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

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Supplementary data
Synthesis of 6.

3,4-Dimethoxythiophene was synthesised from commercial 3,4-dibromothiophene by a literature method\(^1\).

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\begin{align*}
\text{O} & \quad \text{O} \\
\text{3,3'} & \quad \text{2} \\
\text{1,1'} & \quad \text{4} \\
\text{5} & \quad \text{6} \\
\text{7} & \quad \text{8} \\
\text{9}\text{Br} & \\
\end{align*}
\]

4-((6-bromohexyloxy)methyl)-2,2-dimethyl-1,3-dioxolane: To a solution of NaH (3.0 g, 75 mmol) in 80 cm\(^3\) anhydrous THF was added 2,2-dimethyl-1,3-dioxolane-4-methanol (‘solketal’) (10.0 g, 76 mmol) slowly over 20 minutes. After the evolution of gas had ceased, a solution of 1,6-dibromohexane (54.9 g, 225 mmol) in THF (25 cm\(^3\)) was added portionwise with stirring. The solution was then stirred for 12 hours. Solvent was removed in \textit{vacuo} and the brown residue was dissolved in 300 cm\(^3\) of CH\(_2\)Cl\(_2\), washed with distilled water (2 \times 200 cm\(^3\)) and dried over MgSO\(_4\), filtered, and evaporated to yield a yellow viscous oil. Excess 1,6 dibromohexane and any unreacted solketal were largely removed by heating under vacuum. The product was sufficiently pure to be used in the next step. Yield 16.23 g, 73 %. MS (ES\(^+\)), m/z: calc. for C\(_{12}\)H\(_{24}\)O\(_3\)Br\(^+\), [M+H]\(^+\): 295.09088. Found: 295.090154. \(^1\)H NMR (400 MHz) \(\delta\) 1.35, 1.41 (s, 6H, 2 CH\(_3\)), 1.35-1.50 (m, 4H, –CH\(_2\)CH\(_2\)—), 1.55 (m, 2H, J 7.4, –CH\(_2\)—), 1.88 (q, J 7.4, –CH\(_2\)—), 3.41 (t, 1H, J 6.5, H\(^9\)), 3.41-3.50 (overlapping multiplets, 4H, H\(^{3,4}\)), 3.72 (m, 1H, J\(_{1,1'}\) 8.1, J\(_{1,2}\) 6.4, H\(^1\)), 4.05 (dd, 1H, J 6.45, J\(_{1,1'}\) 8.1, H\(^{1'}\)), 4.25 (m, 1H, H\(^2\)). \(^1\)C\(^{1\text{H}}\) NMR (100.6 MHz) \(\delta\) 25.8, 27.2, 28.3, 29.75, 32.9, 34.1, 67.3, 71.9, 72.3, 75.2, 109.7.

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\begin{align*}
\text{HO} & \quad \text{O} \\
\text{3,3'} & \quad \text{2} \\
\text{1,1'} & \quad \text{4} \\
\text{5} & \quad \text{6} \\
\text{7} & \quad \text{8} \\
\text{9}\text{Br} & \\
\end{align*}
\]

3-(6-bromohexyloxy)propane-1,2-diol: 1M aq.HCl (10 cm\(^3\)) was added to a solution of 4-((6-bromohexyloxy)methyl)-2,2-dimethyl-1,3-dioxolane (1.00 g, 3.4 mmol) in THF (20 cm\(^3\)). The
mixture was stirred vigorously for 12 hours at room temperature. Most of the solvent was removed in vacuo and the residue was extracted with CH₂Cl₂ and dried over MgSO₄, then filtered. Solvent was removed in vacuo and the yellow oil was then adsorbed onto silica and eluted with CH₂Cl₂. Yield 0.78 g, 91 %. Anal. calcd. for C₉H₁₉O₃Br: C, 42.33; H, 7.51 %. Found C, 42.55; H, 7.59 %. MS (ES+) m/z: calc. for [M+Na]⁺: 277.0415. Found 277.0419. ¹H NMR (400 MHz): δ 1.35, 1.45, 1.61, 1.88 (m’s, 2H each, –CH₂–), 3.41 (t, 2H, J 6.64, H₉), 3.49-3.41 (overlapping m’s, 4H, H₃,4), 3.68 (m, 2H, J₁,₁’, 11.4, J₁,₂ 7.8, H₁,₁’), 3.85 (m, 1H, J₂,₃, J₂,₁ 5.7, H₂). ¹³C{¹H} NMR (100.6 MHz): δ 25.7, 28.3, 29.7, 32.9, 34.1, 64.5, 71.0, 71.9, 72.7.

2-((6-bromohexyloxy)methyl)-2,3-dihydrothieno[3,4-b][1,4]dioxine, 6: To a 100 cm³ 3-necked flask was added dry toluene (20 cm³) followed by 3,4 dimethoxythiophene (1.00 g, 6.94 mmol), the diol (2.20 g, 8.66 mmol), p-toluenesulfonic acid (0.69 mmol) and water (50 µL). The mixture was heated in a 170 °C oil bath for 20 minutes, the condenser was removed for 5 seconds, and reflux was then continued for 16 hours under a continuous flow of nitrogen. Solvent was removed in vacuo and the residue was extracted into CH₂Cl₂ (50 cm³), washed with water (5 × 5 cm³), dried over MgSO₄, and filtered. Solvent was removed and the yellow oil was then adsorbed onto neutral alumina and eluted with CH₂Cl₂ / hexane (1:1) to separate the pure product as a yellow oil. Yield 1.51 g, 69.7 %. Anal. calcd. for C₁₃H₁₉O₃BrS: C, 46.57; H, 5.71 %. Found C, 47.22; H, 5.78 %. MS (ES+) m/z: calcld. for [M+H]⁺: 335.0317. Found: 335.0313. ¹H NMR (400 MHz): δ 1.37, 1.44 (overlapping m, 4H, –CH₂–), 1.60 (m, 2H, –CH₂–), 1.86 (m, 2H, –CH₂–), 3.41 (t, 2H, J 6.83, H²), 3.50 (t, 2H, J 6.5, H³), 3.65 (m, 2H, J 10.4, 4.9, H₃,₄), 4.05 and 4.22 (m,
2H, J 11.7, 7.6, H¹¹), 4.29 (m, 1H, H²), 6.335, 6.337 (AB, JAB 1.4, thieryl H’s). \(^{13}\text{C}\{^1\text{H}\} \text{ NMR}\) (100.6 MHz): \(\delta\) 25.7, 28.3, 29.7, 33.1, 34.3, 66.6, 69.6, 72.2, 73.0, 99.99, 100.1, 141.9.

Additional electrochemical and EIS data

**Figure S1.** Repetitive scan cyclic voltammograms of (A) EDOT:8a copolymer formation, (B) EDOT:8b copolymer formation in 0.1 M Bu₄NBF₄ / CH₃CN, 100 mV s⁻¹, 0.01 M total monomer concentration, 5:1 EDOT:complex.
XPS spectra of other co-polymers

Figure S2. XPS spectra for copolymer of 5b and EDOT. Clockwise from top left: Pt 4f, P 2p and Cl 2p regions.

Figure S3. XPS spectra for copolymer of 5a and EDOT. Clockwise from top left: Pd 3d, P 2p and Cl 2p regions.
Figure S4. XPS spectra for copolymer of 8b and EDOT. Left: Pt 4f; right: P 2p regions.
Figure S5. Equivalent circuit for ‘transmission line’ model (top), and idealised form of Argand diagram for an electronically conducting polymer film behaving in accord with this model. Frequency decreases from b–c–d–e. R_S is the uncompensated electrolyte resistance, R_e is the electronic resistance of the polymer film, R_i is the ionic resistance of the polymer film.

References