complexes, the most straightforward route is to use terminally-substituted EDOT-phosphines since these are easily prepared. EDOT is readily deprotonated using LiN^iPr_2 in THF, and reaction of LiEDOT with Ph_2PCl gave Ph_2P(5–EDOT), **1**. Reaction of 2 equiv. of this with $[PdCl_2(CH_3CN)_2]$ or $[PtCl_2(PhCN)_2]$ in CH_2Cl_2 gave square planar [$PdCl_2$(**1**)$_2$] (**2a**) and [$PtCl_2$(**1**)$_2$] (**2b**) respectively. For **2b**, the geometry is clearly *trans* as $^1J_{PtP}$ is 2670 Hz. Moreover, the thienyl H resonance is a triplet owing to long-range coupling in a second-order AA′XX′ system to both P atoms ($|J_{PH} + J_{P'H}| = 4.2$ Hz), whereas the corresponding resonance in the free ligand is a doublet ($J_{PH} =$ 0.9 Hz). This is diagnostic of *trans* geometry.[35] Complex **2a** also has a triplet thienyl H resonance ($|J_{PH} + J_{P'H}| = 3.8$ Hz) suggesting that this, too, is *trans*. X-Ray crystal structure determinations confirm these assignments. Fig. 1 shows the molecular structure of complex **2b**.‡Note that there are two slightly different independent molecules in the unit cell; bond lengths and angles for only one of these is given in the caption. Although somewhat long, the metal–ligand bond lengths lie within the usual range for complexes of the type *trans*-[$PtCl_2(PAr_3)_2$] (checked *via* the Cambridge Crystallographic Database),[36] especially where the aryl groups are bulky. For example, in *trans*-[$PtCl_2(PPh_3)_2$], Pt–P is 2.3163(11) Å and Pt–Cl is 2.2997(11) Å,[37] while in *trans*-[$PtCl_2(P\{2\text{-}^iPrC_6H_4\}_3)_2$], Pt–P is 2.3436(11) Å and Pt–Cl is 2.3039(10) Å.[38] A dataset was also obtained for **2a** (deposited with CCDC; reference 699407).† However, the data were very weak and the diffraction peaks broad owing to small crystal size and low crystal quality. Due to the problematic data, anisotropic refinement resulted in physically implausible ellipsoids for the C and O atoms and a low data to parameter ratio. Therefore these atoms were refined isotropically (resulting in a higher than normal final R-factor *ca.* 11 %). Nevertheless, the coordination geometry at the Pd atoms is unequivocally established as being *trans*, with two half molecules of **2a** (and a chloroform of solvation) in the asymmetric unit, and with the Pd atoms lying on inversion centres.

Attempts to electropolymerize these complexes intact, either alone or as copolymers with unsubstituted EDOT, all failed as judged by a combination of cyclic voltammetry, EIS and XPS characterization of the resulting polymers (*q.v.*). We therefore decided to prepare phosphine ligands bearing pendant EDOT

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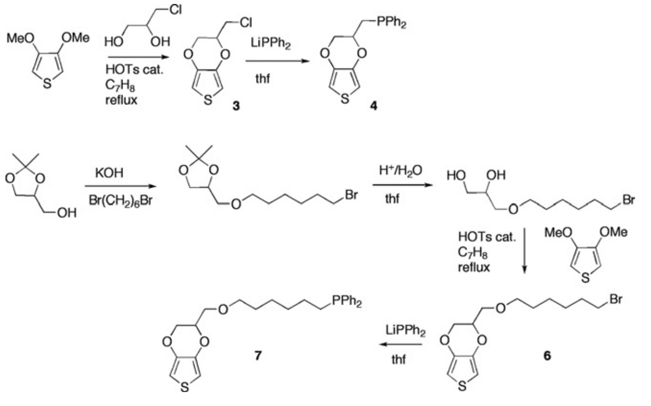
‡ *Crystal data for* **2b**, $C_{36}H_{30}Cl_2O_4P_2PtS_2\cdot C_4H_{10}O$, M_r 992.77, triclinic, $P\bar{1}$ a = 11.379(2), b = 12.109(2), c = 15.524(3) Å, α = 72.370(4)°, β = 89.055(5)°, γ = 66.038(5)°, V = 1848.9(6) Å^3, T = 100 K, Z = 2, 100003 measured reflections, 4981 independent reflections, R_1 ($I > 2\sigma(I)$) 0.0623, wR_2 (all data) 0.0955, CCDC 699408. *Crystal data for* **5a**, $C_{38}H_{34}Cl_2O_4P_2PdS_2$, M_r 858.01 triclinic, $P\bar{1}$ a = 9.244(5), b = 10.182(5), c = 10.679(6) Å, α = 107.001(8)°, β = 96.758(9)°, γ = 106.538(8)°, V = 899.0(8) Å^3, T = 100 K, Z = 1, 3759 measured reflections, 3054 independent reflections, R_1 ($I > 2\sigma(I)$) 0.0417, wR_2 (all data) 0.1035, CCDC 701459.



Scheme 1 Syntheses of ligands **4** and **7**.

groups, in which both of the EDOT α-positions are free for oxidative polymerizations (Scheme 1).

Using literature methods,[32] 3,4-dimethoxythiophene was prepared from 3,4-dibromothiophene, and an acid-catalyzed ether exchange reaction of this with (racemic) 3-chloropropane-1,2-diol gave 2-(chloromethyl)-2,3-dihydrothieno[3,4-*b*][1,4]dioxine (EDOTCH$_2$Cl; **3**). Reaction of **3** with LiPPh$_2$ in THF gave EDOTCH$_2$PPh$_2$, **4** as an air-sensitive oil. Spectroscopic and analytical data indicated that it was sufficiently pure to use as prepared. Reaction of **4** with [PdCl$_2$(CH$_3$CN)$_2$] or [PtCl$_2$(PhCN)$_2$] in CH$_2$Cl$_2$ gave sparingly soluble complexes, **5a** (M = Pd) and **5b** (M = Pt) respectively. Microanalytical and mass spectrometry data were consistent with the expected formulae, [MCl$_2$(**4**)$_2$]. The proton NMR spectra of **5a** and **5b** show complex and quite broad alkyl EDOT unit resonances. Interestingly, while the thienyl proton resonances for **4** are at closely similar chemical shifts with a very small HH coupling, both **5a** and **5b** show two distinct sets of thienyl H resonances, both of which are complex multiplets. The $^{31}P\{^1H\}$ NMR spectrum of **5b** shows two sharp resonances of near–identical intensity, at 9.13 and 10.76 p.p.m., with $^1J_{PtP}$ satellites at almost identical separations, 3664 and 3669 Hz respectively, consistent with *cis* geometry. Since ligand **4** is a mixture of enantiomers, the most likely explanation for the complexity of the ^1H and ^{31}P NMR spectra is that the resulting two diastereomeric complexes comprising **5b** give distinct sets of ^1H and $^{31}P\{^1H\}$ resonances. To add to the complexity, two much less intense resonances, at 12.0 and 13.2 p.p.m., were seen in the $^{31}P\{^1H\}$ spectrum of **5b**. The signal to noise ratio was insufficient to allow $^1J_{PtP}$ to be determined for these minor resonances, but it is possible that they are due to the two diasteromeric *trans* isomers. The $^{31}P\{^1H\}$ NMR spectrum of **5a** showed two singlets of equal intensity at 15.38 and 15.44 p.p.m., and a minor peak at 18.29 p.p.m. Repeated attempts at recrystallization of **5a** eventually yielded crystals suitable for X-Ray analysis, and these proved to be of the *trans* isomer. The molecular structure is illustrated in Fig. 2.‡

Bond lengths and angles are typical of other examples of *trans*-[PdCl$_2$(Ar$_2$PR)$_2$].[36] Preparative-scale recrystallization, to separate either the *cis* and *trans* isomers, or the diastereomers, was unsuccessful for **5a** and **5b**. We therefore decided to attempt the electrochemical polymerization of these complexes as isomer mixtures.

Steric crowding is well known to inhibit electropolymerization for thiophenes in which a bulky substituent is close to the monomer unit, whereas with a longer 'spacer' between the bulky substituent and the thiophene ring, electropolymerization proceeds satisfactorily.[39] Accordingly, we synthesized ligand **7** to complement **4** (Scheme 1). Reaction of glycerine acetone ketal with excess 1,6-dibromohexane, followed by hydrolysis, gave the required functionalized diol, and acid-catalyzed ether exchange with 3,4-dimethoxythiophene gave **6**[33] (for details see the ESI)† which was then treated with LiPPh$_2$ in THF to give **7** as a viscous, air-sensitive oil. Reaction of **7** with [PdCl$_2$(CH$_3$CN)$_2$] or [PtCl$_2$(PhCN)$_2$] in CH$_2$Cl$_2$ gave complexes, **8a** (M = Pd) and **8b** (M = Pt) respectively. Microanalytical and mass spectrometry data were consistent with the expected formulae, [MCl$_2$(**7**)$_2$]. Complexes **8a** and **8b** show singlets in their $^{31}P\{^1H\}$ spectra, with $^1J_{PtP}$ (3657 Hz) consistent with *cis* geometry for **8b**, in spite of the fact that these are also diasteromeric mixtures (the asymmetric centres are far from the coordination sphere).

Electrochemical synthesis of poly(3,4-ethylenedioxythiophene)s copolymers with EDOT-phosphine complexes

When contemplating the electrochemical polymerization of EDOT-containing phosphine complexes, it is necessary to consider the possible redox activity of the metal centre as well as that of the EDOT unit(s). There have been several studies of the irreversible redox behavior of *cis*- and *trans*-[PtCl$_2$(PR$_3$)$_2$], although most of the attention has focussed on reduction to Pt(0).[40–46] Similarly, because of the importance of [Pd(PR$_3$)$_2$] and related species as intermediates in Pd-catalyzed coupling cycles,

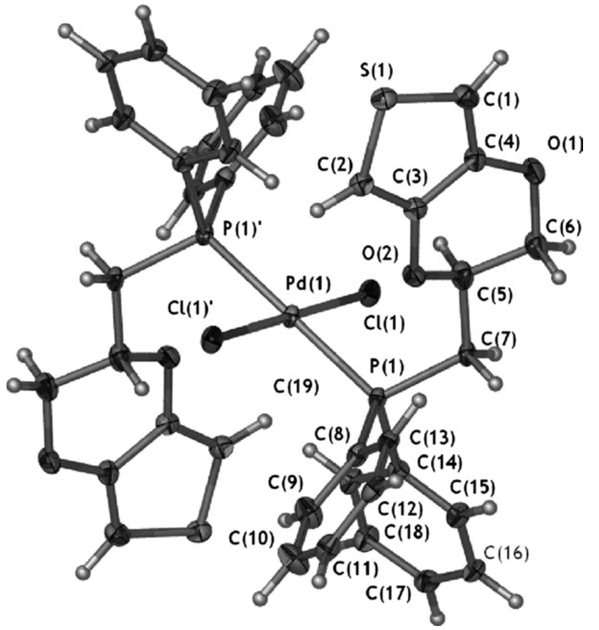


Fig. 2 Thermal ellipsoid plot (50% probability ellipsoids) of molecule of **5a**. The Pd atom lies on an inversion centre, resulting in *trans*-stereochemistry and the inversion related P1′ and Cl1′ atoms are labelled in this figure. Significant bond distances and angles are as follows. Pd(1)–P(1) 2.3027(15), Pd(1)–Cl(1) 2.2791(16), P(1)–C(7) 1.848(4), P(1)–C(8) 1.822(4), P(1)–C(14) 1.821(3) Å; P(1)–Pd(1)–P(1a) 180.0°, P(1)–Pd(1)–Cl(1) 86.45(3)°, P(1)–Pd(1)–Cl(1a) 93.55(3)°, Cl(1)–Pd(1)–Cl(1a) 180.0°.

there has been intensive electrochemical study of Pd(0)/Pd(II) interconversion involving phosphine ligands.[47–50] In contrast, however, few studies have appeared on M(II)/M(IV) couples. In early work, the oxidative behavior of *cis*-[$PtCl_2(PPh_{3-n}R_n)_2$] (R = Me; n = 0–3 and R = Et, n = 3) was reported.[46] The complex *cis*-[$PtCl_2(PPh_3)_2$] showed a small irreversible anodic wave at E_P = +1.78 V, and a much larger irreversible anodic wave at E_P = +2.23 V. These were assigned to the oxidation of, respectively, the *trans*- and *cis*-isomers; it was assumed that the former originated from the latter by isomerisation. Later, a detailed electrochemical study of the oxidation of *cis*- and *trans*-[$PtCl_2(PEt_2)_3$] was published.[40] Both isomers showed very similar voltammetric waves (Pt working electrode, 0.08 M Bu_4NClO_4–CH_3CN), with a small anodic peak near +1.7 V and a larger anodic peak near +2.1 V. On reversing the scan a small cathodic peak was seen at *ca.* +0.8 V. Upon cooling to −10 °C both the small anodic wave at +1.7 V and the cathodic wave at +0.8 V disappeared; the origin of these waves is still unclear, since the irreversible reduction of *cis*-[$PtCl_4(PEt_3)_2$] (studied independently) occurred at *ca.* 0.0 V. Attempts to carry out bulk electrolyses at +2.1 V were hampered by very low current flow, indicating that the electrooxidation was probably a CE or EC process with a slow chemical step. Coulometry could not be performed, and $^{31}P\{^1H\}$ NMR spectroscopic characterization of the products of such electrolyses (incomplete even after several hours) revealed mainly unreacted [$PtCl_2(PEt_3)_2$], with some [$PtCl_4(PEt_3)_2$], and oxidised phosphine.

In view of these results, we anticipated that because our Pt(II) complexes involve less electron-donating ligands of type Ph_2PAr or Ph_2PR, at potentials negative of +2 V (the positive limit in our electropolymerizations), the redox activity of the metal centers during repetitive scan cyclic voltammetry would be limited. No related study of corresponding complexes [$PdCl_2(PPh_{3-n}R_n)_2$] has been performed, but since known examples of Pd(IV)–phosphine complexes are less thermodynamically stable than the corresponding Pt(IV) complexes,[51,52] it is unlikely that our Pd(II) complexes would be significantly oxidised at potentials less positive than the Pt(II) examples.

The electrochemical oxidation of **2a** or **2b** alone did not result in the formation of redox-active polymer films on the electrode surface. Co-polymerization with unsubstituted monomer is a strategy that has often succeeded in cases where a functionalized monomer does not electropolymerize alone,[6,12,29,53] and we therefore attempted to grow polymer films from electrolyte solutions containing both **2a** (or **2b**) and EDOT (5:1 mole ratio; 0.01 M total monomer concentration), using repetitive scan cyclic voltammetry. In these experiments, redox-active polymer films were deposited on the electrodes. The cyclic voltammograms obtained during electrodeposition (Fig. 3) were similar in profile to those obtained during the electrodeposition of PEDOT itself, under the same conditions.

Similarly, we could not prepare redox-active polymer films by electrooxidation of **5a** or **5b** alone. Cyclic voltammograms of the copolymerization of, respectively, **5a** and **5b** with EDOT are shown in Fig. 4. On the first scan, there are two anodic peaks at +1.38 and +1.90 V, and the subsequent evolution of these peaks on repeated scanning is again significantly different from that of the corresponding peaks at +1.36 and +2.00 V seen in the first scan of EDOT itself.

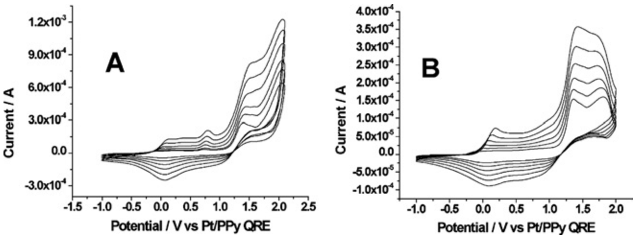


Fig. 3 Repetitive scan cyclic voltammetry experiments to grow PEDOT homopolymer (A) and an EDOT:**2a** copolymer (B). Both experiments used a scan rate of 100 mV s^{-1}, 0.1M Bu_4NBF_4–CH_3CN electrolyte and 0.01 M total monomer concentration. The copolymer experiment used a 5:1 ratio of EDOT:**2a**.

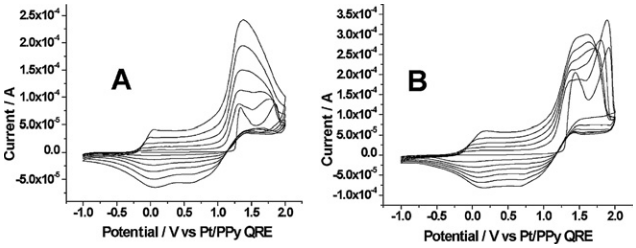


Fig. 4 Repetitive scan cyclic voltammetry copolymerizations of EDOT with (A) **5a** and (B) **5b**. Conditions as in caption to Fig. 3.

In spite of the longer 'spacer' for the ligand **7**, we were not able to electropolymerize the complexes **8a** or **8b** alone, and again resorted to copolymerization. The voltammograms of the EDOT:**8** copolymers are very similar in profile to those of the corresponding EDOT:**5** copolymers (ESI, Fig. S1).† After electrodeposition, all polymer films were characterized by cyclic voltammetry in background electrolyte, electrochemical impedance spectroscopy and X-Ray photoelectron spectroscopy.

XPS characterization of the copolymers

The XPS spectra of polymers prepared using mixtures of **2a** (or **2b**) and EDOT showed that any metal or chlorine present were below the detection limit. However, small but significant P 2p peaks were apparent, at 131.9 eV. For **2a**, the S:P ratio was >20:1, and for complex 2b the S:P ratio was >10:1. This suggests that electrochemical oxidation of complexes **2a** and **2b** results in decomposition, with liberation of **1** (or its oxidation product) that is subsequently incorporated into the growing polymer film. This would explain why the voltammograms in background electrolyte (see below) are characteristic of a polymer somewhat less conjugated than PEDOT (although, interestingly, the electrochemical impedance spectra were very similar). Failure to incorporate intact metal complexes with this ligand into conjugated polymers is in agreement with the failure of earlier attempts to polymerise Mo(0)[30] and W cluster complexes[24] of this and related ligands.

In contrast, the complexes with ligands in which EDOT units are present as a pendant group (**5a**, **5b**, **8a**, **8b**) were successfully copolymerized with EDOT. The data are summarized in Table 1. Characteristic peaks are observed for Pd ($3d_{5/2}$; **5a** and **8a**) and Pt ($4f_{7/2}$; **5b** and **8b**) at binding energies that are very similar to those

Table 1 XPS data for complex copolymers. Note that time constraints prevented collection of high-resolution data for Cl 2p (**8b**), S 2p and O 1s (**5a**, **5b**, **8b** respectively), although these elements were all observed in the survey scans

Copolymer with **5a**	
Pd $3d_{5/2}$, $3d_{3/2}$ 337.9, 343.2 eV	Pd:P 0.63
Cl 2p 198.3, 199.9 eV	Pd:Cl 0.52
P 2p 132.0 eV	
Copolymer with **5b**	
Pt $4f_{7/2}$, $4f_{5/2}$ 73.1, 76.4 eV	Pt:P 0.49
Cl 2p 198.2, 199.8 eV	Pt:Cl 0.51
P2p 131.6 eV	
Copolymer with **8a**	
Pd $3d_{5/2}$, $3d_{3/2}$ 338.1, 343.3 eV	Pd:P 0.66
Cl 2p 198.2, 199.9 eV	Pd:Cl 0.61
P 2p 131.5 eV	Pd:S 0.33
S 2p 163.8, 164.8 eV	Pd:O 0.2
O 1s 532.4 eV	
Copolymer with **8b**	
Pt $4f_{7/2}$, $4f_{5/2}$ 73.0, 76.4 eV	Pt:P 0.41
P 2p 131.6 eV (Cl 2p not determined)	

reported for other neutral Pd(II) or Pt(II) complexes.[54,55] Peaks due to P 2p and Cl 2p are also observed, in approximately the correct element ratios, and at binding energies consistent with coordinated PR_3 and Cl^- respectively.[56,57] Fig. 5 shows the data obtained for the EDOT: **8a** copolymer.

The XPS data supports the contention that the complexes of phosphines with 'pendant' EDOT units are incorporated intact into these copolymers. In particular, irreversible oxidation of the metal centers to M(IV) would result in significant binding energy increases. For example, for $K_2[PtCl_6]$, the $4f_{7/2}$ peak is reported to occur at 75.7 eV,[58] and for the *trans*-$[PdCl_2(en)_2]^{2+}$ unit (in halogen-bridged Pd(II)/Pd(IV) mixed valence complexes), the $3d_{5/2}$ peak is at 340.6 eV.[59] For the copolymer of EDOT with **8a**, high-resolution data were also obtained for S (2p). Interestingly, the mole ratio Pd:S was *ca.* 1:3. This is consistent with a *ca.* 1:1 ratio of EDOT and **8a** in the copolymer, a considerably higher proportion of complex than was used in the monomer feed. A high proportion of incorporated metal complex would lead to a heavily cross-linked polymer, a large volume fraction of which is metal complex, and this might explain the observation that the voltammograms of the copolymers (see below) are so different from that of PEDOT itself.

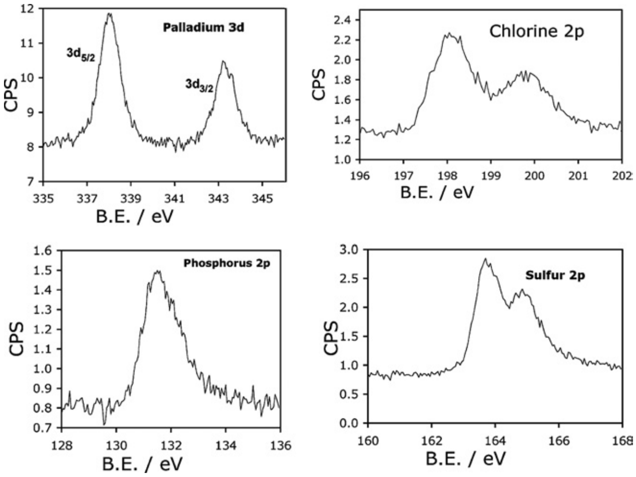


Fig. 5 XPS data for the copolymer made using EDOT and complex **8a**. Clockwise from top: Pd 3d, Cl 2p, S 2p, and P 2p.

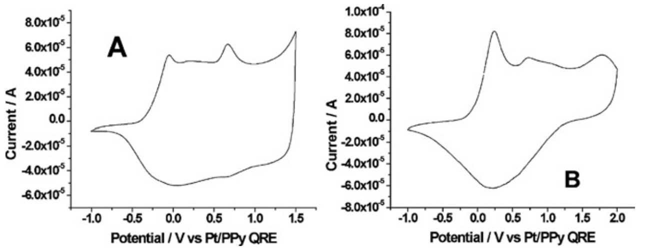


Fig. 6 Cyclic voltammograms (100 mV s^{-1}) of PEDOT homopolymer (A) and 'EDOT:**2a** copolymer' (B) in 0.1 M Bu_4NBF_4–CH_3CN.

The cyclic voltammograms of PEDOT and of a 'copolymer' grown using complex **2a** and EDOT are shown in Fig. 6. The PEDOT voltammogram (Fig. 6, (A)) resembles those observed previously for films grown and cycled in polar aprotic solvents with small, non-nucleophilic anion electrolytes.[26,60] The 'copolymer' obtained using complex **2a** (Fig. 6, (B)) shows somewhat more positive onset and peak potentials for oxidation compared with PEDOT itself, suggesting that the polymer is less conjugated than PEDOT. This is consistent with the XPS evidence that although there is no Pd or Cl in the film, there is some P owing to incorporation of (oxidised) **1**.

Electrochemical impedance spectroscopy

Electrochemical impedance spectroscopy is a powerful yet simple tool to study electronic and ionic resistances associated with electroactive materials. The technique has been extensively used to gather electrical information on electronically conductive polymers. Among the various theories developed to interpret EIS data of electronically conductive polymers, the dual-rail transmission line model proposed by Albery *et al.*[61–64] has been widely used to extract electronic and ionic resistances of such materials as polypyrrole, polyaniline and PEDOT in combination with various anions. In this model, the motion of electrons along the polymer film is described by one resistive rail, R_1, while the motion of the counter ions in the pores of the polymer containing the electrolyte is described by a second resistive rail, R_2. The electrons are driven along the rail by the Nernst potential between the solution phase in the pores and the polymer interface. The Donnan potential between the solution–polymer interface drives the ions into and out of the polymer. The origin of the distributed capacitance, C_p, between the two lines has been clearly explained by Feldberg.[65] (See ESI, Fig. S5.)†

The detailed analysis of the model for the charge transport in electronically conducting polymers will yield the following impedance plot for electronically conducting polymers. At the highest frequency there is a simple resistance, R_S, due to the resistance of the bulk electrolyte. As the frequency is lowered, a semicircular section is found which is caused by the resistance, R_e, of the whole polymer coat transmission line in parallel with the capacitance C_E. Under these conditions the polymer carries charge to the polymer–electrolyte interface, where a small part of the distributed capacitance is charged and discharged. When the semicircle is complete the corresponding resistance in the real axis of the Argand diagram is equal to the sum of the solution

Table 2 Values of electronic resistance R_e and ionic resistance R_I for 'copolymer' films from EIS spectra as a function of electrode potential

E/mV	PEDOT R_e, R_I/Ω	EDOT/**2a** R_e, R_I/Ω	EDOT/**2b** R_e, R_I/Ω	EDOT/**5a** R_e, R_I/Ω	EDOT/**5b** R_e, R_I/Ω	EDOT/**8a** R_e, R_I/Ω	EDOT/**8b** R_e, R_I/Ω
–100	253, 747	335, 870	263, 688	383, 1038	760, 1672	n.d.	352, 1037
+100	225, 663	181, 534	145, 281	357, 1057	697, 2016	546, 1445	670, 1950
+300	170, 512	210, 613	178, 526	265, 774	413, 1140	339, 940	529, 1550
+800	157, 460	174, 410	102, 196	323, 937	281, 764	269, 670	287, 848

resistance and the electronic resistance of the polymer. Thus the diameter of the semicircle provides the electronic resistance, R_e, of the polymer. At moderate frequencies there exists a 45° 'Warburg' region characteristic of the more resistive solution phase of the transmission line. As the frequency is further lowered, the involvement of the distributed capacitance becomes prominent and when the frequency is less than $(R_S C_P)^{-1}$, the characteristic time constant of the transmission line, the whole of the distributed capacitance is involved. This results in a vertical straight line in the Argand diagram. The difference in Z_{real} between the extremes of the Warburg region gives one third of the ionic resistance of the polymer, R_I (ESI Fig. S5).†

The R_e and R_I values extracted from the EIS spectra at selected applied DC potentials for the polymers, together with the respective conductivities, are shown in Table 2. Interestingly, the electrochemical impedance data for the polymers made in the presence of **2a** or **2b** are little different from that of PEDOT itself. The electronic resistances at a given potential are similar to, or even a little lower, than the values for the pure PEDOT film.

Electrochemistry of copolymers

The voltammograms of copolymers of **5** and **8** with EDOT recorded in the absence of monomer are again notably different from those of the PEDOT homopolymer (Fig. 7). The onset of PEDOT polymer oxidation seen at *ca.* −0.3 V in PEDOT (Fig. 6, (A)) is shifted positive, to almost 0.0 V, and the peak potential of the first anodic wave is shifted from −0.05 V in PEDOT to +0.28 V in the copolymer with **5b**. The cyclic voltammogram of the EDOT:**5a** copolymer shows behavior intermediate between that of the PEDOT homopolymer and the EDOT:**5b** copolymer. This suggests that the copolymers have a shorter mean conjugation length (shortest for the EDOT:**5b** copolymer), consistent with the higher electronic resistance values at a given potential from the EIS spectra for these materials (Table 2). Also, whereas there is a significant cathodic current in the PEDOT voltammogram almost immediately after the scan direction is reversed, the re-reduction of the copolymer with **5b** does not commence until +1.2 V, and the main cathodic peak is at a more negative potential (−0.2 V) than that of PEDOT (+0.1 V). Hence, the kinetics of the polymer redox process(es) are, once more, clearly slower in the copolymers.

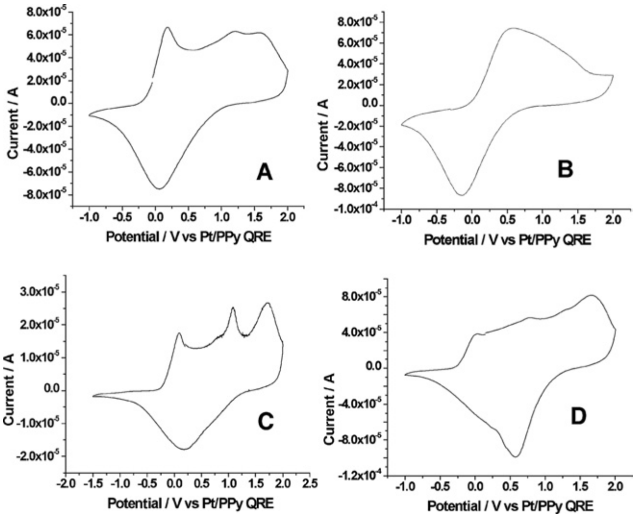


Fig. 7 Cyclic voltammograms (100 mV s^{-1}) of EDOT:**5a** copolymer (A), EDOT:**5b** copolymer (B), EDOT:**8a** copolymer (C) and EDOT:**8b** copolymer (D) in 0.1 M Bu_4NBF_4/CH_3CN.

The voltammograms of copolymers of complexes **8** with EDOT (Fig. 7C and 7D) are also different in profile from that of PEDOT itself, and are likewise consistent with the copolymers having shorter mean conjugation lengths than PEDOT itself, and slower kinetics of redox switching, as expected for such heavily cross-linked materials bearing a large volume of redox-inactive complex.

Interestingly, although the relative peak heights are different, the peak potentials for the oxidation processes seen for the **5a** and **8a** copolymers are similar. However, the **5b** copolymer CV is quite different in profile to that of **5b**.

Conclusions

We have shown that to build PEDOT materials containing covalently-bound square planar Pd(II) and Pt(II) phosphine complexes, it is necessary to use EDOT monomer units with both thiophene α-positions free, and bearing the phosphine moiety as a pendant group, such as **4** or **7**. Complexes of ligands in which the thiophene ring of EDOT is a phosphorus substituent, such as **1**, do not electropolymerize intact, instead undergoing oxidative decomposition with at least partial incorporation of the ligand (or its oxidation product) into the growing polymer.

We are currently extending this work to redox-active Ru(II) complexes, and we are studying applications of the materials in (electro)catalytic reactions. Additionally, we are constructing bidentate and chiral phosphine ligands with pendant EDOT groups.

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