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Metal Coordination and Aggregation Properties of Chiral Polythiophenes and Polythienylethynylenes

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Materials

THF was freshly distilled from sodium-benzophenone ketyl. Toluene was freshly distilled from sodium. All other solvents and reagents were commercial products and were used as supplied.

Procedures

GPC measurements were performed on a Waters 590 GPC, using THF as solvent and a PL Gel column, calibrated with polystyrene standards. The ^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Varian Gemini 400 MHz spectrometer. Chemical shifts are reported in ppm. The UV-vis. spectra were recorded on a Perkin Elmer Lambda 40 spectrophotometer. The PL spectra were recorded on a Perkin Elmer Luminescence Spectrometer LS 50 B. The IR spectra were recorded as films, on a Perkin-Elmer 1600 series FT-IR spectrometer. DSC and TGA data were collected on a Perkin-Elmer DSC 7 apparatus and a Perkin-Elmer TGA 7 apparatus, respectively. GC-MS measurements were performed on a Shimadzu GCMS-QP5000. Crystallographic data were collected on a Nonius KappaCCD diffractometer on rotating Mo anode.

Synthesized Materials

3,4-Dimethoxythiophene was synthesised using a published procedure.[32]

(S)-3,7-Dimethyloctan-1-ol (1)

A solution of citronellol (2.50 g, 16.0 mmol) in ethyl acetate (50 mL) was placed in a parr reaction vessel. Nitrogen gas was bubbled through the solution for 3 min, followed by the addition of 10 % palladium on carbon (100 mg). Nitrogen gas was then bubbled through the suspension for a further 2 min before the top was sealed. The reaction vessel was placed in the parr apparatus and hydrogen gas was introduced to give an over pressure of 20 psi. The pressure was reduced to atmospheric pressure by venting through a bubbler and the vessel repressurised with hydrogen gas to 40 psi. The pressure was again reduced to atmospheric pressure by venting through a bubbler. The vessel was then represurisation with hydrogen gas to 70 psi and the parr apparatus was set in motion. After 1 h more hydrogen gas was introduced to restore the pressure to 70 psi. The apparatus was allowed to run for a further 2 h with no further pressure drop. The suspension was filtered and the solid properly and safely disposed of. The solvent was evaporated from the remaining solution under reduced pressure to give the product, (S)-3,7-dimethyloctan-1-ol, **1**, (2.53 g, 100 %) as a colourless liquid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.75–0.95 (9H, m), 1.03–1.11 (2H, m), 1.11–1.42 (4H, m), 1.42–1.63 (2H, m), 3.59–3.72 (2H, m); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 19.85, 22.80, 24.89, 28.18, 29.73, 37.59, 39.48, 40.21, 61.42.

(S)-1-Bromo-3,7-dimethyloctane (2)

(S)-3,7-Dimethyloctan-1-ol (40.0 g, 252.7 mmol) was added to a solution of triphenyl phosphine (73.0 g, 278.3 mmol) in dichloromethane (200 mL) and cooled to 0 °C. *N*-Bromosuccinimide (49.5 g, 278.1 mmol) was added portion-wise over a period of 2 h, observing complete dissolution between each addition. The solution was allowed to warm to room temperature and then stirred overnight. The solvent was removed under reduced pressure and the remaining paste was lixiviated with *n*-hexane (6 × 150 mL). The combined hexane fractions were filtered and the solvent removed under reduced pressure. The remaining liquid was distilled under reduced pressure to give the product (S)-1-bromo-3,7-dimethyloctane, **2**, (47.00 g, 84.1 %) as a colourless liquid. b.p. 42 °C (0.1 mmHg); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.78–0.93 (9H, m), 1.04–1.19 (2H, m), 1.20–1.38 (2H, m), 1.47–1.57 (1H, m), 1.57–1.71 (2H, m), 1.80–1.95 (1H, m), 3.37–3.48 (2H, m); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 19.18, 22.81, 24.77, 28.17, 31.89, 32.44, 36.94, 39.39, 40.30.

(S)-3,7-dimethyloctane-1-thiol (3)

A solution of thiourea (1.00 g, 13.87 mmol) and (S)-1-Bromo-3,7-dimethyloctane (1.00 g, 4.52 mmol) in ethanol (50 mL) was flushed with argon by bubbling for 2 min then allowed to reflux over night. A solution of potassium hydroxide (785 mg, 14.0 mmol) in water (10 mL) was added and reflux was allowed to continue for a further

6 h. The solution was cooled to room temperature and 90 % of the ethanol was removed under reduced pressure. Dichloromethane (50 mL) and water (10 mL) were added then the phases separated. The aqueous phase was extracted with dichloromethane (2 × 25 mL) and the organic phases were combined. The new organic phase was washed with water (2 × 20 mL) then dried over sodium sulfate. The solvent was removed under reduced pressure to leave the product, (S)-3,7-dimethyloctane-1-thiol, **3**, (725 mg, 92.0 %) as a colourless liquid. ^{1}H NMR (CDCl$_3$, 400 MHz) δ 0.82–0.89 (9H, m), 1.07–1.18 (2H, m), 1.20–1.36 (4H, m) 1.38–1.65 (4H, m), 2.43–2.61 (2H, m); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 19.44, 22.73, 22.92, 24.86, 28.18, 32.05, 37.12, 39.46, 41.74; MS (GCMS-EI$^+$): *m/z* 174 (M)$^+$.

3,4-Bis(3(S),7-dimethyloctyloxy)thiophene (4)

3,4-Dimethoxythiophene (3.00 g, 20.8 mmol), (S)-3,7-dimethyloctan-1-ol, **1**, (10.0 g, 63.2 mmol) and *p*-toluenesulfonic acid (360 mg, 2.09 mmol) were added to a two necked round bottomed flask fitted with a reflux condenser. The solution was stirred at 90 °C for 3 days under a constant gentle flow of nitrogen gas in the second neck and out through the condenser. The excess alcohol was distilled off under reduced pressure and the residue was purified by column chromatography, eluting with *n*-heptane. Evaporation of the solvent under reduced pressure gave the product, 3,4-bis(3,7-dimethyloctyloxy)thiophene, **4**, (7.80 g, 94.5 %), as a colourless liquid. ^{1}H NMR (CDCl$_3$, 400 MHz) δ 0.86 (12H, d, J = 7.0 Hz), 0.93 (6H, d, J = 6.2 Hz), 1.10–1.20 (4H, m), 1.22–1.37 (8H, m), 1.47–1.58 (2H, m), 1.58-1.70 (4H, m), 1.80–1.91 (2H, m), 3.97–4.04 (4H, m), 6.17 (2H, s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 19.94, 22.92, 24.89, 28.20, 30.17, 36.16, 37.53, 39.46, 69.21, 97.04, 147.81; MS (GCMS-EI$^+$): *m/z* 397 (M)$^+$.

3,4-Bis(3(S),7-dimethyloctylthio)thiophene (5)

3,4-Dimethoxythiophene (6.00 g, 41.6 mmol), (S)-3,7-dimethyloctane-1-thiol, **3**, (21.6 g, 123.9 mmol) and *p*-toluenesulfonic acid (717 mg, 4.16 mmol) were added to a two necked round bottomed flask fitted with a reflux condenser. The solution was stirred at 100 °C for 14 days under a constant gentle flow of nitrogen gas in the second neck and out through the condenser. The excess thiol was distilled off under reduced pressure and the residue was purified by column chromatography, eluting with *n*-heptane. Evaporation of the solvent under reduced pressure gave the product, 3,4-bis(3,7-dimethyloctylthio)thiophene, **5**, (17.01 g, 95.3 %), as a colourless liquid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.80–0.90 (18H, m), 1.09–1.21 (4H, m), 1.21–1.35 (8H, m), 1.41–1.73 (8H, m), 2.81–2.97 (4H, m), 7.09 (2H, s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 19.61, 22.85, 24.88, 28.19, 32.42, 32.48, 36.33, 37.15, 39.47, 123.13, 134.22; MS (GCMS-EI$^+$): *m/z* 428 (M)$^+$.

3,4-Bis(3(S),7-dimethyloctyloxy)-2,5-diiodothiophene (6)

N-iodosuccinimide (3.40 g, 15.1 mmol) was added portion-wise to a stirred solution of 3,4-bis(3,7-dimethyloctyloxy)thiophene, **4**, (3.00 g, 7.56 mmol) in DMF (10 mL) in the dark over a period of 1 h. The reaction mixture was allowed to stir in the dark at room temperature for 48 h. Diethyl ether (25 mL) was added and the solution was washed with water (25 mL). The layers were separated and the aqueous layer was washed with diethyl ether (2 × 20 mL). The organic phases were combined and washed with water (2 × 25 mL) then dried over magnesium sulfate. The solvent was removed under reduced pressure and the residue was purified by column chromatography, eluting with 9:1 *n*-hexane:dichloromethane. Evaporation of the solvent under reduced pressure gave the product, 3,4-bis(3,7-dimethyloctyloxy)-2,5-diiodothiophene, **6**, (4.23 g, 86.2 %), as a colourless liquid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.86 (12H, d, *J* = 7.0 Hz), 0.93 (6H, d, *J* = 6.9 Hz), 1.08–1.18 (4H, m), 1.21–1.37 (8H, m), 1.47–1.60 (4H, m), 1.65–1.83 (6H, m), 3.99–4.12 (4H, m); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 19.61, 22.60, 24.66, 27.96, 29.61, 37.07, 37.25, 39.26, 63.46, 72.36, 151.78.

3,4-Bis(3(S),7-dimethyloctylthio)-2,5-diiodothiophene (7)

N-iodosuccinimide (5.25 g, 23.3 mmol) was added portion-wise to a stirred solution of 3,4-bis(3,7-dimethyloctylthio)thiophene, **5**, (5.00 g, 11.7 mmol) in DMF (15 mL) in the dark over a period of 1 h. The reaction mixture was allowed to stir in the dark at room temperature for 48 h. Diethyl ether (50 mL) was added and the solution was washed with water (2 × 50 mL). The layers were separated and the aqueous layer was washed with diethyl ether (2 × 50 mL). The organic phases were combined and dried over sodium sulfate. The solvent was removed under reduced pressure and the residue was purified by column chromatography, eluting with *n*-heptane. Evaporation of the solvent under reduced pressure gave the product, 3,4-bis(3,7-dimethyloctylthio)-2,5-diiodothiophene, **7**, (5.31 g, 66.9 %), as a colourless liquid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.83–0.95 (18H, m), 1.03–1.33 (14H, m), 1.33–1.42 (2H, m), 1.44–1.60 (4H, m), 2.79–2.96 (4H, m); ^{13}C

NMR ($CDCl_3$, 100 MHz) δ 19.57, 22.85, 24.86, 28.19, 32.26, 34.78, 36.72, 37.07, 39.48, 72.36, 141.51.

3,4-Bis(3(S),7-dimethyloctyloxy)-2,5-bis(2-(trimethylsilyl)ethynyl)thiophene (8)

Argon gas was bubbled through a solution of trimethylsilylacetylene (665 mg, 6.77 mmol) and 3,4-bis(3,7-dimethyloctyloxy)-2,5-diiodothiophene, **6**, (2.00 g, 3.08 mmol) in triethylamine (10 mL). Copper(I) iodide (2.5 mg, 13.1 μmol) and bis(triphenylphosphine)palladium dichloride (3.6 mg, 5.13 μmol) were added and the reaction mixture was stirred under argon at room temperature for 4 h. The solvent was removed under reduced pressure and the residue was purified by column chromatography, eluting with 20:3 *n*-hexane:chloroform. Evaporation of the solvent under reduced pressure gave the product, 3,4-bis(3,7-dimethyloctyloxy)-2,5-bis(2-(trimethylsilyl)ethynyl)thiophene, **8**, (1.69 g, 93.0 %), as a colourless liquid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.23 (18H, s), 0.78 (12H, d, *J* = 7.0 Hz), 0.86 (6H, d, *J* = 6.9 Hz), 1.08–1.63 (16H, m), 1.59–1.70 (2H, m), 1.70–1.81 (2H, m), 4.28–4.40 (4H, m); ^{13}C NMR ($CDCl_3$, 100 MHz) δ -0.2, 19.6, 22.7, 24.7, 28.0, 29.6, 36.8, 37.3, 39.3, 71.0, 96.0, 101.8, 103.6, 150.6.

3,4-Bis(3(S),7-dimethyloctylthio)-2,5-bis(2-(trimethylsilyl)ethynyl)thiophene (9)

A solution of 3,4-bis(3,7-dimethyloctylthio)-2,5-diiodothiophene, **7**, (3.00 g, 4.41 mmol) and triethylamine (12.3 mL, 88.3 mmol) in THF (40 mL) was placed under vacuum for 5 s then filled with argon. The 5 s evacuation and refilling with argon was repeated a further 3 times. Copper(I) iodide (168 mg, 882 μmol) and tetrakis(triphenylphosphine)palladium(0) (510 mg, 441 μmol) were added and the vessel was again placed under vacuum for 5 s then filled with argon, 3 times. Trimethylsilylacetylene (1.40 mL, 9.94 mmol) was then added via syringe and the reaction mixture was stirred under argon at room temperature for 16 h. The solvent was removed under reduced pressure and the residue was purified by column chromatography, eluting with *n*-heptane. Evaporation of the solvent under reduced pressure gave the product, 3,4-bis(3,7-dimethyloctylthio)-2,5-bis(2-(trimethylsilyl)ethynyl)thiophene, **9**, (2.61 g, 95.3 %), as a pale yellow liquid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.26 (18H, s), 0.77–0.90 (18H, m), 1.02–1.40 (16H, m), 1.42–1.59 (4H, m), 2.93–3.10 (4H, m); ^{13}C NMR ($CDCl_3$, 100 MHz) δ -0.21, 19.62, 22.83, 24.86, 28.20, 32.26, 32.98, 37.01, 37.16, 39.48, 96.65, 104.86, 124.70, 139.91; MS (GCMS-EI$^+$): *m/z* 621 $(M)^+$.

3,4-Bis(3(S),7-dimethyloctyloxy)-2,5-diethynylthiophene (10)

1 M Tetrabutyl ammonium fluoride (0.70 mL, 0.70 mmol) was added to a solution of 3,4-bis(3,7-dimethyloctyloxy)-2,5-bis(2-(trimethylsilyl)ethynyl)thiophene, **8**, (750 mg, 1.27 mmol) in THF (30 mL). The mixture was then stirred under argon for 10 min at room temperature. The reaction mixture was added directly to the top of a short neutral alumina column and drawn trough under reduced pressure. The column was thoroughly flushed by eluting with 9:1 *n*-hexane:dichloromethane. The solvent was removed under reduced pressure to give the product 3,4-bis(3,7-dimethyloctyloxy)-2,5-diethynylthiophene, **10**, (510 mg, 90.7 %), as a colourless liquid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.78 (12H, d, J = 7.0 Hz), 0.84 (6H, d, J = 6.9 Hz), 1.06–1.64 (16H, m), 1.58–

1.72 (2H, m), 1.69–1.83 (2H, m), 3.50 (2H, s), 4.28–4.40 (4H, m); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 19.6, 22.7, 24.7, 28.0, 29.5, 36.8, 37.3, 39.2, 71.2, 75.4, 83.9, 102.5, 149.7; MS (GCMS-EI$^+$): *m/z* 444.85 $(M)^+$.

3,4-Bis(3(S),7-dimethyloctylthio)-2,5-diethynylthiophene (11)

Nitrogen gas was bubbled through a solution of 3,4-bis(3,7-dimethyloctylthio)-2,5-bis(2-(trimethylsilyl)ethynyl) thiophene, **9**, (1.00 g, 1.61 mmol) in THF (30 mL) for 5 min. 1 M Tetrabutyl ammonium fluoride (3.38 mL, 3.38 mmol) was then added and the mixture was stirred under argon for 15 min at room temperature. The reaction mixture was added directly to the top of a short neutral alumina column and drawn trough under reduced pressure. The column was thoroughly flushed by eluting with 9:1 *n*-heptane:dichloromethane. The solvent was removed under reduced pressure to give the product 3,4-bis(3,7-dimethyloctylthio)-2,5-diethynylthiophene, **11**, (668 mg, 87.0 %), as a colourless liquid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.70–0.93 (18H, m), 0.95–1.78 (20H, m), 2.75–3.23 (4H, m), 3.49 (2H, s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 19.32, 22.62, 24.61, 27.94, 31.99, 33.14, 36.72, 36.87, 39.22, 75.82, 86.24, 124.34, 140.36.

Poly-(3,4-bis(3(S),7-dimethyloctyloxy))-thienylethynylene (12)

Argon gas was bubbled through a solution of 3,4-bis(3,7-dimethyloctyloxy)-2,5-diethynylthiophene, **10**, (510 mg, 1.15 mmol) and triethylamine (0.8 mL) in toluene (6 mL) for 15 min. Under a positive flow of argon tetrakis(triphenylphosphine)palladium(0) (12.0 mg, 10.4 μmol) and copper(I) iodide (4.0 mg, 21.0 μmol) were added. 3,4-Bis(3,7-dimethyloctyloxy)-2,5-diiodothiophene, **6**, (750 mg, 1.15 mmol) was added dropwise and the mixture was stirred under argon at 60 °C for 16 h. The reaction mixture was then cooled to room temperature and poured into methanol (100 mL). The red precipitate that formed was collected my filtration and dried under vacuum at 30 °C for 6 h to give the product poly-(3,4-bis(3,7-dimethyloctyloxy))-thienylethynylene, **12**, (770 mg, 79.9 %), as a red solid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.85 (12H, d, J = 7.0 Hz), 0.94 (6H, d, J = 6.2 Hz), 1.10–1.60 (16H, m), 1.62-1.72 (2H, m), 1.72–1.86 (2H, m), 4.30–4.44 (4H, m); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 19.6, 22.7, 24.7, 28.0, 29.6, 36.9, 37.4, 39.2, 71.2, 87.9, 83.9, 103.5, 150.1; GPC: $M_n = 13370\ \mathrm{gmol^{-1}}$, $M_w = 23440\ \mathrm{gmol^{-1}}$.

Poly-(3,4-bis(3(S),7-dimethyloctylthio))-thienylethynylene (13)

Nitrogen gas was bubbled through a solution of 3,4-bis(3,7-dimethyloctylthio)-2,5-diethynylthiophene, **11**, (668 mg, 1.40 mmol) and triethylamine (3.9 mL) in toluene (5 mL) for 5 min. Under a positive flow of argon tetrakis(triphenylphosphine)palladium(0) (162 mg, 140 μmol) and copper(I) iodide (53 mg, 280 μmol) were added and nitrogen gas was bubbled through for a further 5 min. 3,4-Bis(3,7-dimethyloctylthio)-2,5-diiodothiophene, **7**, (953 mg, 1.40 mmol) was dissolved in toluene (5 mL) and nitrogen gas was bubbled through it for 5 min, after which the solution was added to the reaction mixture and the mixture was stirred under argon at 60 °C for 16 h. The reaction mixture was then cooled to room temperature and poured into methanol (100 mL). The red precipitate that formed was collected my filtration washed with methanol and dried under vacuum to give the product poly-(3,4-bis(3,7-dimethyloctylthio))-thienylethynylene, **13**, (493 mg, 78.2 %), as a red solid. ^{1}H

NMR ($CDCl_3$, 400 MHz) δ 0.70–0.97 (18H, m), 0.99–1.75 (20H, m), 2.77–3.24 (4H, m); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 19.41, 22.64, 24.68, 27.97, 30.31, 32.07, 36.60, 36.96, 39.25, 76.68, 125.51, 135.76; GPC: M_n = 14800 $gmol^{-1}$, M_w = 39600 $gmol^{-1}$.

Poly-(3,4-bis(3(S),7-dimethyloctylthio))-(3',4'-bis(3,7-dimethyloctyloxy))-bis(thienylethynylene) (14)

Nitrogen gas was bubbled through a solution of 3,4-bis(3,7-dimethyloctylthio)-2,5-diethynylthiophene, **11**, (315 mg, 0.66 mmol) and triethylamine (1.0 mL) in toluene (5 mL) for 5 min. Under a positive flow of argon tetrakis(triphenylphosphine)palladium(0) (76 mg, 66 μmol) and copper(I) iodide (25 mg, 130 μmol) were added and nitrogen gas was bubbled through for a further 5 min. 3,4-Bis(3,7-dimethyloctyloxy)-2,5-diiodothiophene, **6**, (428 mg, 0.66 mmol) was dissolved in toluene (5 mL) and nitrogen gas was bubbled through it for 5 min, after which the solution was added to the reaction mixture and the mixture was stirred under argon at 60 °C for 16 h. The reaction mixture was then cooled to room temperature and poured into methanol (100 mL). The red precipitate that formed was collected my filtration, washed with methanol and dried under vacuum to give the product poly-(3,4-bis(3,7-dimethyloctylthio))-(3',4'-bis(3,7-dimethyloctyloxy))-bis(thienylethynylene), **14**, (454 mg, 79.0 %), as a red solid. ^1H NMR ($CDCl_3$, 400 MHz) δ 0.60–0.98 (36H, m), 0.98–1.77 (40H, m), 2.94–3.13 (4H, m), 4.40–4.60 (4H, m); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 19.36, 19.63, 22.61, 22.71, 24.67, 24.72, 27.97, 29.66, 30.38, 32.08, 36.82, 36.93, 37.39, 39.16, 39.24, 39.27, 71.40, 76.67, 103.52, 125.54, 135.72, 150.02; GPC: M_n = 15470 $gmol^{-1}$, M_w = 33700 $gmol^{-1}$.

Poly-(3,4-bis(3(S),7-dimethyloctylthio))-thiophene (15)

Nitrogen gas was bubbled through a stirred solution of 3,4-bis(3,7-dimethyloctylthio)-thiophene, **5**, (500 mg, 1.17 mmol) in chloroform (50 mL) for 5 min. Iron(III) chloride (190 mg, 1.17 mmol) was then cautiously added. The fixture was allowed to stir under argon at room temperature for 16 h. The reaction mixture was then poured into a rapidly stirring fixture of methanol (400 mL) and 25 % aqueous ammonia (100 mL). The orange precipitate that formed was collected my filtration, washed with methanol and dried under vacuum to give the product poly-(3,4-bis(3,7-dimethyloctylthio))-thiophene, **15**, (106 mg, 21.2 %), as an orange solid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.78–0.95 (18H, m), 1.02–1.68 (20H, m), 2.82–2.96 (4H, m); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 19.39, 22.62, 24.71, 27.95, 29.41, 32.36, 34.78, 37.03, 39.30, 143.15, 145.42; GPC: M_n = 11180 gmol^{-1}, M_w = 13570 gmol^{-1}.

3,4-Bis(3(S),7-dimethyloctylthio)thiophene-bis(2,2'-bipyridyl)-ruthenium(II) di(tetrafluoroborate) (16)

3,4-bis(3,7-dimethyloctylthio)thiophene, **5**, (100 mg, 0.23 mmol) and cis-dichloro-bis(2,2'-bipyridyl ruthenium(II) dehydrate (110 mg, 0.23 mmol) were dissolved in ethanol (10 mL) and heated to reflux. Silver tetrafluoroborate (90 mg, 0.46 mmol) was added while stirring and a precipitate was instantly noticeable. Heating continued for 48 h after which the reaction mixture was cooled to room temperature. The reaction mixture was then filtered over celite, which was subsequently washed with ethanol. The solvent was removed from the combined ethanol fractions under reduced pressure. The residue was then dissolved in ethanol (5 mL) and hexane (10 mL) was layered on. Crystallisation gave the product 3,4-bis(3,7-dimethyloctylthio)thiophene-bis(2,2'-bipyridyl)-ruthenium(II) di(tetrafluoroborate), **16**, (14.3 mg, 62.0 %), as a red solid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.62–0.90 (18H, m), 0.90–1.18 (8H, m), 1.18–1.37 (4H, m), 1.38–1.50 (4H, m), 1.53–1.82 (4H, m), 2.12–2.22 (4H, m), 7.42-7.54 (2H, m), 7.66-7.74 (4H, m), 7.82-7.88 (2H, m), 7.94-8.06 (2H, m), 8.22-8.37 (2H, m), 8.41-8.56 (2H, m), 8.58-8.63 (2H, m), 9.03-9.14 (2H, m). Crystal data: $[C44H60N4RuS3]^{2+}.2\ BF_4^-$, M = 1015.86, orange, needle-shaped crystal (0.03 x 0.09 x 0.33 mm), monoclinic, space group P21 (no. 4) with a = 13.719(2), b = 12.0218(10), c = 15.802(2) Å, beta = 110.727(12) °, V = 2437.5(5) Å^3, Z = 2, Dc = 1.384 g cm^{-3}, mu(Mo K alpha) = 0.516 mm^{-1}, T = 150 K, 61776 reflections measured, 11199 independent, R int = 0.0534, R sigma = 0.0482. Atoms C404--C498 of one of the aliphatic side-chains are disordered and described with a two-site disorder model. Restraints were necessary to maintain a reasonable geometry. Refinement of 549 parameters converged at a final wR2 value of 0.1405 (all data), R1 = 0.0521 [for 9196 reflections with I > 2 sigma(I)], S = 1.024, -0.57 < Delta rho < 1.45 e Å^{-3}. The Flack x-parameter is -0.02(3), confirming the absolute configuration of the starting material.