Supplementary Information

Monotelechelic Poly(*p*-phenylenevinylene)s by Ring Opening Metathesis Polymerisation

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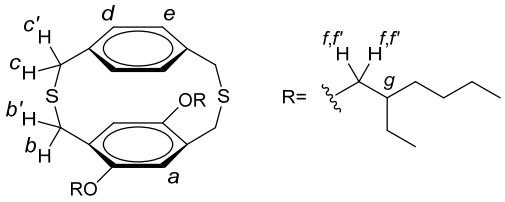
1.1 General Procedures

Nuclear magnetic resonance (NMR) spectra were obtained on either 400 MHz or 500 MHz Brucker spectrometers. Chemical shifts are reported in ppm relative to the indicated residual solvent (^{1}H NMR spectroscopy; 7.26 ppm for [D]chloroform and 7.16 ppm for [D_6]-benzene. ^{13}C NMR spectroscopy; 77.16 ppm for [D]-chloroform, 128.06 ppm for [D_6]-benzene). The following abbreviations are used to indicate the multiplicity of the signals; s = singlet, d = doublet, m = multiplet, br m = broad multiplet. Matrix-assisted laser desorption/ionisation time-of-flight mass spectrometry (MALDI-TOF-MS) was conducted using a Shimadzu Biotech AXIMA Confidence MALDI mass spectrometer in linear (positive) mode, referencing against poly(propylene glycol), M_n = 4.0 kg mol^{-1}. 50 μL of polymer solution (1 mg mL^{-1} in THF) was mixed with 50 μL of a 10 mg mL^{-1} solution of the matrix (dithranol) in THF. A drop of this solution was spotted onto a MALDI plate and the solvent allowed to evaporate at room temperature. Elemental compositions of carbon, hydrogen and sulfur atoms were measured using a Flash 2000 Organic Elemental Analyser (Thermo Scientific). Elemental composition of bromine was determined by titration against silver nitrate using an 888 Titrando (Metrohm). Nominal and high resolution electrospray mass spectrometry were carried out using SQD2 and QTOF Spectrometers (Waters). Infrared spectroscopy was conducted using a Nicolet iS5 (Thermo Scientific) with iD5 ATR accessory. Gel permeation chromatography (GPC) was conducted in THF using a Viscotek GPCmax VE2001 solvent/sample module with 2 × PL gel 10 μm MIXED-B + 1 × PL gel 500A columns, a

Viscotek VE3580 RI detector and a VE 3240 UV-Vis multichannel detector. The flow rate was 1 mL min^{-1} and the system was calibrated with narrow PDI polystyrene standards in the range of 0.2 – 1,800 kg mol^{-1} from Polymer Laboratories. The analysed samples contained *n*-dodecane as a flow marker. UV-Vis absorption spectra and optical densities were recorded on a Varian Cary 5000 UV-Vis-NIR spectrophotometer and photoluminescence spectra were recorded on Cary Eclipse Fluorescence Spectrophotometer. Slow additions were performed using a 205S Watsons-Marlow peristaltic pump.

THF was distilled over sodium/benzophenone and all other anhydrous solvents were purchased from Sigma-Aldrich or Alfa Aesar and used as received. All other reagents were purchased from Sigma-Aldrich, Fisher Scientific, Alfa Aesar or Acros and used has received. Column chromatography was performed using silica gel (60 Å, 230−400 mesh). Petroleum ether refers to the fraction obtained at 40-60 ˚C. All reactions were carried out using standard Schlenk techniques under argon, unless stated otherwise. Degassed solvents were prepared either by purging with argon/nitrogen or by freeze-pump-thaw (three times) for reactions involving organometallic reagents. For ATRP; methyl methacrylate was passed through a short alumina column (activated, basic, Brockmann I) and degassed by three freeze-pump-thaw cycles. Xylenes (mixture of isomers) were distilled over calcium hydride and degassed by three freeze-pump-thaw cycles. Copper(I) bromide was refluxed in glacial acetic acid for 1 hour, filtered and washed with glacial acetic acid, ethanol, diethyl ether then dried under vacuum at room temperature for 48 hours. 4,4'-Dinonyl-2,2'-dipyridyl (dNbpy) was used has received from Alfa Aesar.

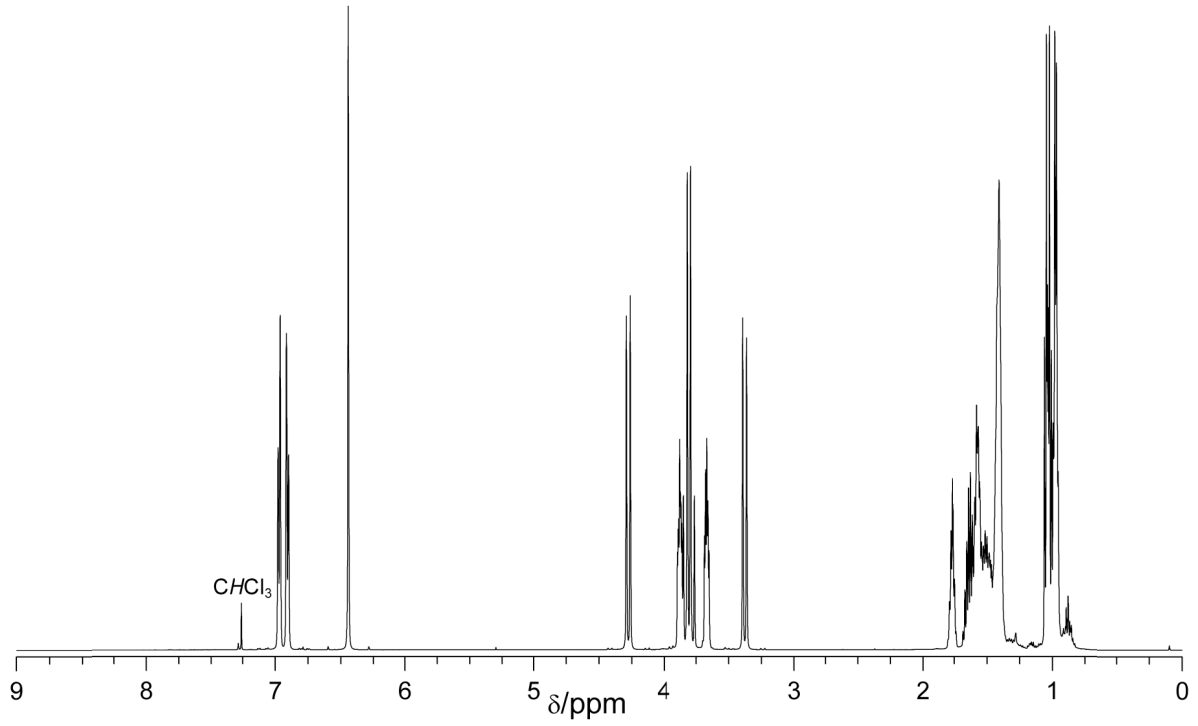
1.2 Synthesis of 5,8-Diethylhexyloxy-2,11-dithia[3.3]paracyclophane

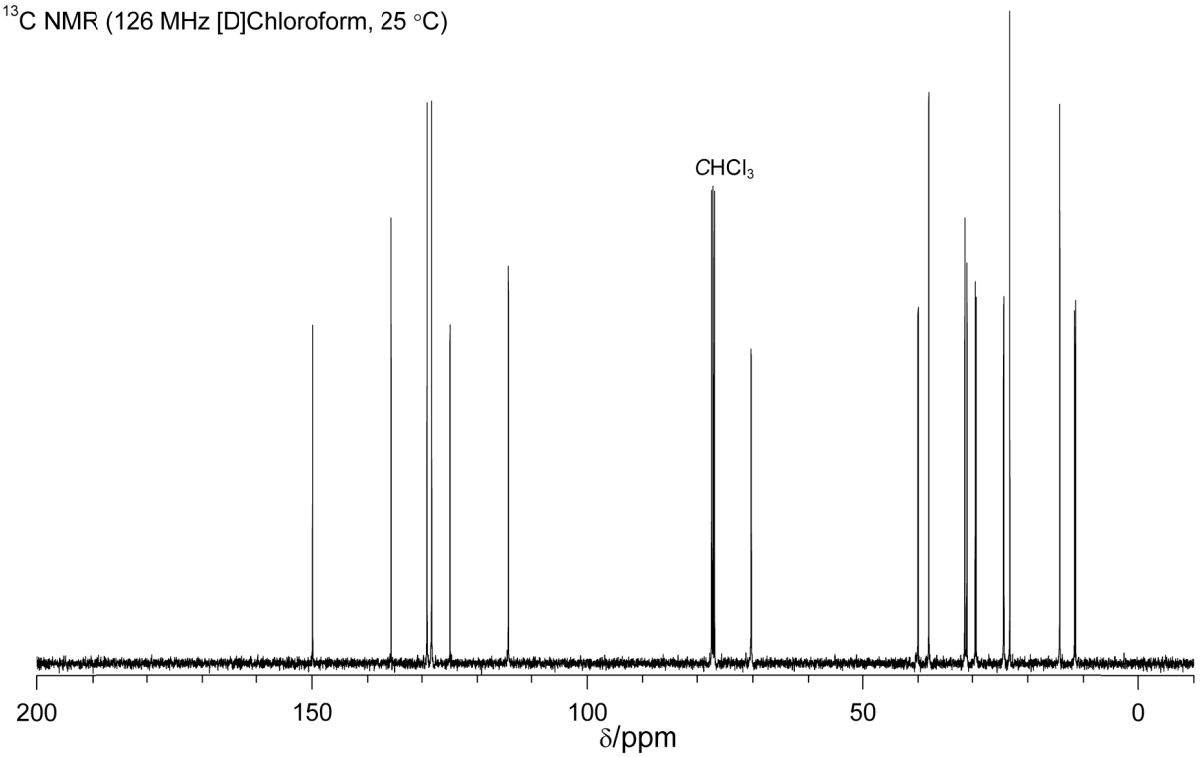


1,4-Benzenedimethanethiol (14.42 g, 84.7 mmol) and 2,5-bis(bromomethyl)-1,4-diethylhexyloxybenzene (44.07 g, 84.7 mmol) were dissolved in deoxygenated toluene (1000

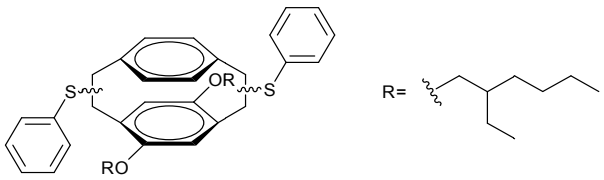
mL) under argon. This solution was added dropwise over 72 hours to potassium hydroxide (14.25 g, 254 mmol) in deoxygenated ethanol (2500 mL), at room temperature under argon. After an additional 2 hours stirring the solvent was removed *in vacuo* and the residue dissolved in dichloromethane (1 × 500 mL) and water (1 × 500 mL). The organic layer was separated and the aqueous layer extracted with dichloromethane (2 × 500 mL). The organic layers were combined, dried over magnesium sulfate, filtered and the solvent removed *in vacuo* to reveal an orange oil. Purification was performed *via* column chromatography (dichloromethane : petroleum ether, 20 : 80) to reveal a colourless oil (21.57 g, 48%). ^{1}H NMR (500 MHz, [D]Chloroform, 25°C): δ = 6.98 (d, ^{3}J(H,H) =8 Hz, 2H; H-*e*), 6.92 (d, ^{3}J(H,H) = 8 Hz, 2H; H-*d*), 6.45 (s, 2H; H-*a*), 4.29 (d, ^{2}J(H,H) = 15 Hz, 2H; H-*b*'), 3.90-3.85 (m, 2H; H-*f*,*f*'), 3.83 (d, ^{2}J(H,H) = 15 Hz, 2H; H-*c'*), 3.79 (d, ^{2}J(H,H) = 15 Hz, 2H; H-*c*), 3.70-3.66 (m, 2H; H-*f*,*f'*), 3.39 (d, ^{2}J(H,H) = 15 Hz, 2H; H-*b*), 1.72-1.62 (m, 2H; H-*g*), 1.70-1.37 (m, 16H; CH_2), 1.09-0.94 ppm (m, 12H; CH_3). ^{13}C NMR (126 MHz, [D]Chloroform, 25°C): 149.91, 135.59, 129.08, 128.26, (124.94, 124.92), (114.37, 114.35), (70.33, 70.29), (40.01, 39.95), 38.04, 31.32, (30.96, 30.93), (29.46, 29.29), (24.38, 24.30), 23.26, (14.29, 14.27), (11.61, 11.43), (peaks in brackets indicate signal doubling has a result of the presence of enatiomers (*R*,*R* and *S*,*S*) and diastereoisomers (*R*,*S* and *S*,*R*) has a consequence of the racemic 2-(*R*/*S*)ethylhexyl). IR (film): ν cm^{-1}: 1037, 1206, 1422, 1464, 1505, 2856, 2924, 2956. HR-MS (EI, M^{+}) for $C_{32}H_{48}O_2S_2$ calc.: 528.3106, found: *m*/*z* 528.3093.

^{1}H NMR (500 MHz [D]Chloroform, 25 °C)



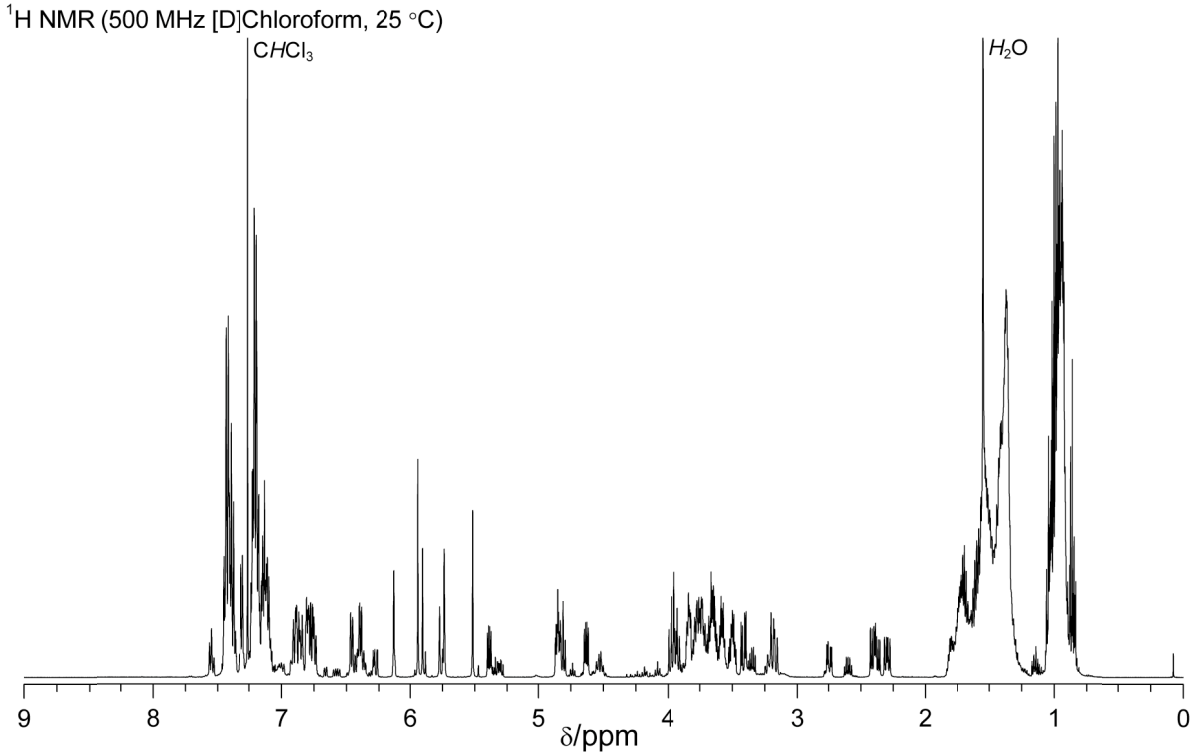


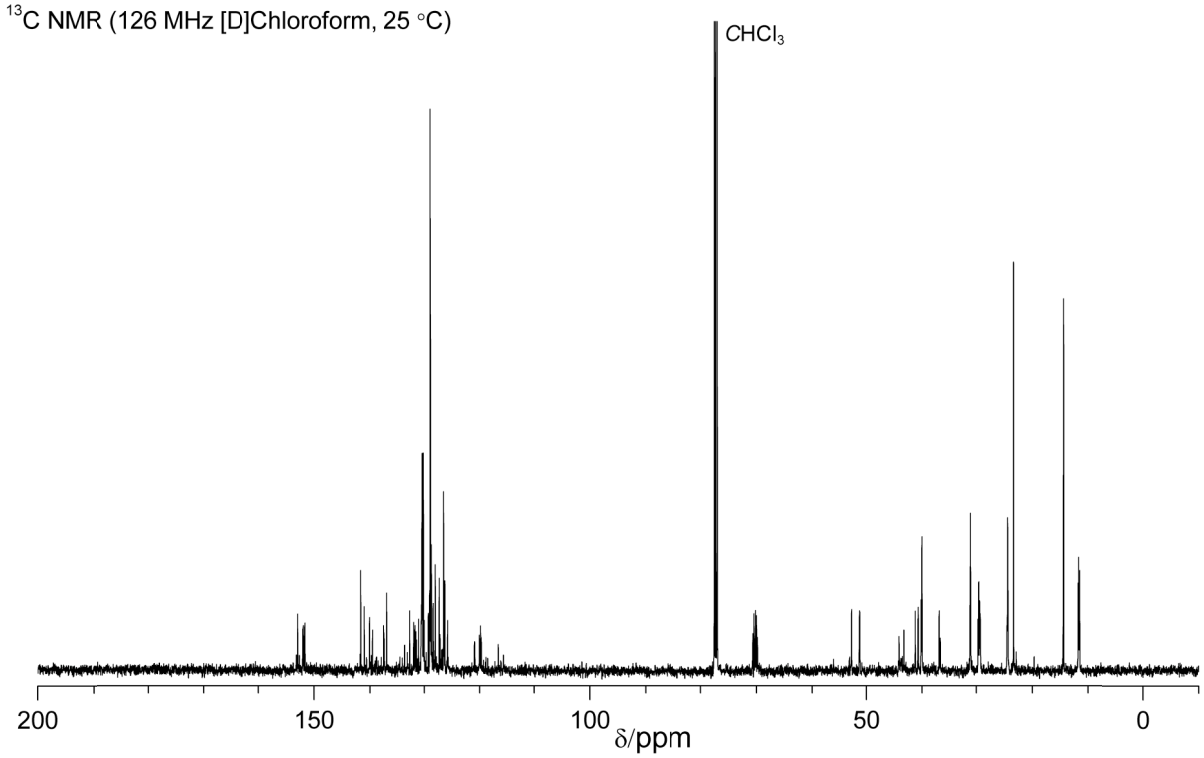
1.3 Benzyne Induced Stevens Rearrangement of 5,8-Diethylhexyloxy-2,11-dithia[3.3]paracyclophane (7)



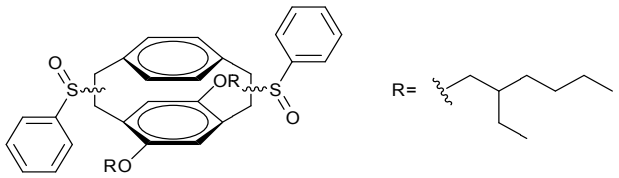
5,8-Diethylhexyloxy-2,11-dithia[3.3]paracyclophane (10.11 g, 19.1 mmol) and 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (14.26 g, 47.5 mmol) were dissolved in anhydrous THF (350 mL) under argon and stirred at room temperature. Tetrabutylammonium fluoride trihydrate (18.09 g, 57.4 mmol) was dissolved in THF (100 mL) and added dropwise to the former solution over 2 hours. The solution was stirred for an additional hour and the solvent removed in *vacuo* revealing a pale yellow solid. The residue was purified by column chromatography (dichloromethane : petroleum ether, 20 : 80), resulting in compound **7** as a pale yellow semi-solid product (11.20 g, 86%). IR (film): ν cm^{-1}: 1026, 1193, 1210, 1480,

1584, 2858, 2924, 2956, 2058. HR-MS (EI, M^+) for $C_{44}H_{56}O_2S_2$ calc: 680.3716, found: *m*/*z* 680.3697.

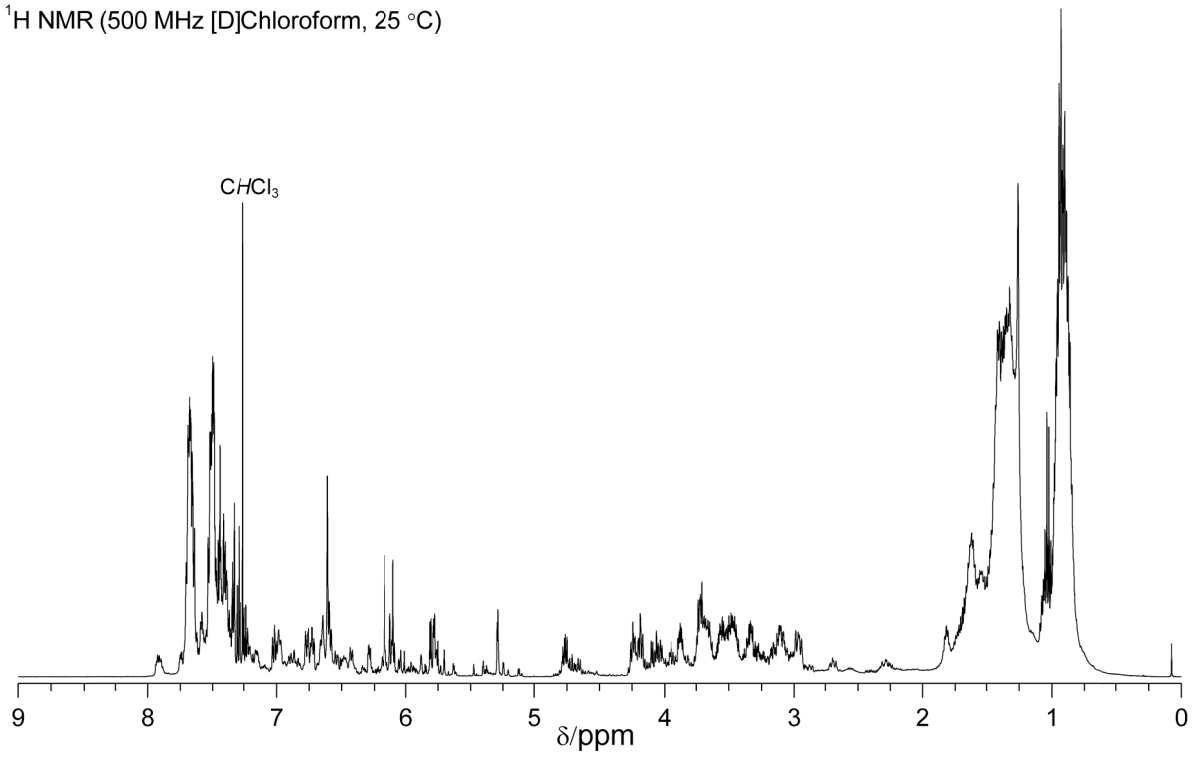




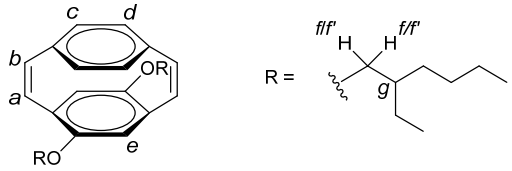
1.4 Oxidation of Phenyl Sulfides of Compound 7 (8)



Compound **7** (6.10 g, 9.0 mmol) was dissolved in toluene (200 mL) and acetic acid (80 mL) under argon. At 0 ˚C hydrogen peroxide (30 wt. % in H_2O, 2.0 mL, 19.7 mmol) was added dropwise over a period of 30 minutes, followed by warming to room temperature. After 20 hours the organic layer was washed with water (3 × 100 mL), saturated sodium bicarbonate (1 × 100 mL), dried over magnesium sulfate and filtered. The solvent was removed *in vacuo* to reveal compound **8** has a highly viscous oil (5.80 g, 92%), which was used without further purification. IR (film): ν cm^{-1} 1030, 1210, 1499, 1584, 2925, 3058. HR-MS (EI, M^+) for $C_{44}H_{56}O_4S_2$ calc.: 712.3615, found: *m*/*z* 712.3596.

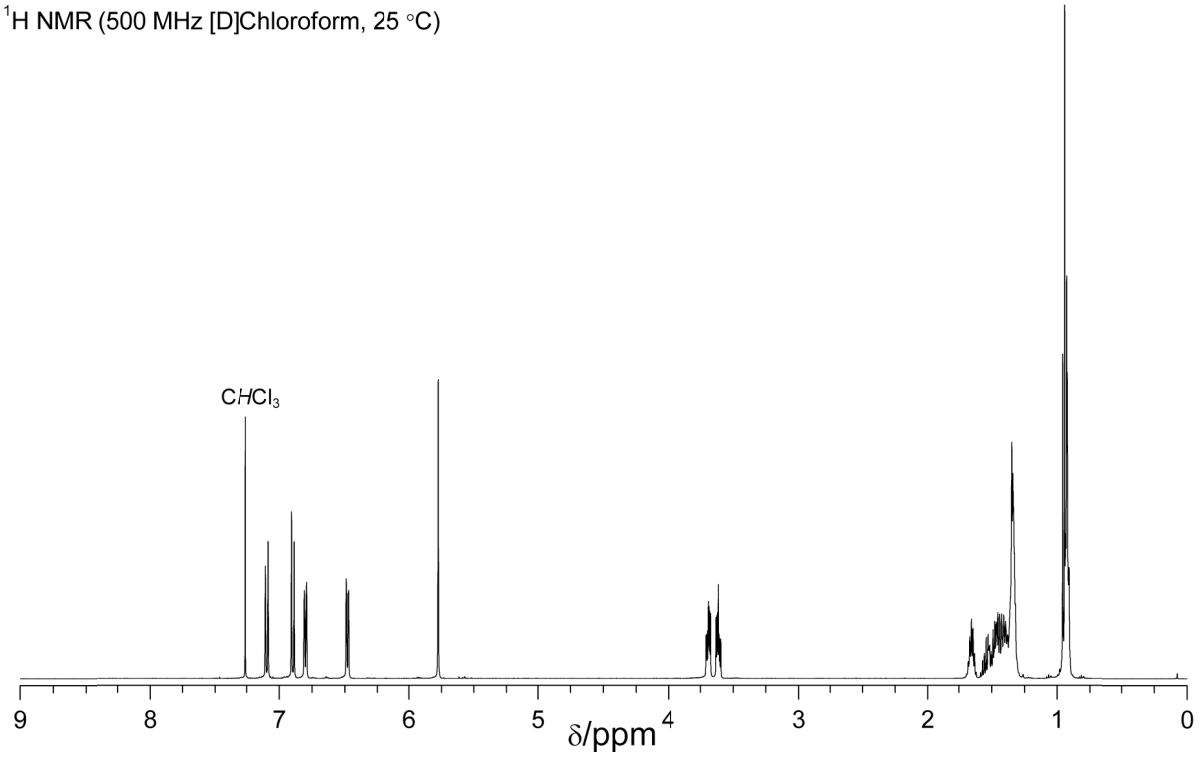


1.5 Synthesis of 4,7-Diethylhexyloxy-[2.2]paracyclophane-1,9-diene (1)

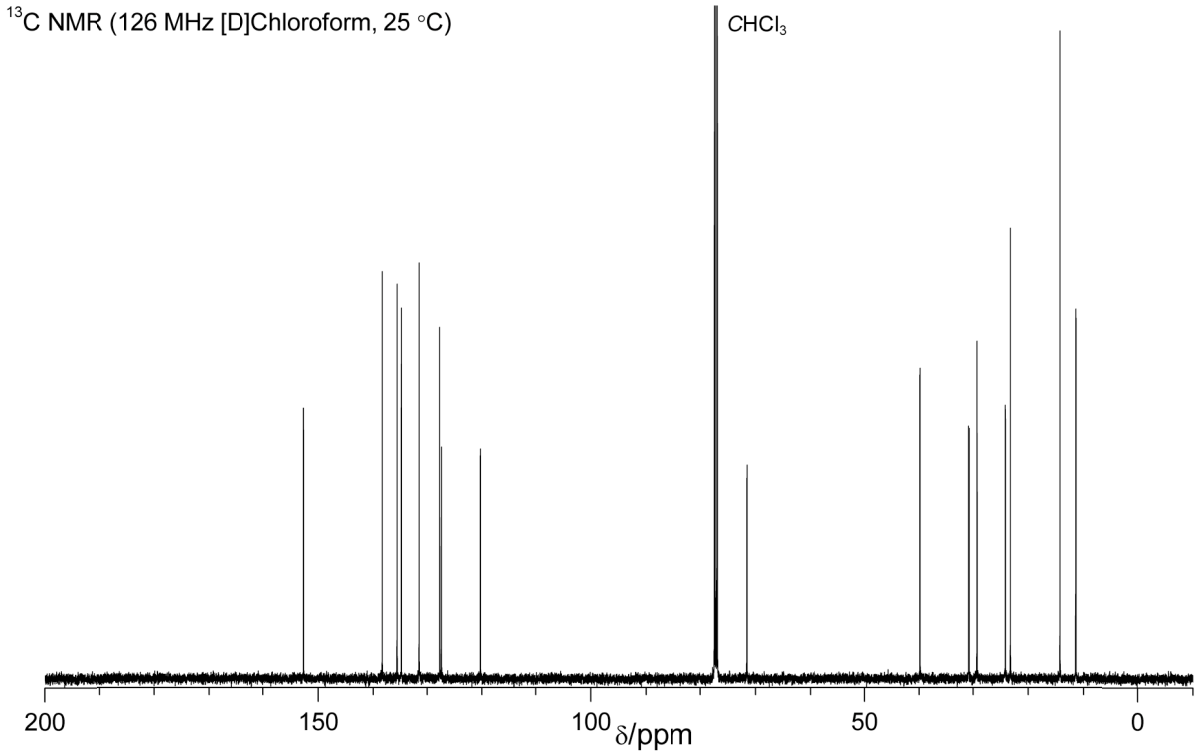


Compound **8** (5.70 g, 8.0 mmol) was dissolved in anhydrous deoxygenated *N*,*N*-dimethylacetamide (300 mL) and heated to 156 ˚C with an argon purge. After 20 hours the reaction was cooled to room temperature and the solvent removed *in vacuo* to reveal a dark brown oil. The crude product was purified by column chromatography (hexane to dichloromethane : hexane, 20 : 80) to obtain a colourless oil (1.37 g, 37 %). ^{1}H NMR (500 MHz, [D]Chloroform, 25°C): 7.12 (d, ^{3}J(H,H) = 10 Hz, 2H; H-*a*), 6.92 (d, ^{3}J(H,H) = 10 Hz, 2H; H-*b)*, 6.82 (d, ^{3}J(H,H) = 8 Hz, 2H; H-*d*), 6.50 (d, ^{3}J(H,H) = 8 Hz, 2H; H-*c*), 5.80 (s, 2H; H-*e*), 3.74-3.66 (m, 2H; H-*f*/*f'*), 3.66-3.57 (m, 2H; H-*f*/*f'*), 1.73-1.59 (m, 2H; H-*g*), 1.59-1.25 (m, 16H), 1.04-0.79 (m, 12H). ^{13}C NMR (126 MHz, [D]Chloroform, 25°C): 152.63, 138.37, 135.47, 134.67, 131.44, 127.69, (127.37, 127.35), (120.29, 120.25), (71.56, 71.52), (39.88, 39.86), (30.81, 30.71), (29.30, 29.27), (24.16, 24.13), (23.24, 23.23), 14.26, (11.42, 11.35), (peaks in brackets indicate signal doubling, *as per explanation in 1.2*). IR (film): ν cm^{-1}: 697(m), 894(m), 1036(m), 1193(m), 1377(m), 1463(m), 1488(m), 2858 (m), 2926(m), 2957(m). HR-MS (EI, M^{+}) for $C_{32}H_{44}O_2$ calc.: 460.3336, found: *m*/*z* 460.3341. Elemental analysis: found; C, 83.06; H, 9.73%. Calc. for $C_{32}H_{48}O_2$; C, 83.43; H, 9.63%.

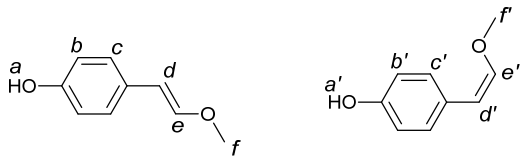
^{1}H NMR (500 MHz [D]Chloroform, 25 °C)



^{13}C NMR (126 MHz [D]Chloroform, 25 °C)

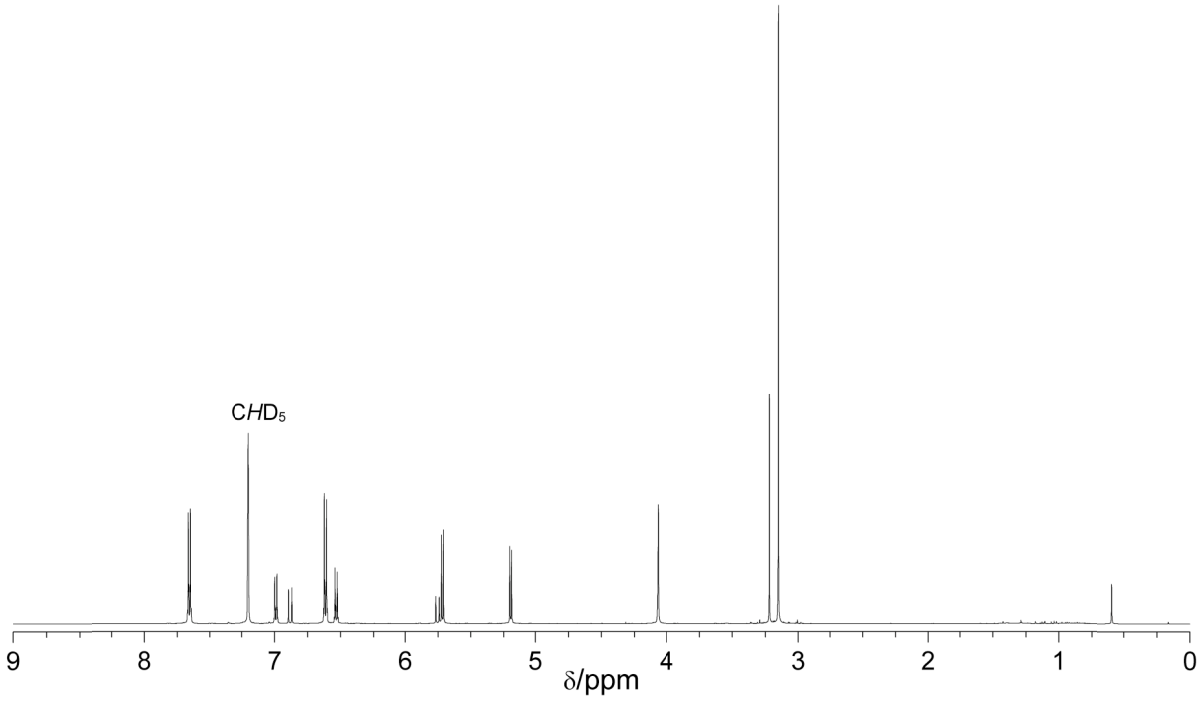


1.6 Synthesis of 4-[(*E*/*Z*)-2-Methoxyvinyl]phenol

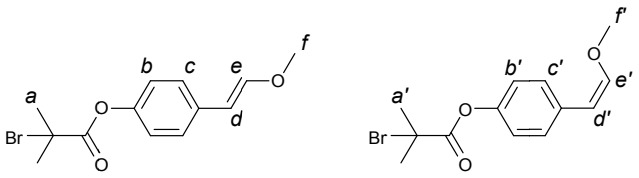


4-Hydroxybenzaldehyde (4.75 g, 38.9 mmol) and (methoxymethyl)triphenylphosphonium chloride (16.00 g, 46.7 mmol) were added to an oven dried Schlenk tube under argon. Anhydrous THF (80 mL) was added and the mixture cooled to 0 °C. Potassium *tert*-butoxide (10.91 g, 97.2 mmol) was added portionwise over a period of 2 hours under an argon stream, warmed to room temperature and stirred overnight. The reaction was quenched by the addition of saturated aqueous ammonium chloride (100 mL) and extracted with dichloromethane (3 × 100 mL). The organic layers were collected, dried over magnesium sulfate, filtered and the solvent removed *in vacuo*. The pale orange oil was purified by column chromatography (diethyl ether : petroleum ether, 20 : 80) to reveal a colourless viscous oil (4.72 g, 81%). The product constituted of an inseparable mixture of *E*/*Z*-vinylene isomers in a ratio of 1.5 : 1 (by integration of the methoxy protons in ^{1}H NMR spectroscopy). The compound was unstable in storage even under argon at -25 °C and was used quickly in subsequent reactions. ^{1}H NMR (500 MHz, [D$_6$]Benzene, 25°C): δ = (*E* isomer); 7.05 (AA'BB', ^{3}J(H,H) = 9 Hz, 2H; H-*c*), 6.94 (d, ^{3}J(H,H) = 13 Hz, 1H; H-*e*), 6.59 (AA'BB', ^{3}J(H,H) = 9 Hz, 2H; H-*b*), 5.80 (d, ^{3}J(H,H) = 13 Hz, 1H; H-*d*), 4.13 (s, 1H; H-*a*), 3.28 (s, 3H; H-*f*). (*Z* isomer); 7.72 (AA'BB', ^{3}J(H,H) = 9 Hz, 2H; H-*c'*), 6.67 (AA'BB', ^{3}J(H,H) = 9 Hz, 2H; H-*b*'), 5.78 (d, ^{3}J(H,H) = 7 Hz, 1H; H-*e'*), 5.26 (d, ^{3}J(H,H) = 7 Hz, 1H; H-*d'*), 4.13 (s, 1H; H-*a'*), 3.21 (s, 3H, H-*f'*).^{13}C NMR (126 MHz, [D]CDCl$_3$, 25°C): (*E*/*Z* isomer) 154.55, 154.43, 147.74, 146.26, 130.17, 129.36, 129.26, 126.76, 115.87, 115.42, 105.99, 105.19, 59.92, 55.97. IR (film): ν cm^{-1}: 836, 1228, 1650, 1510, 1650, 2935, 3033, (EI$^+$) GC-MS *m*/*z*: found; (retention time: 10.09 min); [M]$^+$ 150, [M-CHOCH$_3$]$^+$ 107, calc.; [M]$^+$ 150, [M-CHOCH$_3$]$^+$ 107 and (retention time: 10.14 min); [M]$^+$ 150, [M-CHOCH$_3$]$^+$ 107, calc.; [M]$^+$ 150, [M-CHOCH$_3$]$^+$ 107. HR-MS (EI, M$^+$) for $C_{32}H_{44}O_2$ calc.: 460.3336, found: *m*/*z* 460.3341.

^{1}H NMR (500 MHz [D_6] Benzene, 25 °C)



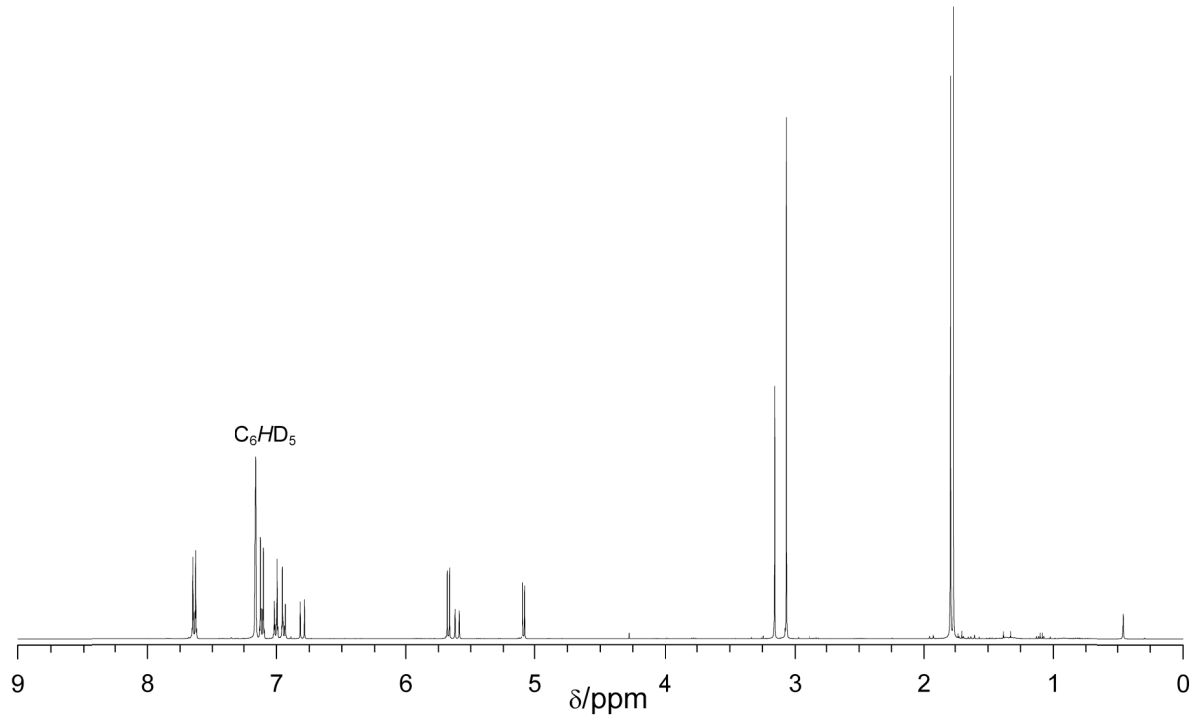
1.7 Synthesis of 4-[(*E*/*Z*)-2-Methoxyvinyl]phenyl-2-bromoisobutyrate (2)

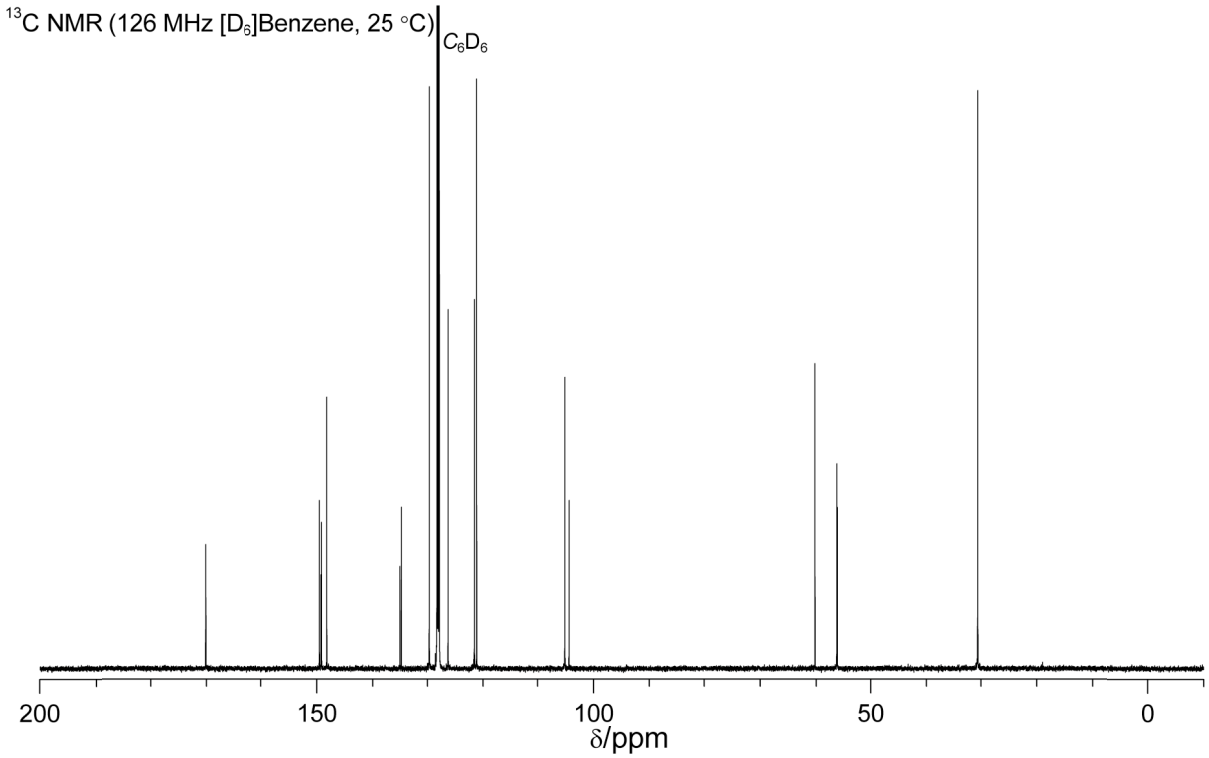


The compound 4-[(*E*/*Z*)-2-methoxyvinyl]phenol (350 mg, 2.33 mmol), anhydrous dichloromethane (10 mL) and anhydrous triethylamine (472 mg, 4.66 mmol) were added to an oven dried flask and the solution cooled to 0 °C under argon. α-Bromoisobutyryl bromide (643 mg, 2.80 mmol) was added dropwise over a period of 1 hour, warmed to room temperature and stirred for 18 hours. Saturated aqueous sodium hydrogen carbonate was added (10 mL) and the organic layer was separated. The organic layer was further washed with saturated aqueous sodium hydrogen carbonate (2 × 10 mL) and 1 M aqueous hydrochloric acid (3 × 10 mL). The organic layer was dried over magnesium sulfate, filtered and the solvent removed *in vacou*. The orange oil was purified by column chromatography

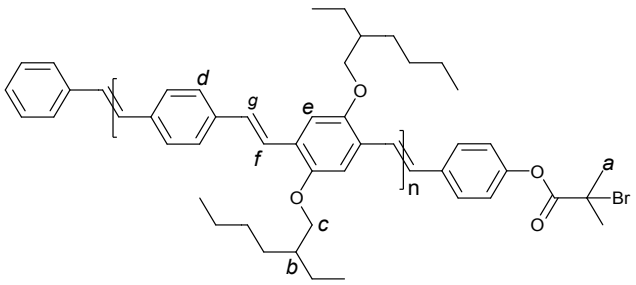
(diethyl ether : petroleum ether, 20 : 80) to reveal a viscous colourless oil (679 mg, 97%) consisting of *E*/*Z*-vinylene isomers in a ratio of 1 : 1.25 (by integration of the methoxy protons in ^{1}H NMR spectroscopy). The product was stored at -25 °C in an argon filled glovebox. ^{1}H NMR (500 MHz, [D_6]Benzene, 25°C): δ = (*Z* isomer); 7.64 (AA'BB', ^{3}J(H,H) = 9Hz, 2H; H-*c'*), 7.11 (AA'BB', ^{3}J(H,H) = 9 Hz, 2H; H-*b'*), 5.67 (d, ^{3}J(H,H) = 7 Hz, 1H; H-*e'*), 5.09 (d, ^{3}J(H,H) = 7 Hz, 1H; H-*d'*), 3.07 (s, 3H; H-*f'*), 1.77 (s, 6H; H-*a'*). (*E* isomer); 7.01 (AA'BB', ^{3}J(H,H) = 9 Hz, 2H; H-*c*), 6.94 (AA'BB', ^{3}J(H,H) = 9 Hz, 2H; H-*b*), 6.80 (d, ^{3}J(H,H) = 13 Hz, 1H; H-*e*), 5.61 (d, ^{3}J(H,H) = 13 Hz, 2H; H-*d*), 3.16 (s, 3H; H-*f*), 1.80 (s, 6H; H-*a*). ^{13}C NMR (126 MHz, [D_6]Benzene, 25°C): (*E*/*Z* isomer); 170.11, 170.07, 149.55, 149.26, 149.15, 148.22, 134.95, 134.68, 129.66, 126.67, 121.55, 121.12, 105.10, 104.35, 60.21, 56.10, 56.00, 55.98, 30.56, 30.55. IR (film): ν cm^{-1}: 731, 823, 878, 935, 1090, 1137, 1166, 1189, 1264, 1503, 1651, 1746, 2934. Elemental analysis: Found: C, 51.90; H, 5.07; Br, 26.76. Calc. for $C_{13}H_{15}O_3Br$: C, 52.19; H, 5.05; Br, 26.71%. HR-MS (EI, M^+) for $C_{13}H_{15}O_3Br$ calc.: 298.0199, found: *m/z* 298.0199.

^{1}H NMR (500 MHz [D_6]Benzene, 25 °C)



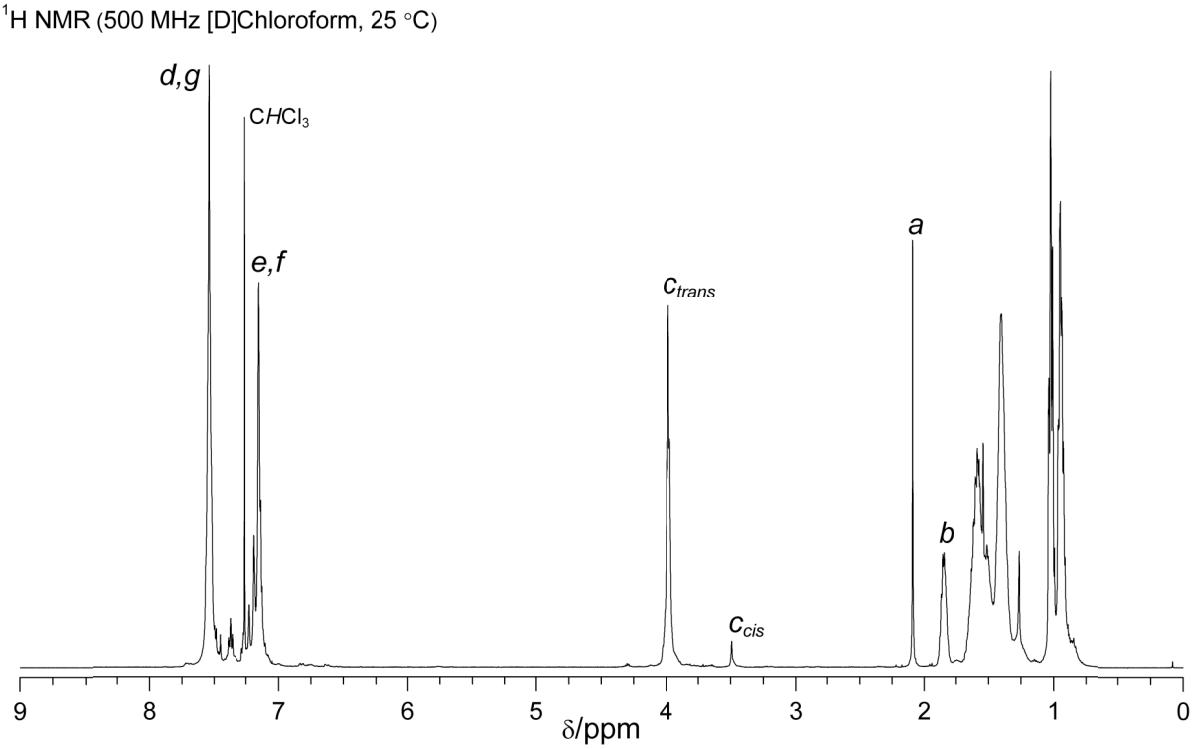


1.8 Synthesis of α-Bromoester Functionalised Monotelechelic Poly(*p*-phenylenevinylene-2,5-diethylhexyloxy-*p*-phenylenevinylene)s (4a-d)

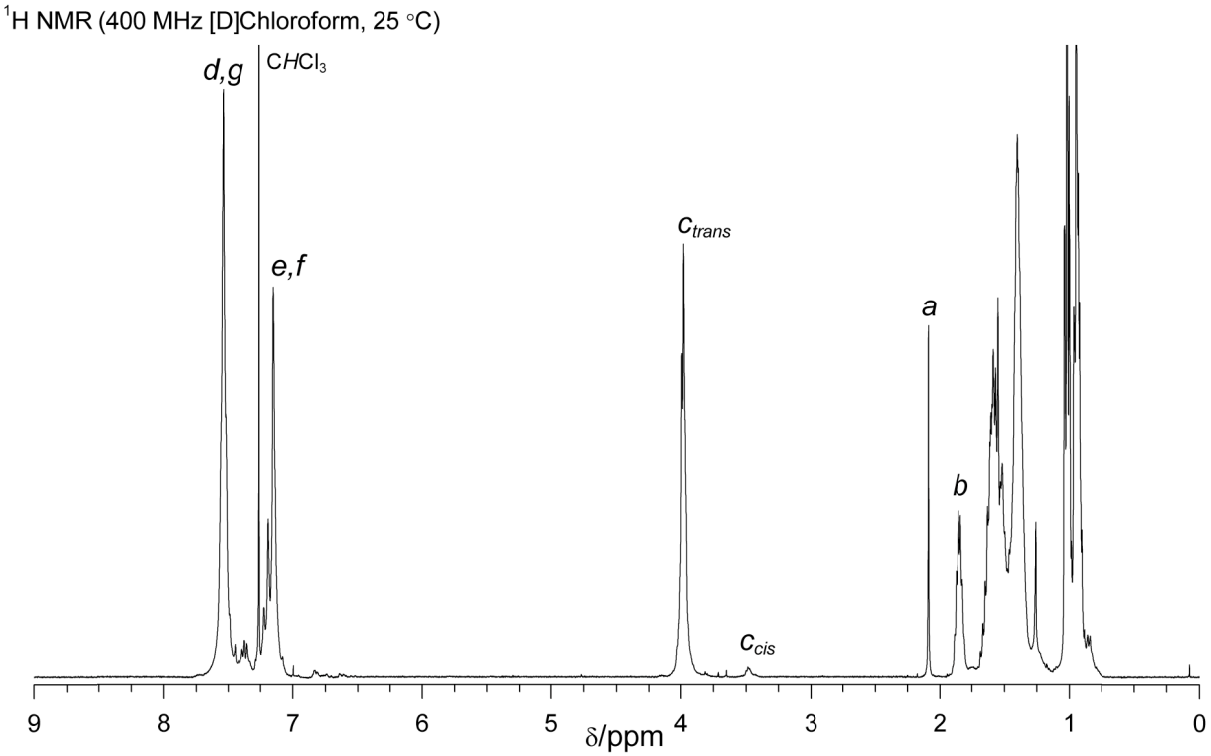


General polymerisation method for α-bromoester functionalised monotelechelic poly(*p*-phenylenevinylene-2,5-diethylhexyloxy-*p*-phenylenevinylene)s (**4a-d**): (Polymer **4a**) In an argon filled glove box cyclophanediene **1**, (100 mg, 217 μmol, 5 *eq*.) and Grubbs 2 (36.9 mg, 43.3 μmol, 1 *eq*.) were added to a vial with a stirrer bar, followed by THF ($[\mathbf{1}]_I = [0.1]_I = 2.17$ mL). The vial was sealed and removed from the glove box, wrapped in foil and stirred at room temperature for 10 mins. The polymerisation was placed in a preheated oil bath at 40 °C and stirred for 8 hours. The polymerisation was cooled to room temperature and transferred back into the glove box. Vinyl ether **2** (260 mg, 868 μmol, 20 *eq*.) was added, the

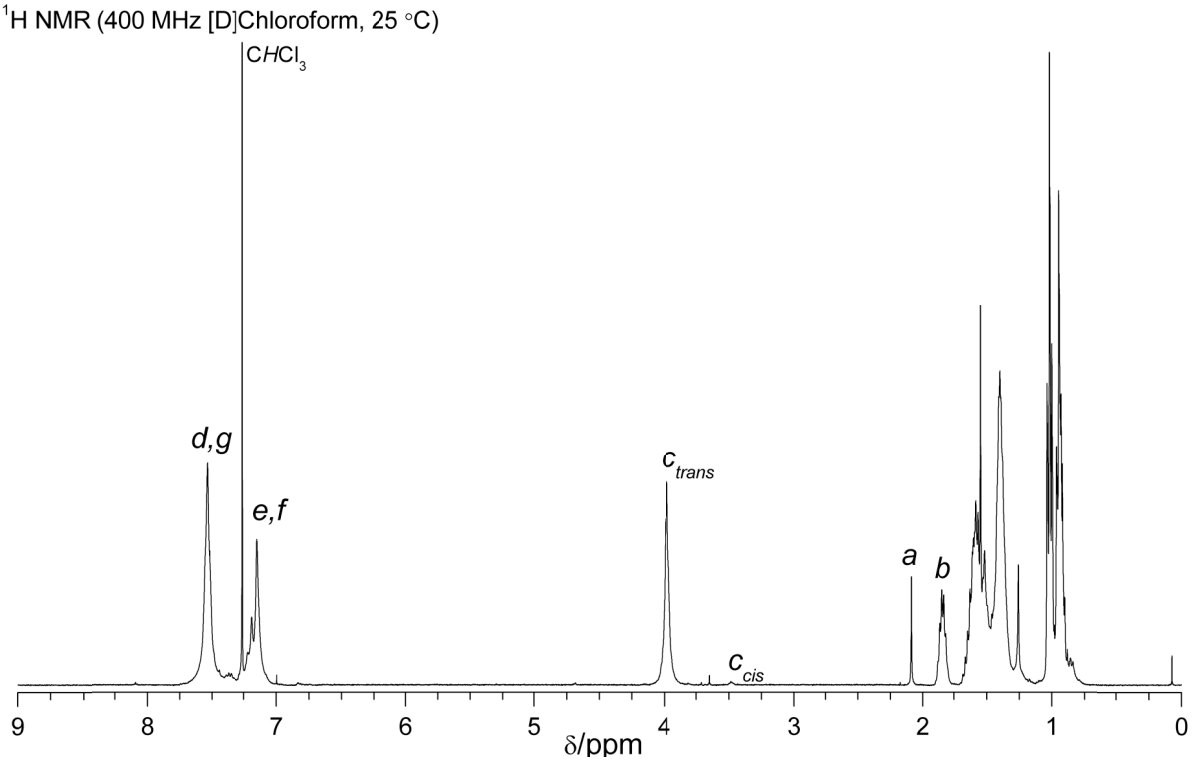
vial sealed, wrapped in foil and removed from the glove box. The reaction was heated at 40 °C, stirred for an additional 24 hours and cooled to room temperature. The reaction was precipitated into a short methanol/Celite plug, washed with methanol, the polymer extracted with hot chloroform and the solvent removed in *vacuo*. The precipitation procedure was repeated to yield polymer **4a** has an orange film (96 mg, 83%), after evaporation of the solvent. ^{1}H NMR (500 MHz, [D]Chloroform, 25 °C): δ = 7.66-7.31 (br m, 6H, H-*d*, H-*g*), 7.30-7.04 (br m, 4H, H-*e,* H-*f*), 4.06-3.89 (br m, 3.85H, H-c_{trans}), 3.52-3.46 (br m, 0.15H, H-c_{cis}), 2.09 (s, 1.10H, H-*a*), 1.92-1.72 (br m, 2H, H-*b*), 1.70-1.20(br m, 16H), 1.10-0.81 (br m, 12H). GPC(THF): M_n = 4.7 kg mol^{-1}, $Đ_M$ = 1.36.



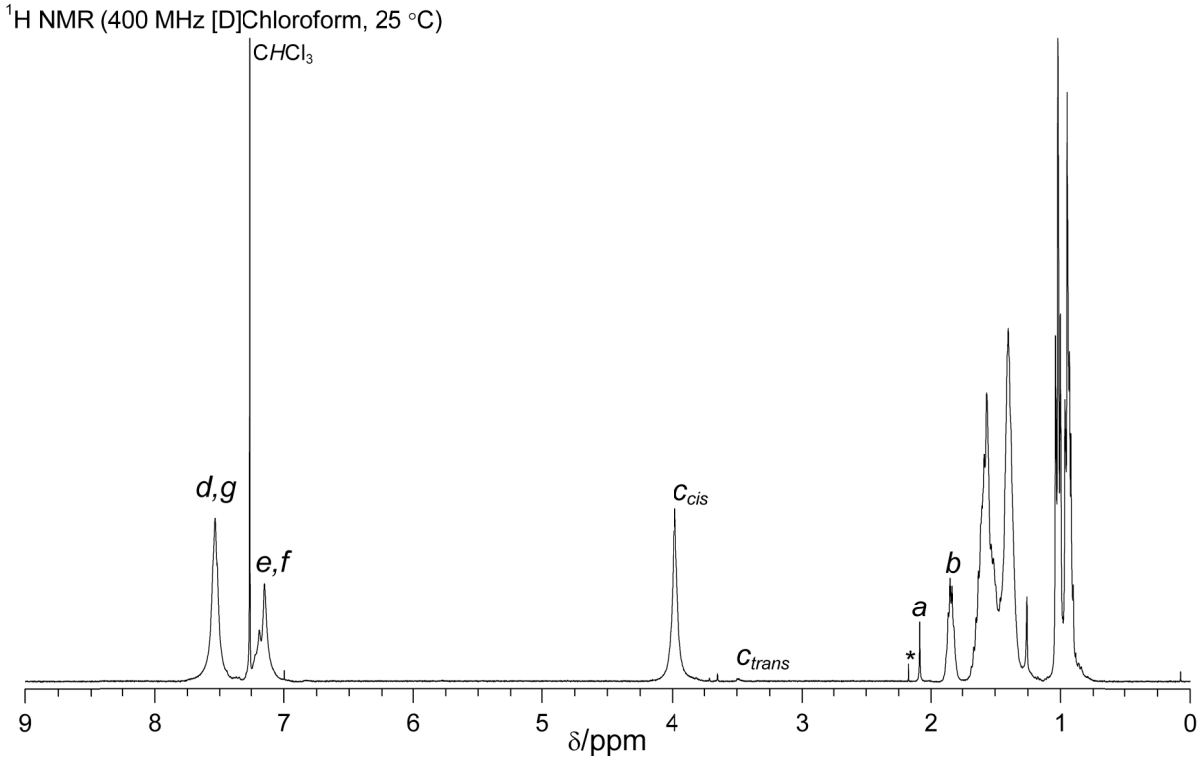
(Polymer **4b**) Following the general polymerisation procedure for polymer **4a**. Cyclophanediene **1** (102 mg, 221 μmol, 10 *eq*.), Grubbs 2 (18.8 mg, 22.1 μmol, 1 *eq*.) and THF ($[\mathbf{1}]_I$ = $[0.1]_I$ = 2.21 mL) stirred at 40 °C for 20 hours. Termination reaction performed with vinyl ether **2** (132 mg, 443 μmol, 20 *eq*.) at 40 °C for 24 hours and polymer **4b** was isolated as an orange film (98 mg, 89%). ^{1}H NMR (400 MHz, [D]Chloroform, 25 °C): δ = 7.67-7.40 (br m, 6H, H-*d*, H-*g*), 7.26-7.01 (br m, 4H, H-*e,* H-*f*), 4.06-3.85 (br m, 3.89H, H-c_{trans}), 3.55-3.40 (br m, 0.11H, H-c_{cis}), 2.09 (s, 0.59 H, H-*a)*, 1.90-1.79 (br m, 2H, H-*b*), 1.70-1.20 (br m, 16H), 1.07-0.87 (br m, 12H). GPC(THF): M_n = 9.0 kg mol^{-1}, $Đ_M$ = 1.51.



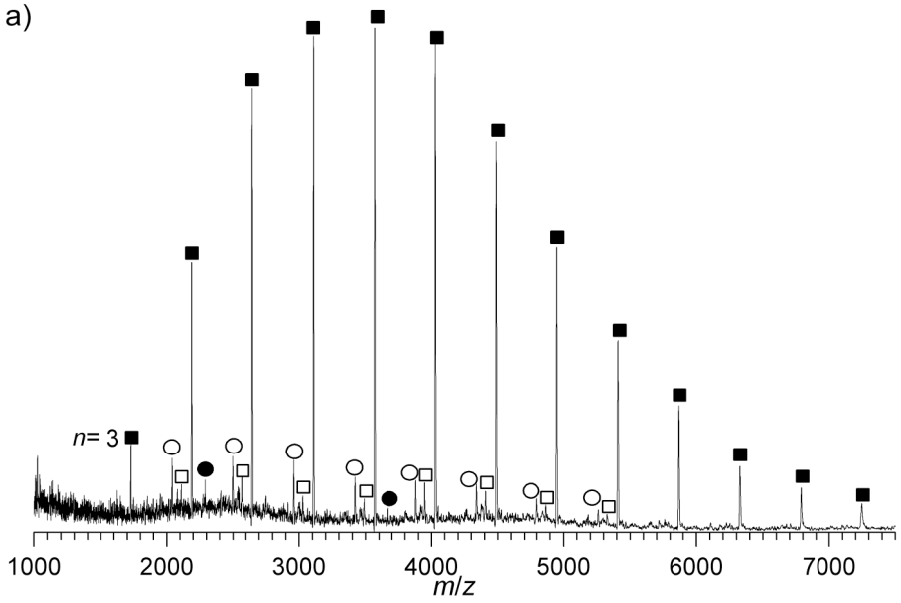
(Polymer **4c**) Following the general polymerisation procedure for polymer **4a**. Cyclophanediene **1** (107 mg, 232 μmol, 20 *eq*.), Grubbs 2 (9.9 mg, 11.6 μmol, 1 *eq*.) and THF ($[\mathbf{1}]_I = [0.1]_I$ = 2.32 mL) stirred at 40 °C for 30 hours. Termination reaction performed with vinyl ether **2** (69.5 mg, 232 μmol, 20 *eq*.) at 40 °C for 24 hours and polymer **4c** was isolated as an orange film (97 mg, 87%). ^{1}H NMR (400 MHz, [D]Chloroform, 25 °C): δ = 7.71-7.34 (br m, 6H, H-*d*, H-*g*), 7.30-7.01 (br m, 4H, H-*e,* H-*f*) 4.11-3.83 (br m, 3.96H, H-c_{trans}), 3.51-3.45 (br m, 0.04H, H-c_{cis}), 2.09 (s, 0.32 H, H-*a)*, 1.92-1.78 (br m, 2H, H-*b*), 1.70-1.20 (br m, 16H), 1.08-0.81 (br m, 12H). GPC(THF): M_n = 22.8 kg mol^{-1}, $Đ_M$ = 1.44.

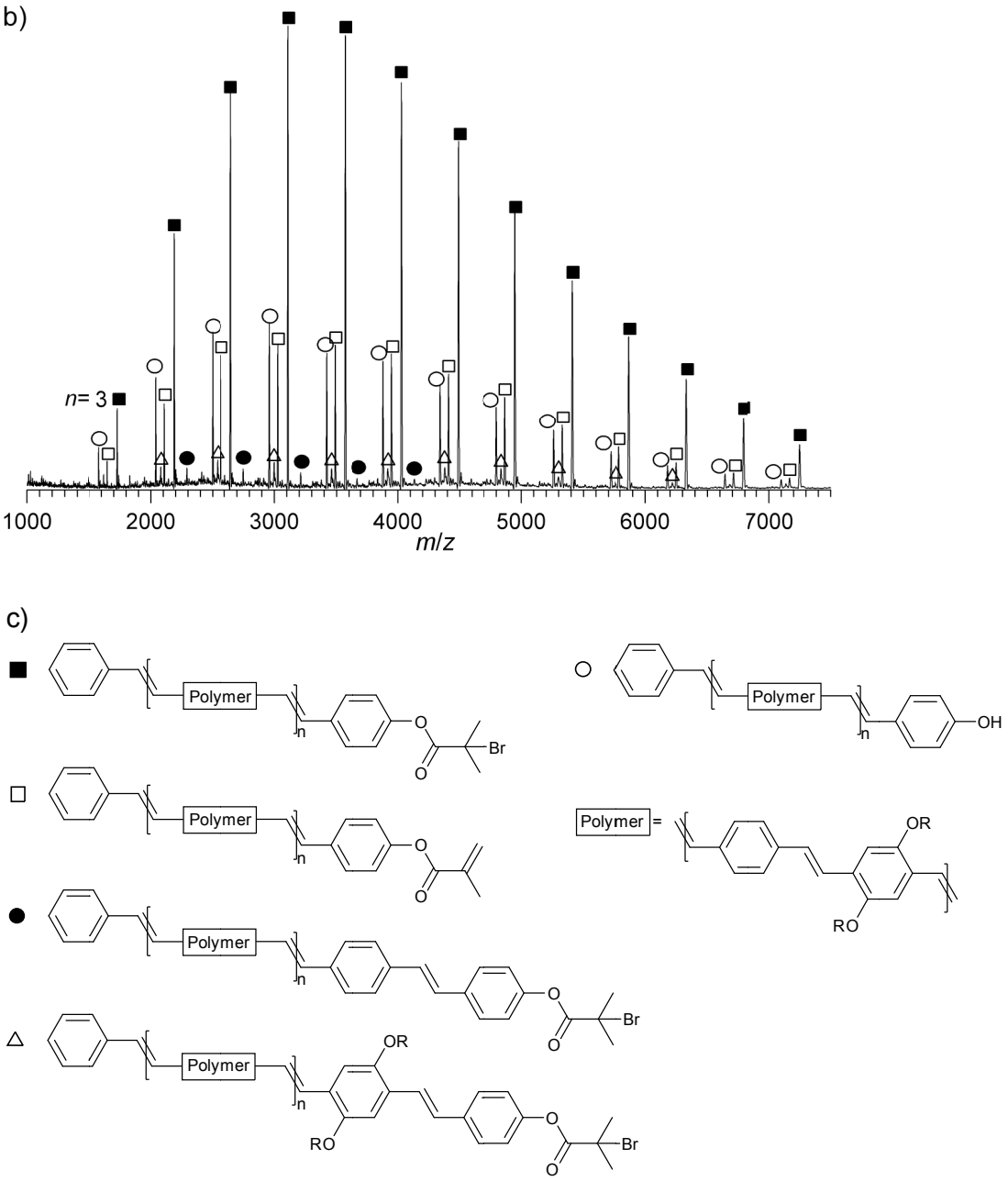


(Polymer **4d**) Following the general polymerisation procedure for polymer **4a**. Cyclophanediene **1** (111 mg, 241 μmol, 30 *eq*.), Grubbs 2 (6.8 mg, 8.0 μmol, 1 *eq*.) and THF ($[\mathbf{1}]_I = [0.1]_I = 2.41$ mL) stirred at 40 °C for 40 hours. Termination reaction performed with vinyl ether **2** (48.0 mg, 161 μmol, 20 *eq*.) at 40 °C for 24 hours and polymer **4d** was isolated as an orange film (103 mg, 90%). ^{1}H NMR (400 MHz, [D]Chloroform, 25 °C): δ = 7.83-7.34 (br m, 6H, H-*d*, H-*g*), 7.32-6.96 (br m, 4H, H-*e,* H-*f*), 4.20-3.73 (br m, 4H, H-c_{trans}), 2.09 (s, 0.18 H, H-*a)*, 1.94-1.75 (br m, 2H, H-*b*), 1.71-1.20 (br m, 16H), 1.08-0.80 (br m, 12H). GPC(THF): $M_n = 39.0$ kg mol^{-1}, $Đ_M = 1.45$.



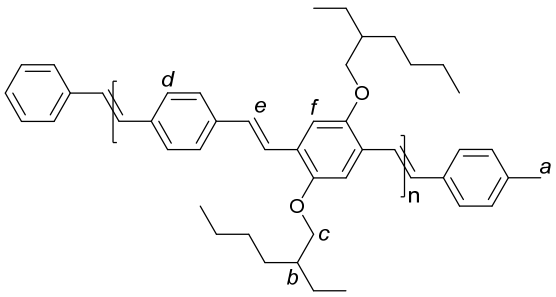
1.9 MALDI-TOF-MS of α-Bromoester Functionalised Monotelechelic Poly(*p*-phenylenevinylene-2,5-diethylhexyloxy-*p*-phenylenevinylene) (4b)



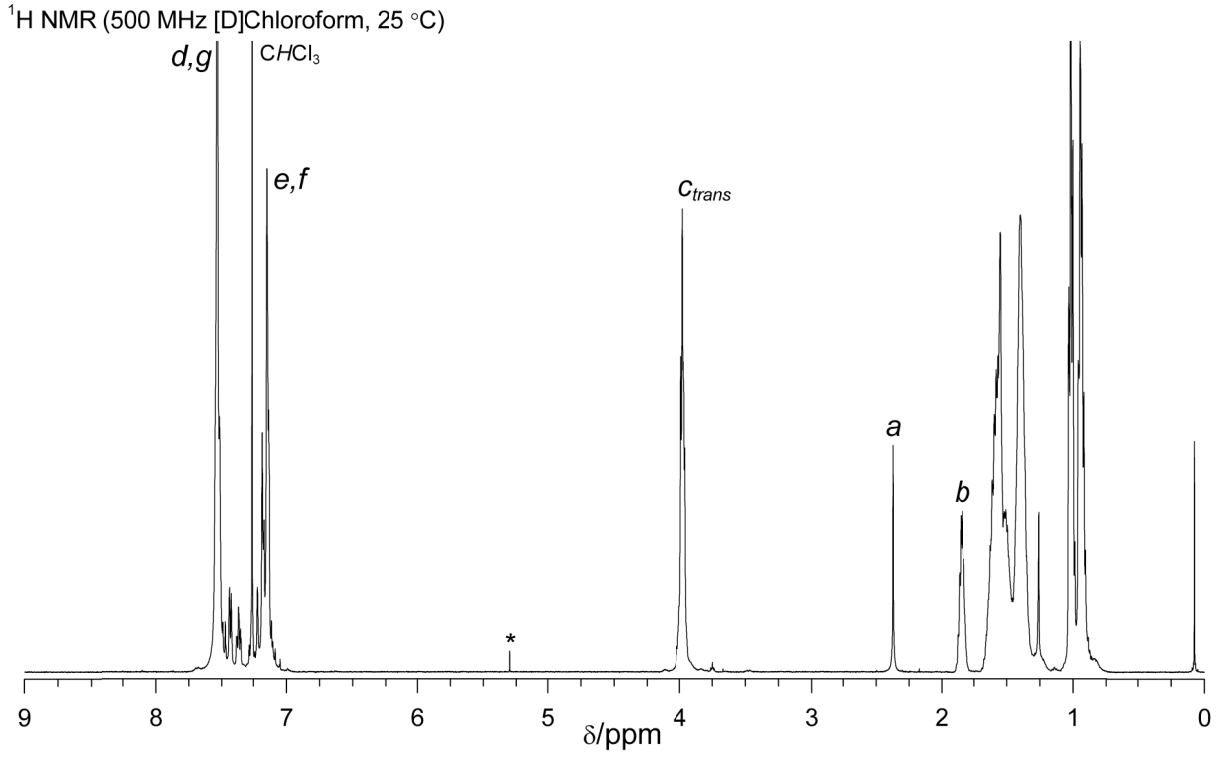


a) MALDI-TOF-MS of polymer **4b** at low laser power, b) MALDI-TOF-MS of polymer **4b** with increased laser power and c) polymer series observed in MALDI-TOF-MS.

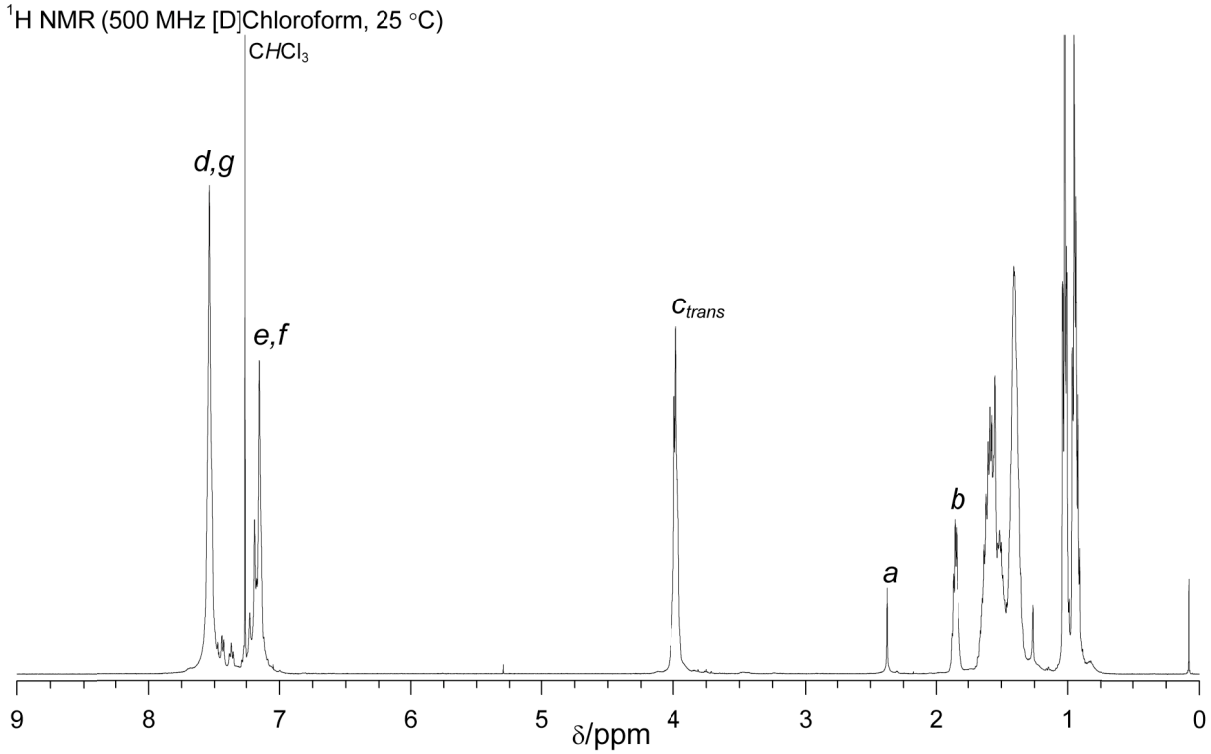
1.10 Synthesis of Tolyl Functionalised Monotelechelic Poly(p-phenylenevinylene-2,5-diethylhexyloxy-p-phenylenevinylene)s (5a-d)



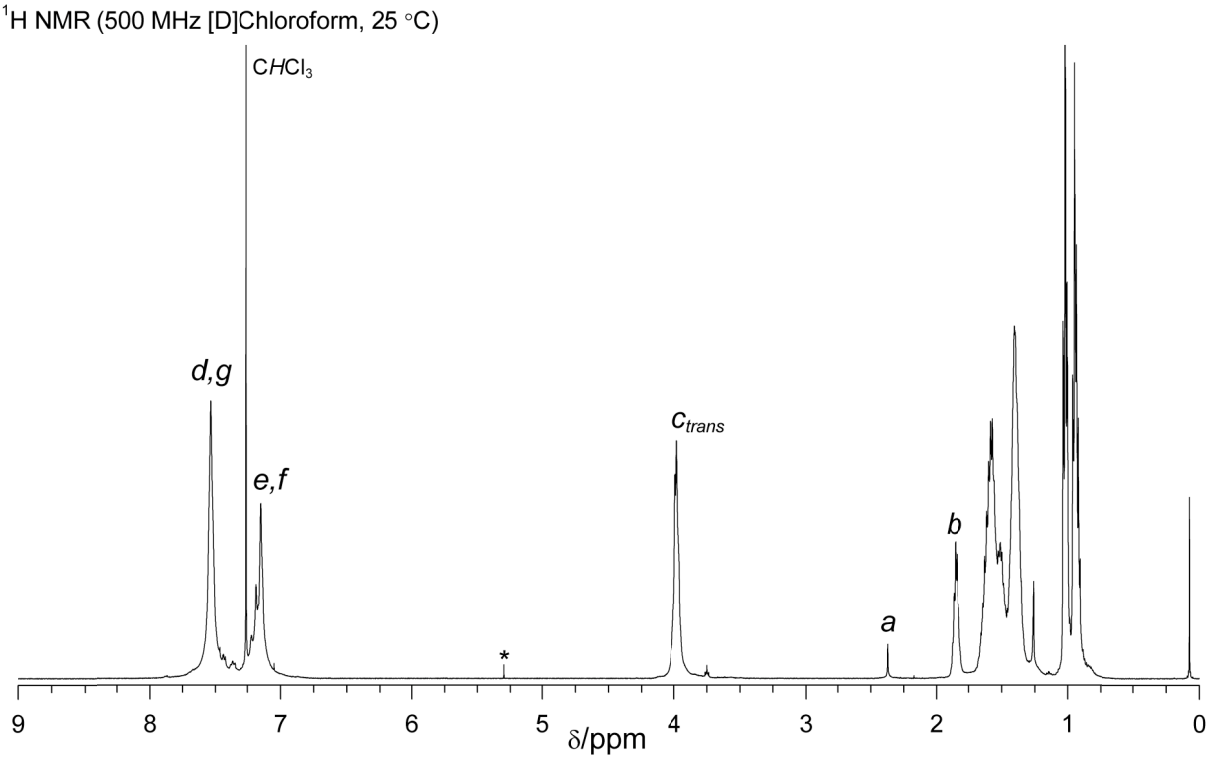
General polymerisation method for tolyl functionalised monotelechelic poly(*p*-phenylenevinylene-2,5-diethylhexyloxy-*p*-phenylenevinylene)s (**5a-d**): (Polymer **5a**) In an argon filled glove box cyclophanediene **1** (32 mg, 69.5 μmol, 5 *eq*.) and Grubbs 2 (11.8 mg, 13.9 μmol, 1 *eq*.) were added to a vial with a stirrer bar, followed by THF ($[\mathbf{1}]_I = [0.1]_I = 0.69$ mL). The vial was sealed, removed from the glove box, wrapped in foil and stirred at room temperature for 10 mins. The polymerisation was placed in a preheated oil bath at 40 °C and stirred for 8 hours. The polymerisation was cooled to room temperature and transferred back into the glove box. Vinyl ether **3** (41 mg, 278 μmol, 20 *eq*.) was added, the vial sealed, wrapped in foil removed from the glove box. The reaction was heated at 40 °C, stirred for an additional 24 hours and cooled to room temperature. The polymerisation was precipitated into a short methanol/Celite column, washed with methanol and the polymer extracted with hot chloroform. The polymer was dissolved in THF (50 mL), the solution purged with argon for 2 hours and subjected in *h*υ (365 nm) for 24 hours. The solvent volume was reduced to ~2mL and the precipitation procedure repeated to yield polymer **5a** has an orange film, after evaporation of the solvent. (29 mg,84%). ^{1}H NMR (500 MHz, [D]Chloroform, 25 °C): δ = 7.64-7.34 (br m, 6H, H-*d*, H-*g*), 7.24-7.04 (br m, 4H, H-*e,* H-*f*), 4.10-3.87 (br m, 4H, H-*c*), 2.37 (s, 1.14H, H-*a)*, 1.91-1.77 (br m, 2H, H-*b*), 1.70-1.30 (br m, 16H), 1.07-0.87 (br m, 12H). GPC(THF): $M_n = 3.7$ kg mol^{-1}, $Đ_M = 1.50$.



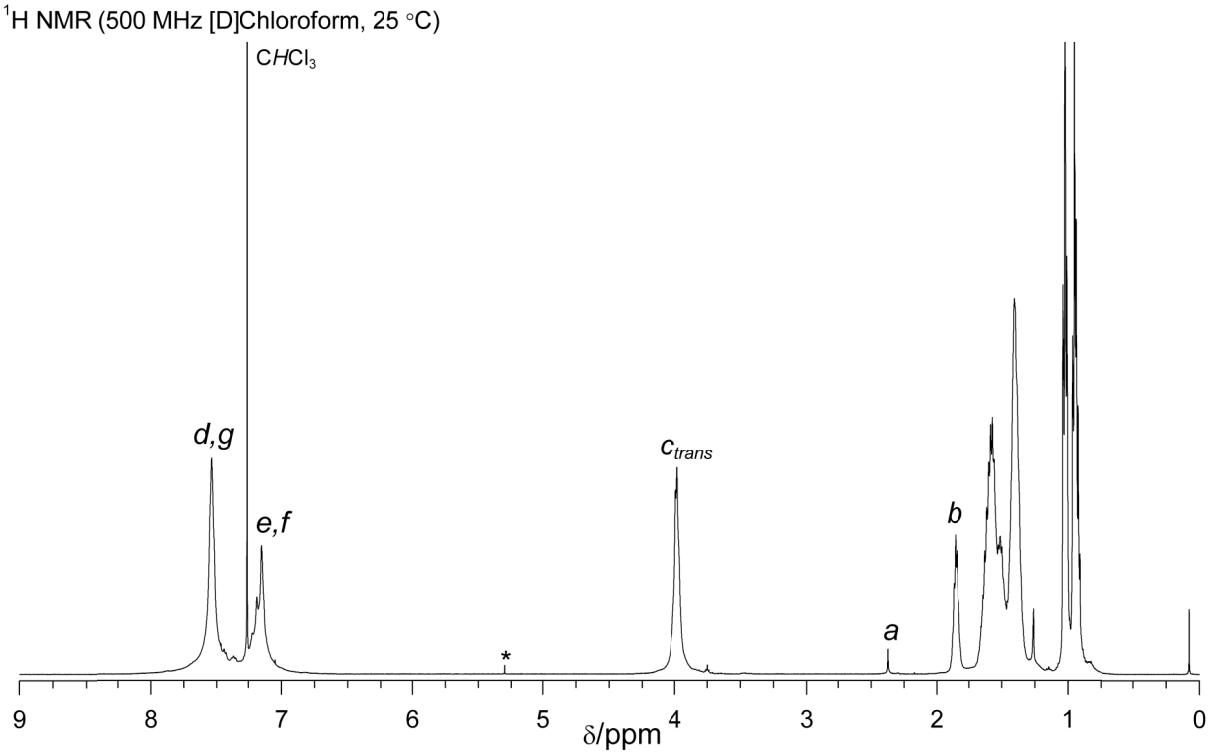
(Polymer **5b**) Following the general polymerisation procedure for polymer **5a**. Cyclophanediene **1** (38 mg, 82.5 μmol, 10 *eq*.), Grubbs 2 (7.0 mg, 8.3 μmol, 1 *eq*.) and THF ($[\mathbf{1}]_I = [0.1]_I = 0.83$ mL) stirred at 40 °C for 20 hours. Termination reaction performed with vinyl ether **3** (25 mg, 165 μmol, 20 *eq*.) for 24 hours and polymer **5b** was isolated as an orange film (33 mg, 83%), after photoisomerisation. ^{1}H NMR (500 MHz, [D]Chloroform, 25 °C): δ = 7.71-7.30 (br m, 6H, H-*d*, H-*g*), 7.24-7.00 (br m, 4H, H-*e,* H-*f*), 4.10-3.88 (br m, 4H, H-*c*), 2.37 (s, 0.55H, H-*a)*, 1.91-1.79 (br m, 2H, H-*b*), 1.72-1.28 (br m, 16H), 1.09-0.83 (br m, 12H). GPC(THF): $M_n = 8.8$ kg mol^{-1}, $Đ_M = 1.51$.



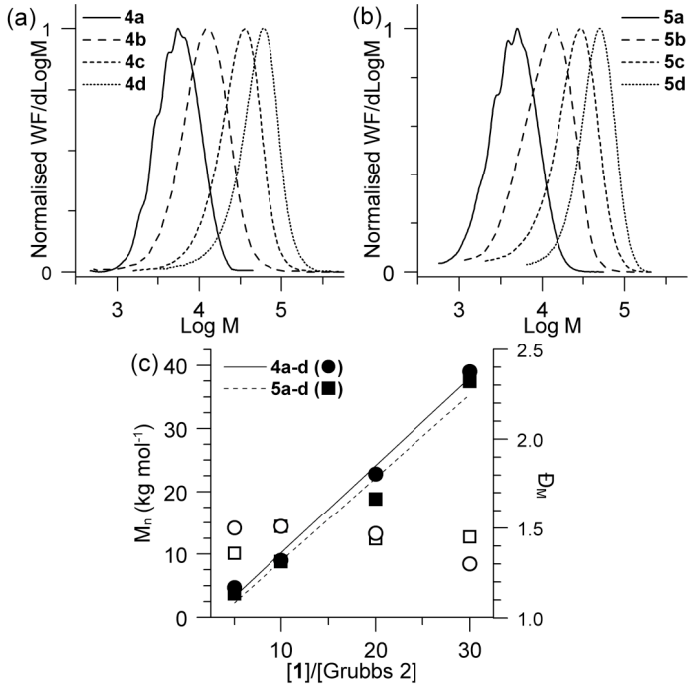
(Polymer **5c**) Following the general polymerisation procedure for polymer **5a**. Cyclophanediene **1** (37 mg, 80.3 μmol, 20 *eq*.), Grubbs 2 (3.4 mg, 4.0 μmol, 1 *eq*.) and THF ($[\mathbf{1}]_I = [0.1]_I = 0.80$ mL) stirred at 40 °C for 30 hours. Termination reaction performed with vinyl ether **3** (12 mg, 80.3 μmol, 20 *eq*.) at 40 °C for 24 hours and polymer **5c** was isolated as an orange film (34 mg, 89%), after photoisomerisation. ^{1}H NMR (500 MHz, [D]Chloroform, 25 °C): δ = 7.91-7.33 (br m, 6H, H-*d*, H-*g*), 7.30-6.96 (br m, 4H, H-*e,* H-*f*), 4.14-3.80 (br m, 4H, H-*c*), 2.37 (s, 0.25H, H-*a)*, 1.92-1.78 (br m, 2H, H-*b*), 1.70-1.27 (br m, 16H), 1.10-0.81 (br m, 12H). GPC(THF): $M_n = 18.8$ kg mol^{-1}, $Đ_M = 1.47$.



(Polymer **5d**) Following the general polymerisation procedure for polymer **5a**. Cyclophanediene **1** (54 mg, 117 µmol, 30 *eq*.), Grubbs 2 (3.3 mg, 3.9 µmol, 1 *eq*.) and THF ($[\mathbf{1}]_I = [0.1]_I = 1.17$ mL) stirred at 40 °C for 40 hours. Termination reaction performed with vinyl ether **3** (12 mg, 78 µmol, 20 *eq*.) for 24 hours and polymer **5d** was isolated as an orange film (48 mg, 87%), after photoisomerisation. ^{1}H NMR (500 MHz, [D]Chloroform, 25 °C): δ = 7.87-7.32 (br m, 6H, H-*d*, H-*g*), 7.25-6.93 (br m, 4H, H-*e,* H-*f*), 4.15-3.82 (br m, 4H, H-*c*), 2.37 (s, 0.18H, H-*a)*, 1.96-1.77 (br m, 2H, H-*b*), 1.71-1.29 (br m, 16H), 1.13-0.85 (br m, 12H). GPC(THF): $M_n = 37.4$ kg mol^{-1}, $Đ_M = 1.30$.

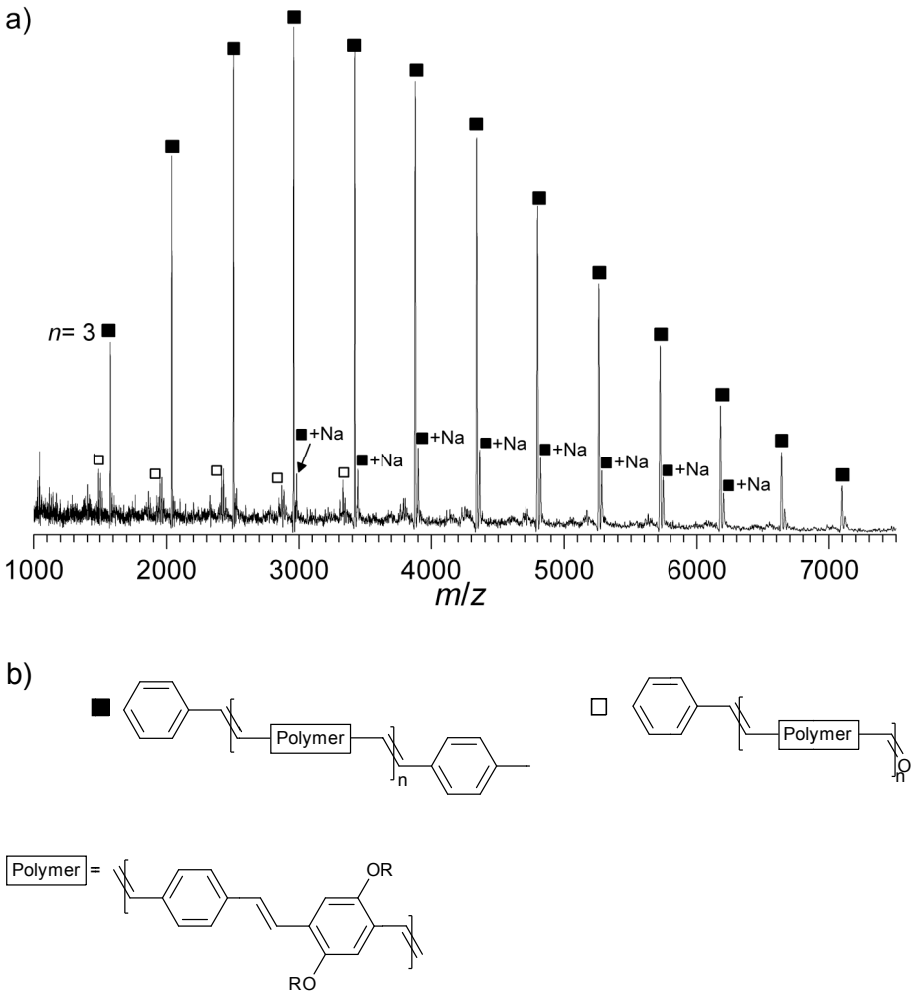


1.11 Molecular Weight Distribution of Polymers 4a-d and 5a-d and Dependence with [1]/[Grubbs 2] Ratio



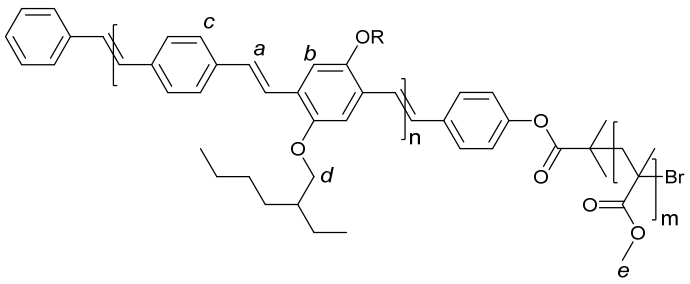
(a) Molecular weight distribution of polymers **4a-d**, (b) molecular weight distribution of polymers **5a-d**, (c) M_n dependence of polymers **4a-d** and **5a-d** with [**1**]/[Grubbs 2] ratio and $Đ_M$ of polymers **4a-d** (○) and **5a-d** (□).

1.12 MALDI-TOF-MS of Tolyl Functionalised Monotelechelic Poly(*p*-phenylenevinylene-2,5-diethylhexyloxy-*p*-phenylenevinylene)s (5b)



a) MALDI-TOF-MS of polymer **5b** after photoisomerisation. b) Polymer series observed in MALDI-TOF-MS.

1.13 Synthesis of Poly(*p*-phenylenevinylene-2,5-diethylhexyloxy-*p*-phenylenevinylene)-*b*-poly(methyl methacrylate) (Polymers 6a-l)



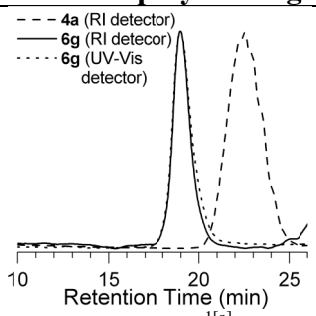
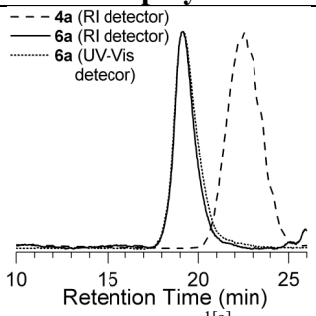
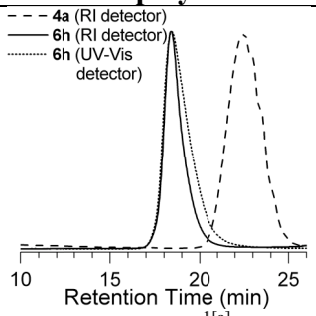
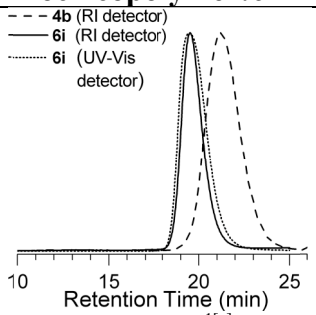
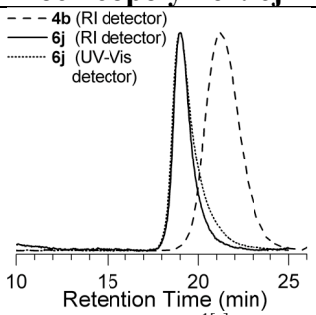
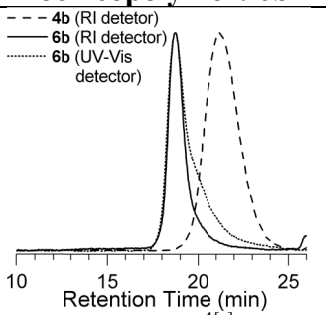
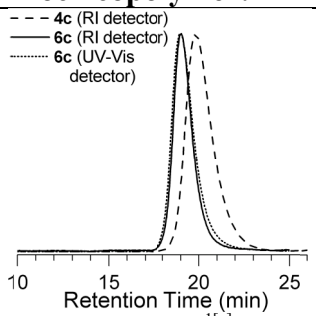
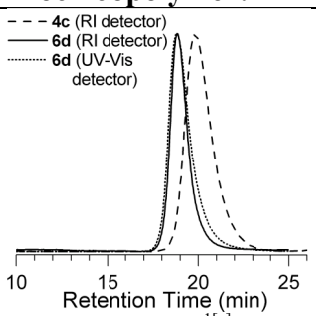
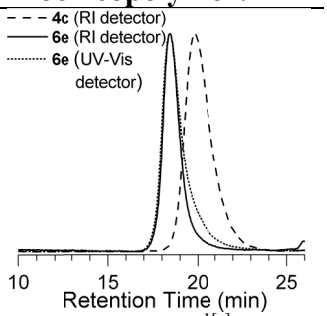
General procedure for the preparation of poly(*p*-phenylenevinylene-2,5-diethylhexyloxy-*p*-phenylenevinylene)-*b*-poly(methyl methacrylate) block copolymers (polymers **6a-l**). (Polymers **6g**, **6a** and **6h**): methyl methacrylate (18.86 g, 188 mmol, 800 *eq*.), xylenes (20.00 g, 188 mmol, 800 *eq*.), copper(I) bromide (33.8 mg, 235 μmol, 1 *eq*.), copper(II) bromide (2.6 mg, 11.8 μmol, 0.05 *eq*.) and dNby (192 mg, 471 μmol, 2 *eq*.) were prepared has described in **section 1.1** and added to a Schlenk tube. The solution was degassed by one further freeze-pump-thaw cycle and macroinitiator **4a** (84 mg, 31.7 μmol) was dissolved in the methyl methacrylate solution (3.00 g) under argon at 40 °C. Once a homogenous solution was obtained the polymerisation was placed in a preheated oil bath at 90 °C and samples taken at 15 minutes, 60 minutes and 180 minutes. The samples were cooled to room temperature, exposed to air, precipitated into methanol and the solid filtered. The resulting solid was dissolved in chloroform, precipitated into diethyl ether, filtered and washed with diethyl ether. After drying under vacuum the polymers were isolated has orange powders with masses of; 55 mg after 15 minutes (**6g**), 115 mg after 60 minutes (**6a**) and 138 mg after 180 minutes (**6h**).

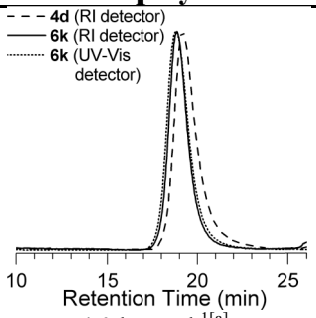
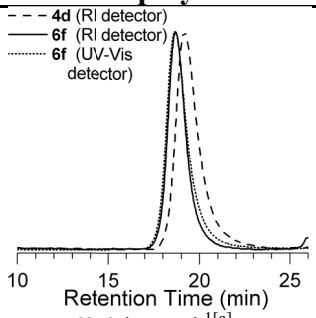
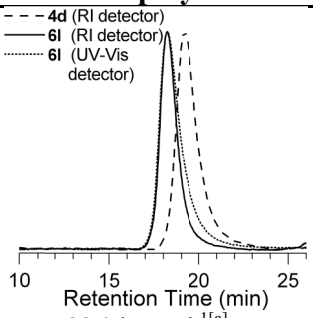
(Polymers **6i**, **6j** and **6b**) Following the general procedure for the preparation of poly(*p*-phenylenevinylene-2,5-diethylhexyloxy-*p*-phenylenevinylene)-*b*-poly(methyl methacrylate) block copolymers (polymers **6a-l**). Macroinitiator **4b** (98 mg, 19.8 μmol) was dissolved in the methyl methacrylate solution (3.00 g) at 40 °C and the polymerisation conducted at 90 °C. The polymers were isolated has orange powders with masses of; 33 mg after 15 minutes (**6i**), 82 mg after 60 minutes (**6j**) and 124 mg after 180 minutes (**6b**).

(Polymers **6c**, **6d** and **6e**) Following the general procedure for the preparation of poly(*p*-phenylenevinylene-2,5-diethylhexyloxy-*p*-phenylenevinylene)-*b*-poly(methyl methacrylate) block copolymers (polymers **6a-l**). Macroinitiator **4c** (90 mg, 9.4 μmol) was dissolved in the methyl methacrylate solution (3.50 g) at 40 °C and the polymerisation conducted at 90 °C. The polymers were isolated has orange powders with masses of; 76 mg after 15 minutes (**6c**), 46 mg after 60 minutes (**6d**) and 146 mg after 180 minutes (**6e**).

(Polymers **6k**, **6f** and **6l**) Following the general procedure for the preparation of poly(*p*-phenylenevinylene-2,5-diethylhexyloxy-*p*-phenylenevinylene)-*b*-poly(methyl methacrylate) block copolymers (polymers **6a-l**). Macroinitiator **4d** (96 mg, 6.8 μmol) was dissolved in the monomer solution (4.00 g) at 40 °C and the polymerisation conducted at 90 °C. The polymers were isolated has orange powders with masses of; 47 mg after 15 minutes (**6c**), 59 mg after 60 minutes (**6f**) and 141 mg after 180 minutes (**6l**).

1.14 Gel Permeation Chromatography Data for Poly(*p*-phenylenevinylene-2,5-diethylhexyloxy-*p*-phenylenevinylene)-*b*-poly(methyl methacrylate) (6a-l)

	Polymerisation Time		
	15 Minutes	**60 Minutes**	**180 Minutes**
Macroinitiator	**Block copolymer: 6g**	**Block copolymer:6a**	**Block copolymer: 6h**
4a			
	$\mathbf{M_n}$ = 42.0 kg mol^{-1}[a] $\mathbf{M_p}$ = 58.7 kg mol^{-1}[a] $\mathbf{Đ_M}$ = 1.26[a] $\mathbf{M_n}$ = 57.6 kg mol^{-1}[b] **Structure:** PPV$_5$-*b*-PMMA$_{550}$[b]	$\mathbf{M_n}$ = 62.0 kg mol^{-1}[a] $\mathbf{M_p}$ = 76.4 kg mol^{-1}[a] $\mathbf{Đ_M}$ = 1.19[a] $\mathbf{M_n}$ = 82.7 kg mol^{-1}[b] **Structure:** PPV$_5$-*b*-PMMA$_{820}$[b]	$\mathbf{M_n}$ = 92.0 kg mol^{-1}[a] $\mathbf{M_p}$ = 123.0 kg mol^{-1}[a] $\mathbf{Đ_M}$ = 1.30[a] $\mathbf{M_n}$ = 171.8 kg mol^{-1}[b] **Structure:** PPV$_5$-*b*-PMMA$_{1690}$[b]
	Block copolymer:6i	**Block copolymer: 6j**	**Block copolymer: 6b**
4b			
	$\mathbf{M_n}$ = 32.0 kg mol^{-1}[a] $\mathbf{M_p}$ = 44.0 kg mol^{-1}[a] $\mathbf{Đ_M}$ = 1.32[a] $\mathbf{M_n}$ = 29.9 kg mol^{-1}[b] **Structure:** PPV$_{10}$-*b*-PMMA$_{250}$[b]	$\mathbf{M_n}$ = 46.0 kg mol^{-1}[a] $\mathbf{M_p}$ = 61.0 kg mol^{-1}[a] $\mathbf{Đ_M}$ = 1.21[a] $\mathbf{M_n}$ = 36.9 kg mol^{-1}[b] **Structure:** PPV$_{10}$-*b*-PMMA$_{320}$[a]	$\mathbf{M_n}$ = 57.0 kg mol^{-1}[a] $\mathbf{M_p}$ = 82.0 kg mol^{-1}[a] $\mathbf{Đ_M}$ = 1.33[a] $\mathbf{M_n}$ = 79.9 kg mol^{-1}[b] **Structure:** PPV$_{10}$-*b*-PMMA$_{750}$[a]
	Block copolymer:	**Block copolymer:**	**Block copolymer:**
4c			
	$\mathbf{M_n}$ = 46.0 kg mol^{-1}[a] $\mathbf{M_p}$ = 64.0 kg mol^{-1}[a] $\mathbf{Đ_M}$ = 1.32[a] $\mathbf{M_n}$ = 54.5 kg mol^{-1}[b] **Structure:** PPV$_{20}$-*b*-PMMA$_{450}$[b]	$\mathbf{M_n}$ = 53.0 kg mol^{-1}[a] $\mathbf{M_p}$ = 73.0 kg mol^{-1}[a] $\mathbf{Đ_M}$ = 1.28[a] $\mathbf{M_n}$ = 87.6 kg mol^{-1}[b] **Structure:** PPV$_{20}$-*b*-PMMA$_{780}$[b]	$\mathbf{M_n}$ = 76.0 kg mol^{-1}[a] $\mathbf{M_p}$ = 105.0 kg mol^{-1}[a] $\mathbf{Đ_M}$ = 1.31[a] $\mathbf{M_n}$ = 143.0 kg mol^{-1}[b] **Structure:** PPV$_{20}$-*b*-PMMA$_{1340}$[b]

Macroinitiator	Block copolymer: 6k	Block copolymer: 6d	Block copolymer: 6l
4d			
	$\mathbf{M_n}$ = 54.0 kg mol^{-1}[a] $\mathbf{M_p}$ = 72.0 kg mol^{-1}[a] $\mathbf{Đ_M}$ = 1.34[a] $\mathbf{M_n}$ = 68.1 kg mol^{-1}[b] **Structure:** PPV$_{30}$-*b*-PMMA$_{540}$[b]	$\mathbf{M_n}$ = 62.0 kg mol^{-1}[a] $\mathbf{M_p}$ = 82.0 kg mol^{-1}[a] $\mathbf{Đ_M}$ = 1.31[a] $\mathbf{M_n}$ = 92.1 kg mol^{-1}[b] **Structure:** PPV$_{30}$-*b*-PMMA$_{780}$[b]	$\mathbf{M_n}$ = 88.0 kg mol^{-1}[a] $\mathbf{M_p}$ = 123.0 kg mol^{-1}[a] $\mathbf{Đ_M}$ = 1.38[a] $\mathbf{M_n}$ = 200.2 kg mol^{-1}[b] **Structure:** PPV$_{30}$-*b*-PMMA$_{1860}$[b]

[a] Determined by GPC with RI detection, calibrated against narrow $Đ_M$ polystyrene standards [b] determined by ^{1}H NMR spectroscopy.

1.15 Measurement of Quantum Yields of Poly(*p*-phenylenevinylene-2,5-diethylhexyloxy-*p*-phenylenevinylene) (5a-d) and Poly(*p*-phenylenevinylene-2,5-diethylhexyloxy-*p*-phenylenevinylene)-*b*-poly(methyl methacrylate) (6a-f)

Photoluminescence quantum yields (PLQYs) were measured in dilute solutions of the polymers (**5a-d** and **6a-f**) in dichloromethane against fluorescein as a reference in 0.1 M aqueous sodium hydroxide (PLQY at 22 °C = 0.95). For each sample the optical density at 470 nm and the integrated fluorescence (480-800 nm, λ_{ex} = 470 nm) were measured for solutions of the polymer in dichloromethane, at five different concentrations with optical densities between 0.01 and 0.1. PLQYs were calculated for each sample using Equation 1.

$$Q = Q_R \frac{I}{I_R} \frac{OD_R}{OD} \frac{n^2}{n_R^2} \text{ (Equation 1)}$$

Q = quantum yield, I = integrated intensity, n = refractive index of the solvent, OD = optical density and the subscript *R* refers to the reference fluorophore (fluorescein).

A PLQY value was calculated for each of the five solutions with a final PLQY value for the polymer determined by discarding the highest and lowest PLQY values and taking an average

of the remaining three. Values for OD_R and I_R were obtained by measuring both the optical density at 470 nm and the integrated fluorescence (480-800 nm, λ_{ex} = 470 nm), with solutions of fluorescein at five different concentrations (optical densities between 0.01 and 0.1). Plotting of the optical density *vs*. the integrated fluorescence of the five solutions resulted in a linear gradient and the single set of values which fitted most closely to a linear gradient were used as the values of OD_R and I_R.

References

1 J. R. Lakowicz, Principles of Fluorescence Spectroscopy, 3rd ed., Springer, Singapore, 2006.