

Supplementary information

Polymer colour converter with very high modulation bandwidth for visible light communications

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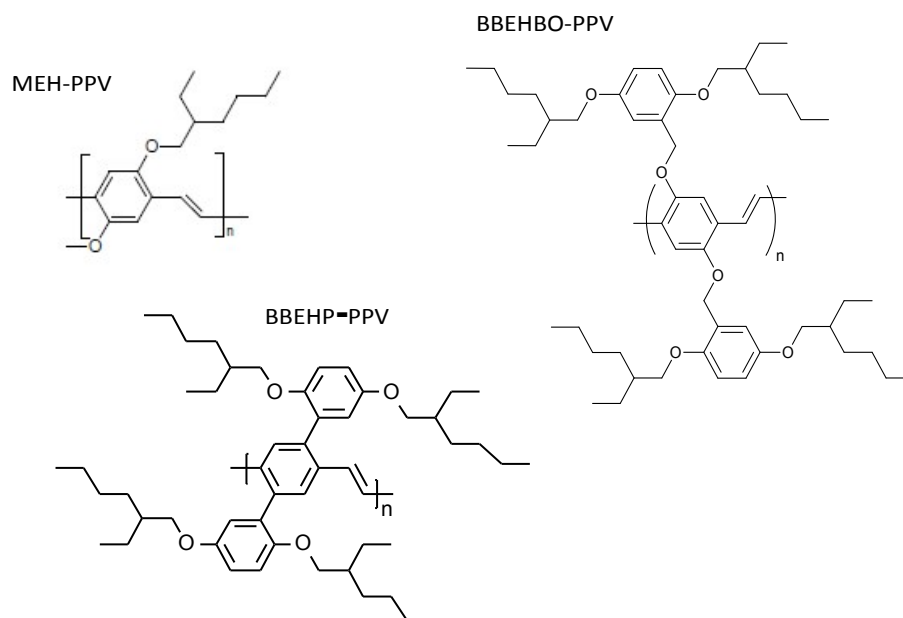


Figure S1: Molecular structures of MEH-PPV, BBEHP-PPV and in comparison, BBEHBO-PPV.

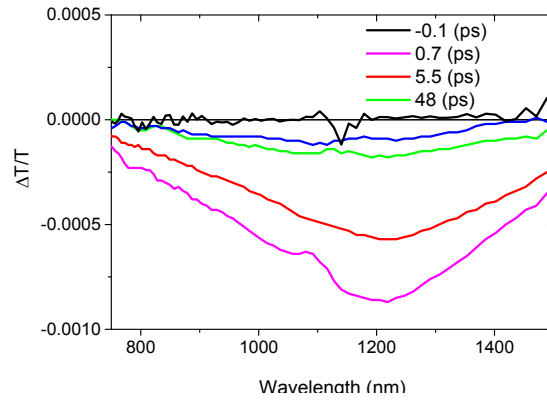


Figure S2: Transient absorption spectra showing excited state regime of BBEHBO-PPV.

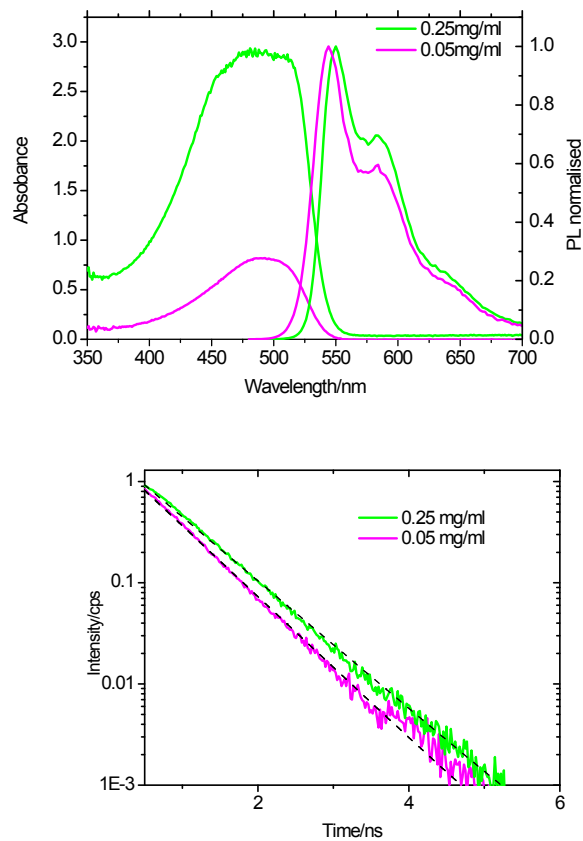


Figure S3: Top: Absorption and PL spectra of BBEHBO-PPV in solution at concentrations of 0.25 and 0.05 mg/ml.

Bottom: PL lifetime of BBEHBO-PPV in solution at concentrations of 0.25 and 0.05 mg/ml, showing a small increase in PL lifetime at concentrations appropriate for LED colour converters.

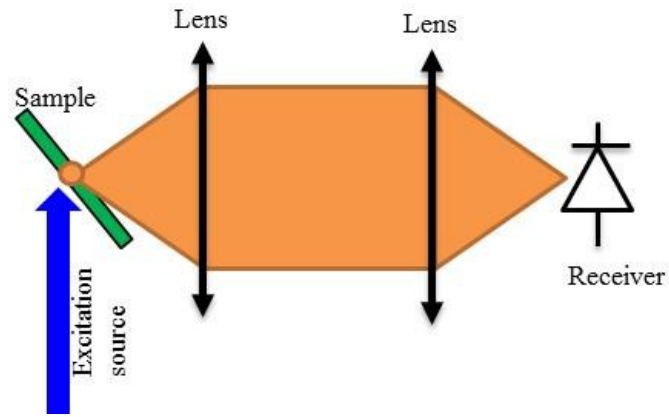


Figure S4: Schematic of experimental configuration for colour convertor bandwidth measurement.

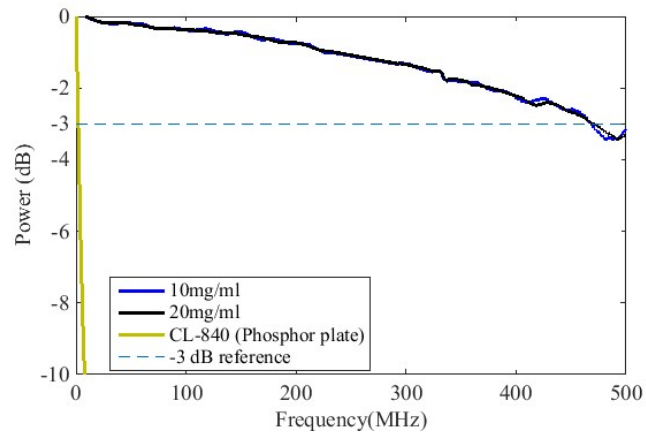


Figure S5: Top: Plot of electrical power vs frequency of BBEHBO-PPV films spin coated from solutions of 10 and 20 mg/ml. The dotted line shows the reference -3 dB bandwidth point. The frequency response of commercial phosphor plate (CL-840) is also shown for comparison.

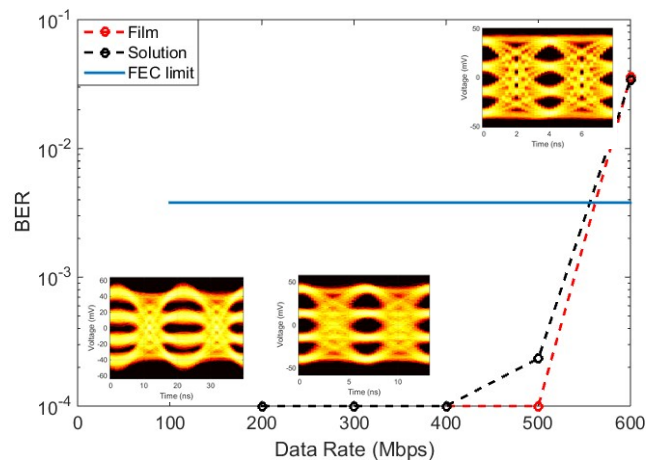


Figure S6. BER vs data rate using PAM-4 scheme. Inset: the eye diagrams at 100, 300 and 500 Mbps.

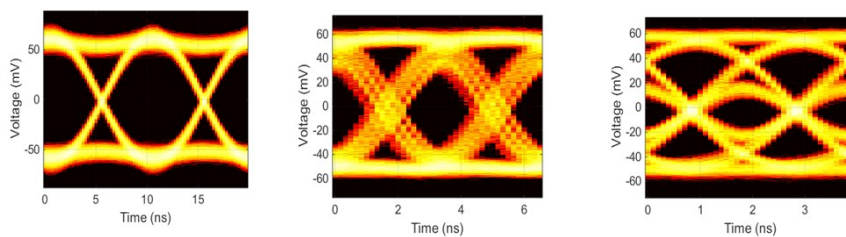
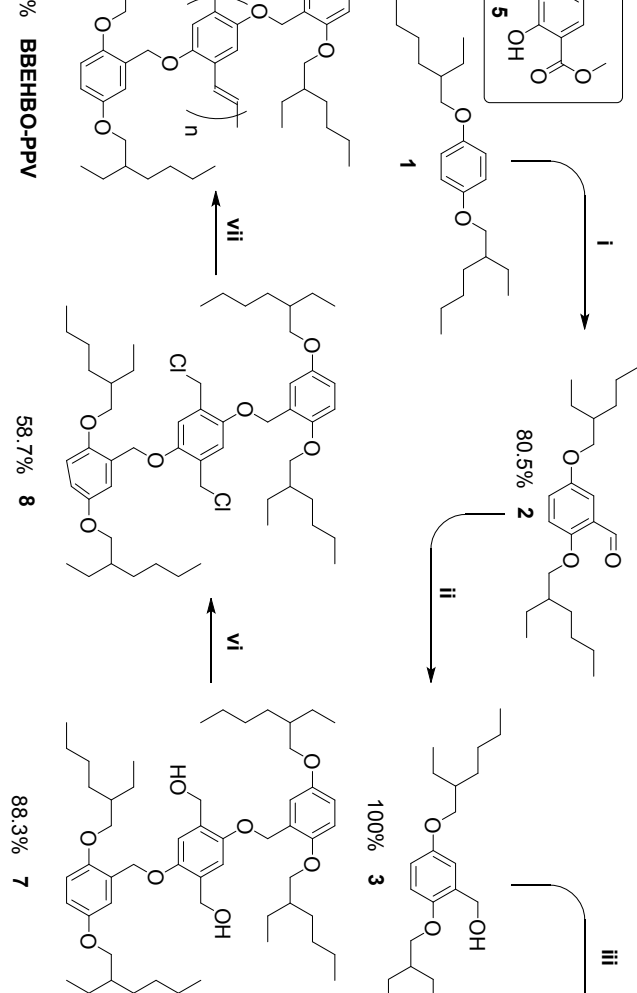


Figure S7. The eye diagrams at 100, 300 and 500 Mbps for PAM-2 scheme.

Table S1: Lifetime fitting results of BBEHBO-PPV, MEH-PPV and BBEHP-PPV in solution.

Material	Concentration (mg/ml)	τ_1 /ns	A_1	Radiative lifetime/ns
BBEHBO-PPV solution	0.25	0.75	1	1.11
BBEHBO-PPV solution	0.05	0.64	1	0.95
BBEHBO-PPV solution	0.025	0.65	1	0.97
MEH-PPV	0.01	0.4	1	
BBEHP-PPV	0.05	0.7	1	

Polymer synthesis



Scheme S1: The synthesis of the BBEHBO-PPV. Reagent and conditions: (i) BuLi, TMEDA, hexane, then DMF; (ii) NaBH₄, methanol; (iii) CBr₄, (C₆H₅)₃P, THF; (iv) K₂CO₃, DMF, 80°C, 3 days; (v) LiAlH₄, THF; (vi) (C₆H₅)₃P, CCl₄, MW 120°C, 2 hours; (vii) tert-BuOK, THF.

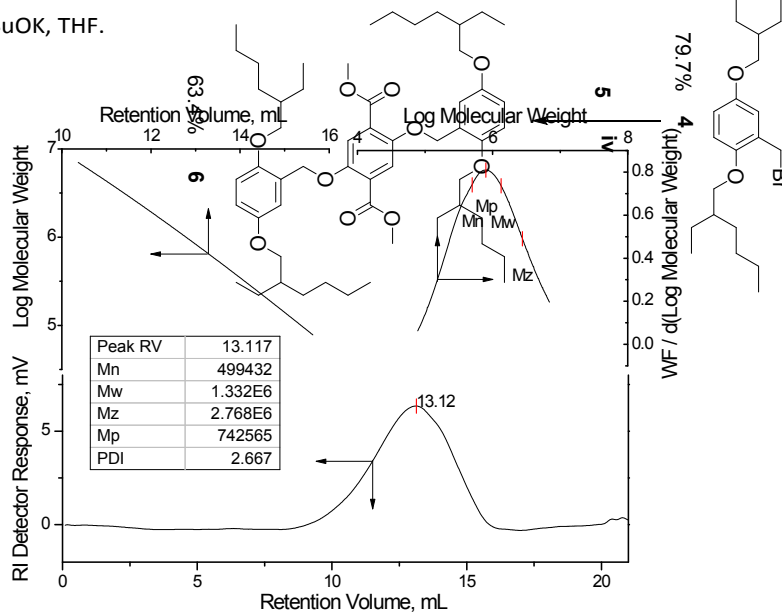


Figure S8 GPC results for BBEHBO-PPV.

The polymer 9 turned out to be fairly thermally stable. Thermogravimetric analysis (Figure 1, solid line) revealed a decomposition temperature of 290°C (5% weight loss). Due to the bulky substituents and high internal volume of the polymer repeat unit the target compound 9 exhibited a low glass transition temperature ($T_g = -17^\circ\text{C}$) in a

differential scanning calorimetry experiment (Figure S9, dashed line), which is responsible for the resin-like appearance of the polymer 9 at ambient temperature.

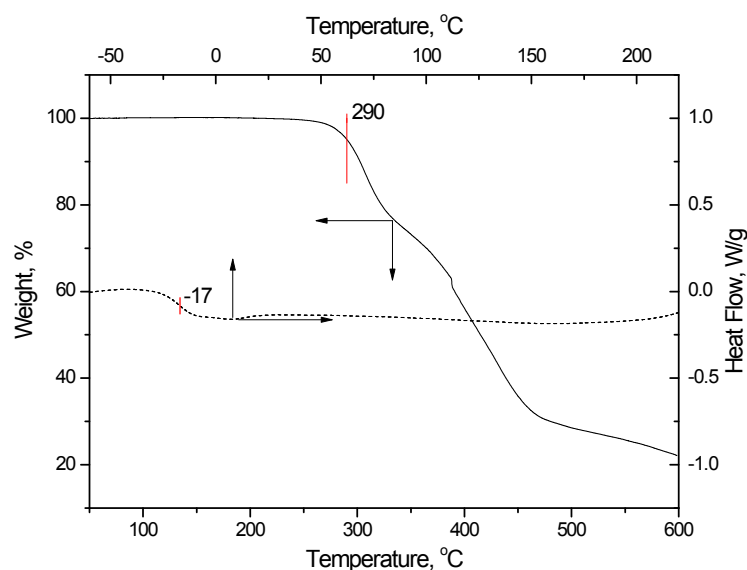


Figure S9. Thermal analysis of the polymer 9. Solid line: TGA (at the rate of 10 °C/min, under Ar flow). Dashed line: DSC (standard Heat – Cool – Reheat procedure, removal of thermal history on the first heat (30 – 225°C, 10 °C/min) then cooling (225 – -70°C, 10°C/min) and the final heat (shown on the graph, -70 – 225°C, 5°C/min).

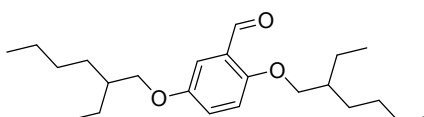
1,4-bis((2-ethylhexyl)oxy)benzene^{20, 21} and 2,5-dihydroxyterephthalate²² were prepared as described in the literature. Water- and oxygen-free THF and hexane were obtained from solvent purification system Innovative Technology SPS-400-5. Carbon tetrachloride was refluxed over CaH₂ and distilled prior to the synthesis. All other solvents and reagents were purchased from Aldrich and used as received.

Appel reaction for preparation of the monomer was performed under microwave irradiation in Biotage Initiator+ EU 356006 (P_{max} = 400 W, f = 2450 MHz). Melting point for the monomer was taken using a Stuart Scientific Electrothermal Melting Point apparatus and is uncorrected. ¹H and ¹³C NMR spectra were recorded on a Bruker Avance/DPX400 apparatus at 400.13 for ¹H, 100.61 MHz for ¹³C in CDCl₃. Chemical shifts are given in ppm; all J values are in Hz.

Elemental analyses were obtained on a Perkin-Elmer 2400 analyser. CI mass spectra were performed on Agilent 5975C inert XL/CI MSD with Triple Axis Detector. ES+APCI MS were carried on Agilent 6130 dual source mass spectrometer. LDI-TOF and MALDI-TOF mass spectra were run on a Shimadzu Axima-CFR spectrometer (mass range 1-150 000 Da) using dithranol as a matrix for MALDI-TOF.

Thermogravimetric analysis was performed on Perkin Elmer Thermogravimetric Analyser TGA 7. Differential scanning calorimetry was conducted on TAINstruments Q10. Gel Permeation Chromatography was carried out using a Viscotek GPC Max1000 system which includes a refractive index detector and two columns (KF-805L Shodex). Eluent was chloroform. The columns were calibrated against polystyrene standards.

2,5-bis((2-ethylhexyl)oxy)benzaldehyde (**2**)



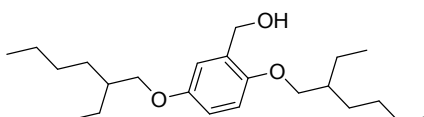
To a solution of 1,4-bis((2-ethylhexyl)oxy)benzene (18.7 g, 55.8 mmol) and TMEDA (18.5 ml) in 90 ml of hexane (27.0 ml, 58.0 mmol) of BuLi solution in hexane (2.15 M) was added dropwise for over half an hour at room temperature. After completing addition the mixture was cooled on petrole – liquid nitrogen bath down to -90°C, and 15 ml (194 mmol) of DMF was added. The mixture was allowed to warm to room temperature, stirred overnight and poured onto ice cold mixture of diluted HCl. The organic layer was separated, while the water one was extracted with ether. The organic layer was combined with the ether extracts, washed with brine, saturated NaHCO₃ solution and dried over MgSO₄. After evaporating the solvent the crude product was subjected to the column on silica eluting with hexane : ethyl acetate (100 : 1). The main fraction provided 16.3 g (44.9 mmol, 80.5%) of the yellowish oil.

MS (ES+APCI): 363.3 ([M+H]⁺).

¹H NMR (400 MHz, δ, CDCl₃): 10.48 (1H, s), 7.32 (1H, d, ⁴J=3.2 Hz), 7.12 (1H, dd, ³J=9.0 Hz, ⁴J=3.2 Hz), 6.93 (1H, d, ³J=9.1 Hz), 3.94 (1H, dd, ²J=9.2 Hz, ³J=5.4 Hz), 3.91 (1H, dd, ²J=9.2 Hz, ³J=5.6 Hz), 3.84 (1H, dd, ²J=9.1 Hz, ³J=5.7 Hz), 3.81 (1H, dd, ²J=9.1 Hz, ³J=5.9 Hz), 1.84 – 1.64 (2H, m), 1.58 – 1.22 (16H, m), 1.10 – 0.70 (12H, m).

¹³C NMR (101 MHz, δ, CDCl₃): 189.86, 156.66, 153.45, 125.31, 124.27, 114.37, 111.05, 71.65, 71.42, 39.71, 39.56, 30.79, 30.66, 29.25, 29.21, 24.15, 24.00, 23.19, 23.15, 14.20, 11.32, 11.22.

(2,5-bis((2-ethylhexyl)oxy)phenyl)methanol (**3**)



To a solution of 2,5-bis((2-ethylhexyl)oxy)benzaldehyde (2.02g, 5.56 mmol) in 75 ml of dry methanol sodium borohydride (249 mg, 6.57 mmol) was added. The mixture was stirred until complete consumption of the starting aldehyde (TLC control, approx. half an hour). Aqueous work up afforded the colourless oil that was pure enough and used without further purification. The yield of the product was quantitative (2.03 g).

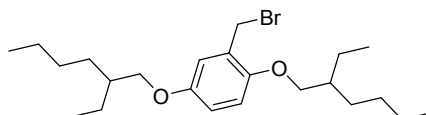
MS (CI): 364 (M+), 347.2 ([M-(OH-)]+).

¹H NMR (400 MHz, δ , CDCl₃): 6.88 (1H, d, ⁴J=2.4 Hz), 6.79 (1H, d, ³J=8.6 Hz), 6.76 (1H, dd, ³J=8.9 Hz, ⁴J=2.7 Hz), 4.66 (2H, d, ³J=6.5 Hz)*, 3.87 (1H, dd, ²J=9.2 Hz, ³J=5.4 Hz), 3.85 (1H, dd, ²J=9.2 Hz, ³J=5.6 Hz), 3.81 (1H, dd, ²J=9.1 Hz, ³J=5.7 Hz), 3.79 (1H, dd, ²J=9.1 Hz, ³J=5.8 Hz), 2.37 (1H, t, ³J=6.5 Hz)*, 1.80 – 1.62 (2H, m), 1.55 – 1.25 (16H, m), 1.00 – 0.80 (12H, m).

*In some instances the doublet at 4.66 ppm and the triplet at 2.37 ppm appeared as a singlet and a broad singlet respectively due to exchange with water in acidic CDCl₃ (Figure S12).

¹³C NMR (101 MHz, δ , CDCl₃): 153.50, 151.16, 130.36, 115.55, 113.86, 112.05, 71.34, 70.94, 62.50, 39.71, 39.62, 30.88, 30.68, 29.24, 24.27, 24.02, 23.20, 23.17, 14.22, 14.18, 11.32, 11.24.

2-(bromomethyl)-1,4-bis((2-ethylhexyl)oxy)benzene (**4**)



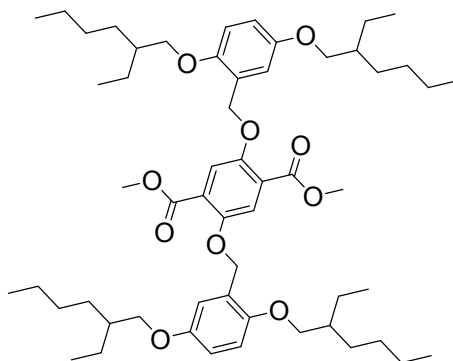
To a solution of (2,5-bis((2-ethylhexyl)oxy)phenyl)methanol (5.38 g, 14.8 mmol) in 70 ml of THF carbon tetrabromide (2.01 g, 6.06 mmol) and triphenylphosphine (1.57 g, 5.98 mmol) were added and the reaction mixture was stirred for 1 hour. The other portions of carbon tetrabromide (3.23 g, 9.74 mmol) and triphenylphosphine (2.48 g, 9.46 mmol) were added and the reaction allowed to stir for another 25 hours. The solvent was evaporated and the residue was treated in an ultrasonic bath with hexane and filtered through the silica plug, washing the residue on the silica plug with hexane. The combine filtrates were evaporated affording the product as colourless oil with a yield of 5.03 g (11.8 mmol, 79.7 %)

MS (ES+APCI): 426.1 (M⁺).

¹H NMR (400 MHz, δ , CDCl₃): 6.90 (1H, d, ⁴J=2.6 Hz), 6.81 (1H, dd, ³J=8.9 Hz, ⁴J=2.7 Hz), 6.77 (1H, d, ³J=8.8 Hz), 4.53 (2H, s), 3.86 (2H, d, ³J=5.4 Hz), 3.79 (1H, dd, ²J=9.1 Hz, ³J=5.6 Hz), 3.77 (1H, dd, ²J=9.1 Hz, ³J=5.9 Hz), 1.80 – 1.63 (2H, m), 1.62 – 1.25

(16H, m), 1.00 – 0.80 (12H, m) ^{13}C NMR (101 MHz, δ , CDCl_3): 153.14, 151.32, 127.03, 117.17, 115.83, 112.76, 71.29, 70.97, 39.77, 39.62, 30.80, 30.67, 29.28, 29.24, 24.18, 24.00, 23.21, 14.25, 11.39, 11.26.

Dimethyl 2,5-bis((2,5-bis((2-ethylhexyl)oxy)benzyl)oxy)terephthalate (**6**)

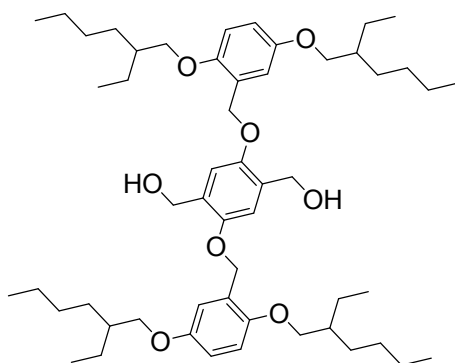


To a mixture of dimethyl 2,5-dihydroxyterephthalate (1.11 g, 4.89 mmol) and K_2CO_3 (3.83 g, 27.7 mmol) in 20 ml of DMF benzyl bromide (5.03 g, 11.8 mmol) in 5 ml of DMF was added, followed by washing with 3x5ml of DMF. The reaction mixture was stirred at 80 °C for three days. After cooling to room temperature the reaction was quenched with brine and extracted with ether. The combined extracts were dried over MgSO_4 . After evaporation the solvent the crude product was subjected to column on silica, eluting with hexane : ethyl acetate, starting 100 : 1 and ramping up to 100 : 3. The yield of the product as a colourless oil was 2.85 g (3.10 mmol, 63.4%)

MS (LDI+): 917.27 (M^+).

^1H NMR (400 MHz, δ , CDCl_3): 7.52 (2H, s), 7.27 (2H, d, $^4J=1.4$ Hz), 6.83 – 6.74 (4H, m), 5.16 (4H, s), 3.92 (6H, s), 3.87 – 3.80 (8H, m), 1.78 – 1.65 (4H, m), 1.54 – 1.25 (32H, m), 0.98 – 0.82 (24H, m). ^{13}C NMR (101 MHz, δ , CDCl_3): 166.25, 153.65, 152.00, 150.15, 126.55, 124.91, 117.51, 114.71, 113.97, 112.08, 71.38, 71.27, 66.92, 52.37, 39.62, 30.83, 30.72, 29.25, 29.22, 24.20, 24.04, 23.22, 23.17, 14.21, 11.31, 11.24.

(2,5-bis((2,5-bis((2-ethylhexyl)oxy)benzyl)oxy)-1,4-phenylene)dimethanol (**7**)



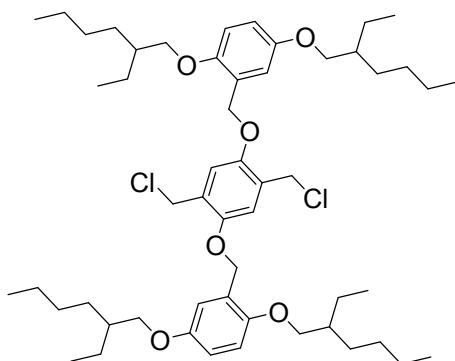
To a suspension of LiAlH_4 (593 mg, 15.6 mmol) in 32 ml of THF, cooled to -15 C , the solution of diester (2.85 g, 3.10 mmol) in 18 ml of THF was added at such a rate as to keep the temperature of the reaction at -12 C (for ca. 15 min), followed by rinsing with further portions of THF (2x10 ml). The reaction was left overnight allowing the temperature slowly to rise to the ambient. Then reaction mixture was cooled to -16 C and quenched with 8 ml of cold water, acidified (pH 4), keeping the temperature below -3 C , and extracted with CH_2Cl_2 . The combined extracts were washed with brine and dried with MgSO_4 . Evaporation of the solvent afforded 2.56 g of the crude product, which was purified by column on silica, eluting first with hexane : CH_2Cl_2 1:1 and ramping to pure CH_2Cl_2 . The yield of the product as a colourless oil was 2.36 g, 2.74 mmol, 88.3%.

MS (MALDI+): 862.85 (M^+), 885.25 ($\text{M}+\text{Na}^+$); MS (MALDI-): 862.12 (M^-).

^1H NMR (400 MHz, δ , CDCl_3): 7.00 (2H, d, $^4J=2.3\text{ Hz}$), 6.97 (2H, s), 6.87 – 6.78 (4H, m), 5.08 (4H, s), 4.68 (4H, d, $^3J=6.6\text{ Hz}$), 3.85 (4H, d, $^3J=5.8\text{ Hz}$), 3.85 – 3.75 (4H, m), 2.53 (2H, t, $^3J=6.5\text{ Hz}$), 1.78 – 1.64 (4H, m), 1.56 – 1.22 (32H, m), 0.97 – 0.82 (24H, m).

^{13}C NMR (101 MHz, CDCl_3) δ 153.49, 151.03, 150.95, 129.82, 126.55, 115.86, 114.43, 113.27, 112.61, 71.53, 71.35, 66.62, 62.40, 39.59, 39.51, 30.74, 30.65, 29.20, 24.08, 23.98, 23.20, 23.16, 14.23, 14.20, 11.23.

2,2'-(((2,5-bis(chloromethyl)-1,4-phenylene)bis(oxy))bis(methylene))bis(1,4-bis((2-ethylhexyl)oxy)benzene) (**8**)



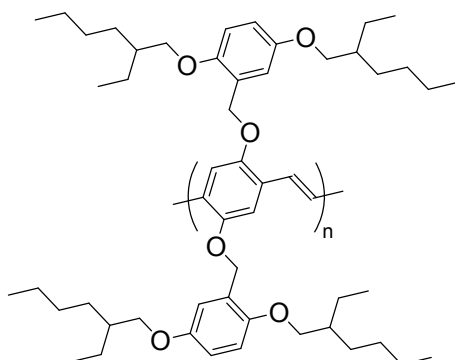
The 2 ml microwave vial was charged with 58.8 mg (68.1 μmol) of diol, 0.30 ml (3.1 mmol) of CCl_4 and 52.3 mg (199 μmol) of triphenylphosphine, degased with argon and heated at microwave at 80 $^\circ\text{C}$ for 10 min, at 100 $^\circ\text{C}$ for 10 min and at 120 $^\circ\text{C}$ for 2 hours. The excess of CCl_4 was removed in vacuum and the residue was purified by two subsequent columns on silica the first one was eluted with CH_2Cl_2 : hexane 1:5 and the other one – with toluene : hexane 1:1. The yield of the white solid with m.p. 76-78 $^\circ\text{C}$ was 36.0 mg (40.0 μmol , 58.7%)

MS (MALDI-): 897.41 (M⁺). Anal. Calcd for $\text{C}_{54}\text{H}_{84}\text{Cl}_2\text{O}_6$: C, 72.05; H, 9.41%. Found: C, 72.29; H, 9.26%.

^1H NMR (400 MHz, δ , CDCl_3): 7.13 (2H, d, $^4\text{J}=1.8$ Hz), 7.03 (2H, s), 6.86 – 6.77 (4H, m), 5.14 (4H, s), 4.68 (4H, s), 3.86 (4H, d, $^3\text{J}=5.6$ Hz), 3.82 (2H, dd, $^2\text{J}=9.2$ Hz, $^3\text{J}=5.7$ Hz), 3.80 (2H, dd, $^2\text{J}=9.2$ Hz, $^3\text{J}=6.1$ Hz), 1.80 – 1.63 (4H, m), 1.54 – 1.24 (32H, m), 0.98 – 0.85 (24H, m)

^{13}C NMR (101 MHz, δ , CDCl_3): 153.59, 150.77, 150.48, 127.59, 126.59, 115.11, 114.83, 114.66, 112.38, 71.47, 71.39, 66.19, 41.68, 39.71, 39.56, 30.86, 30.66, 29.28, 29.20, 24.21, 23.98, 23.21, 23.15, 14.23, 11.34, 11.22.

Poly(2,5-bis((2,5-bis((2-ethylhexyl)oxy)benzyl)oxy)-1,4-phenylene vinylene) (BBEHBO-PPV)



To a solution of 130 mg (145 μ mol) of the monomer in 12 ml of THF, 1.12 ml of 1.08 M solution of tert-BuOK in THF was added over 1 hour, and the reaction mixture was stirred for 5 hours. The reaction mixture was quenched with methanol (~ 200 ml), cooled and filtered. The crude product was washed in Soxhlet overnight successively with methanol and acetone and extracted with CH_2Cl_2 . After evaporation of the solvent the polymer was re-precipitated from THF : methanol and THF : acetone mixtures and dried in the vacuum. The yield of the polymer as a red resin-like solid was 81.8 mg (68.4%).

T_d (5% weight loss) = 290 $^\circ\text{C}$, T_g = -17 $^\circ\text{C}$, M_n = 499 kDa, PDI = 2.67

^1H NMR (400 MHz, δ , CDCl_3): 7.02 (4H, br), 6.67 (6H, br), 5.05 (4H, br), 3.75 (4H, br), 3.65 (4H, br), 1.58 (4H, br), 1.40 – 1.15 (32H, m), 0.8 – 0.6 (24H, m).

Anal. Calcd for $[\text{C}_{54}\text{H}_{82}\text{O}_6]_n$: C, 78.40; H, 9.99%. Found: C, 77.81; H, 9.93%.

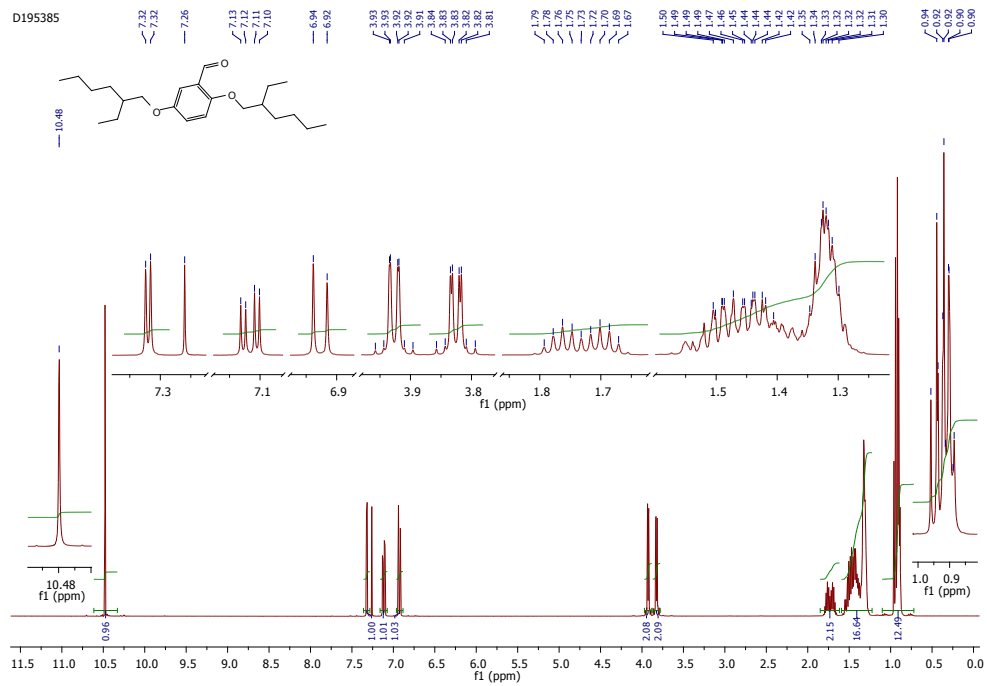


Figure S10. ^1H NMR spectrum of aldehyde 2.

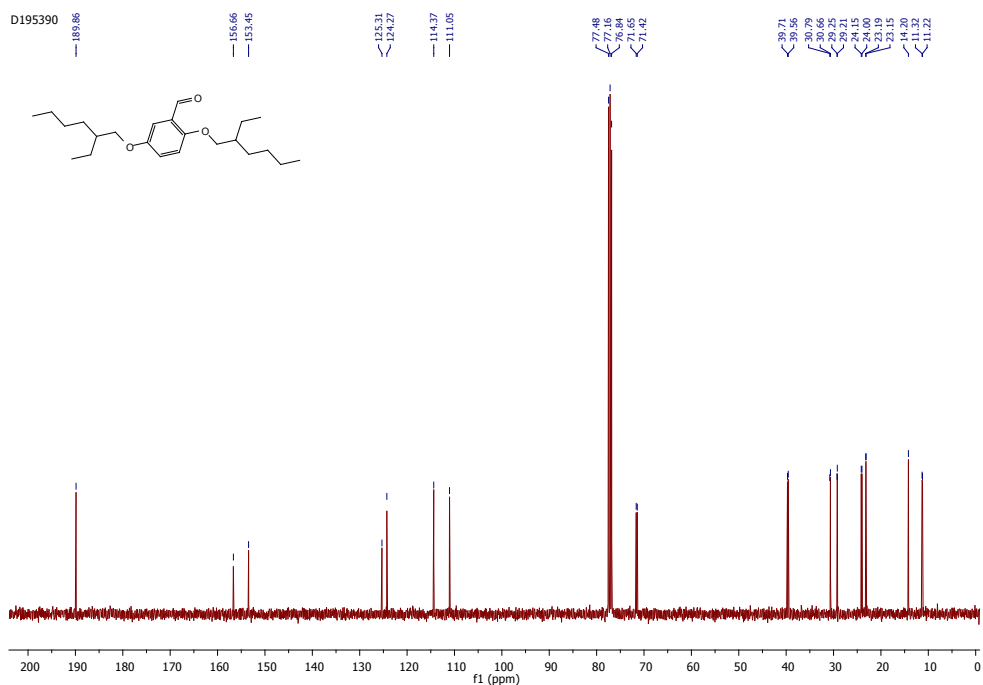


Figure S11. ^{13}C NMR spectrum of aldehyde 2.

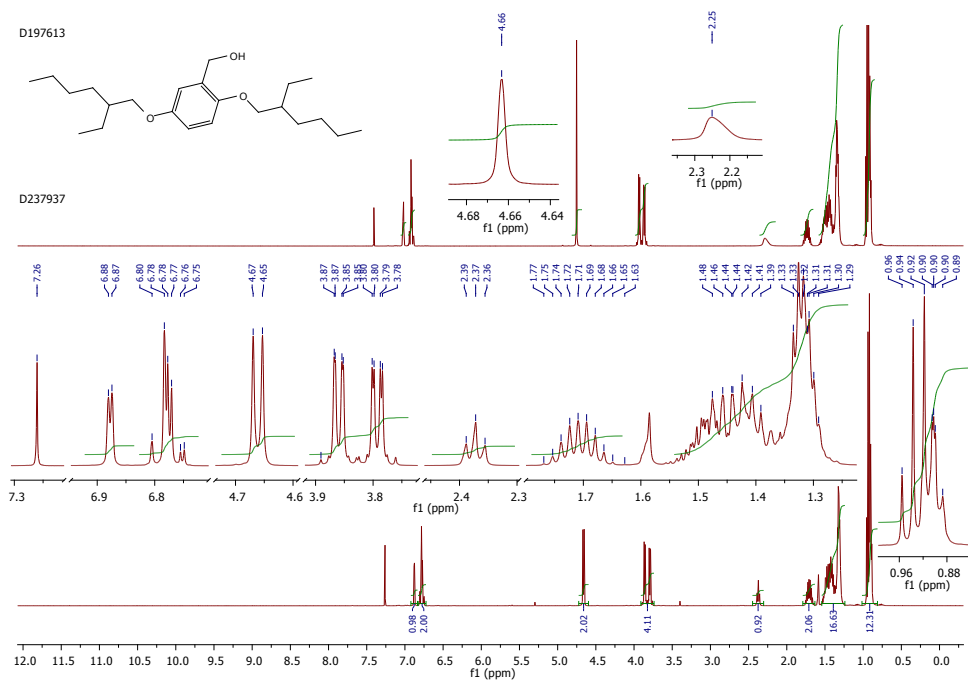


Figure S12. ^1H NMR spectrum of compound **3**. The top spectrum shows the case when $-\text{CH}_2-$ and $-\text{OH}$ protons of the carbinol group appear as singlet and broad singlet respectively due to exchange with water in acidic CDCl_3 .

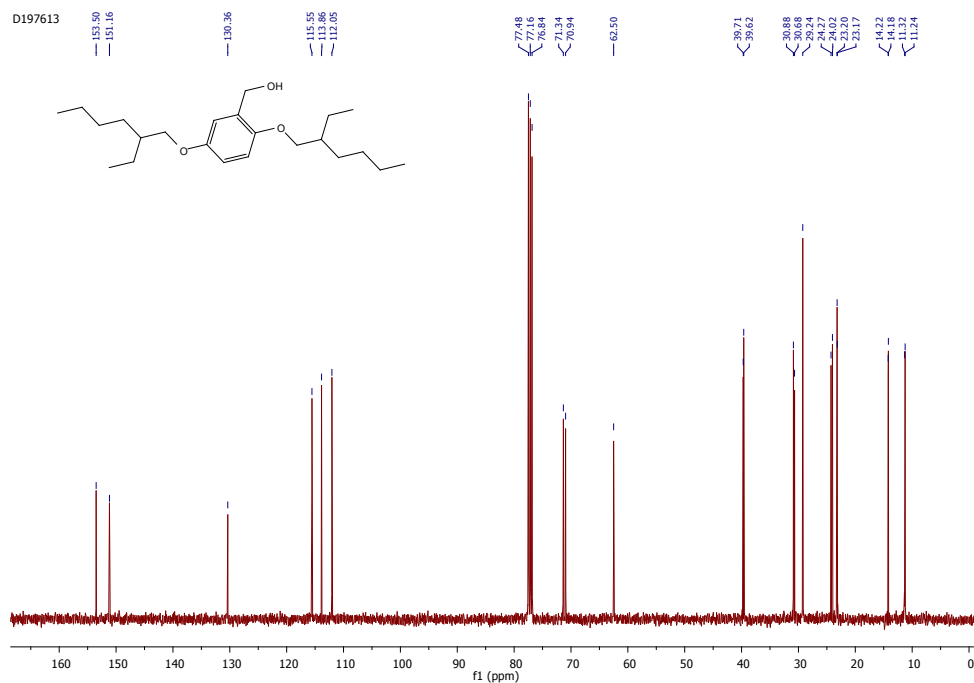


Figure S13. ^{13}C NMR spectrum of carbinol **3**.

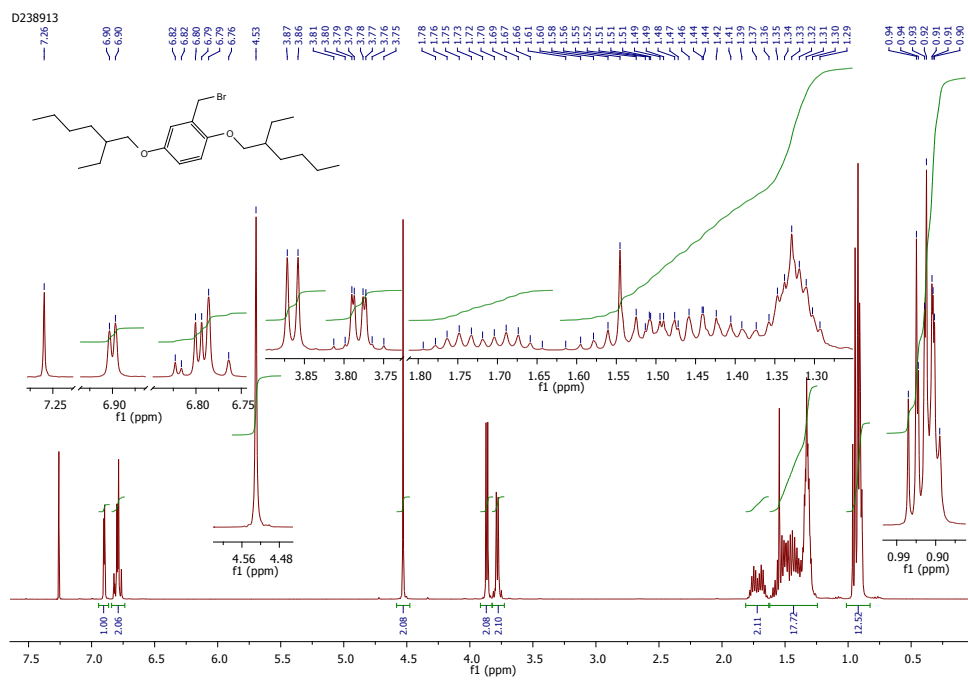


Figure S14. ^1H NMR spectrum of compound 4.

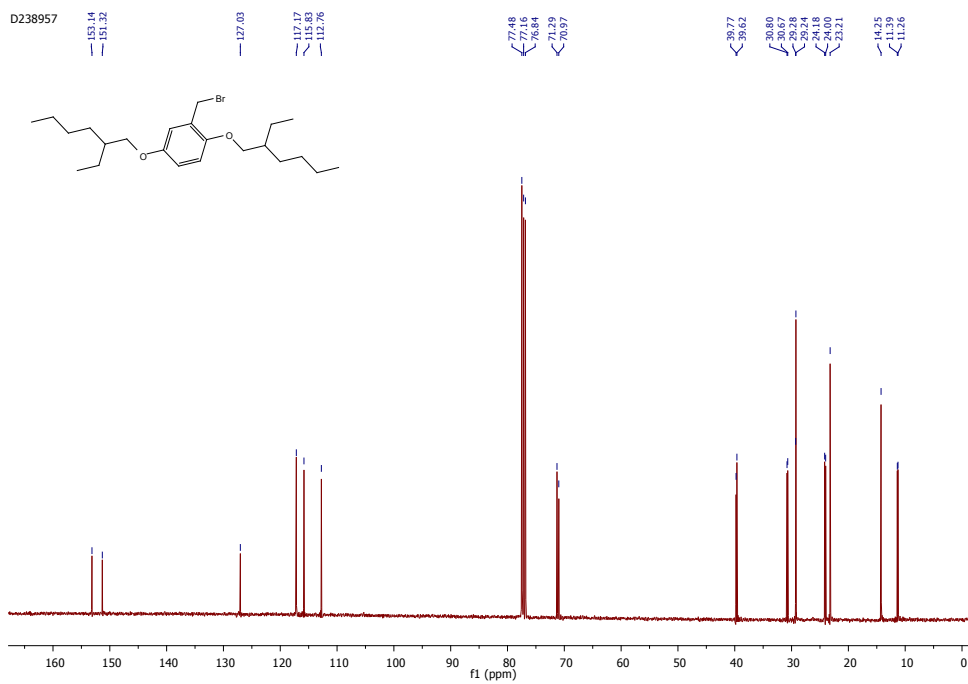


Figure S15. ^{13}C NMR spectrum of compound 4.

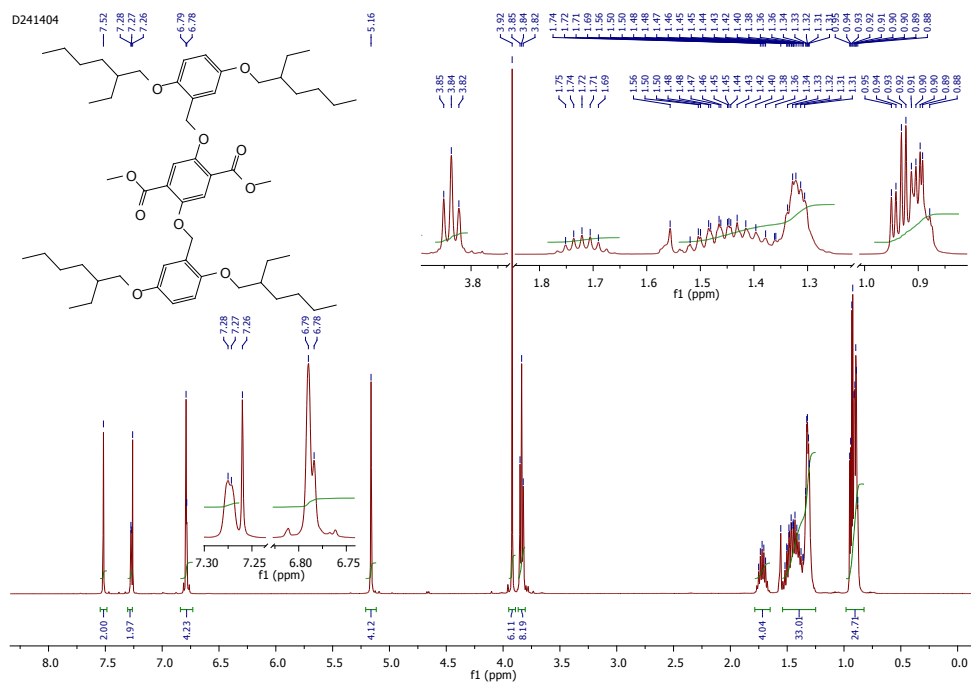


Figure S16. ^1H NMR spectrum of compound 6.

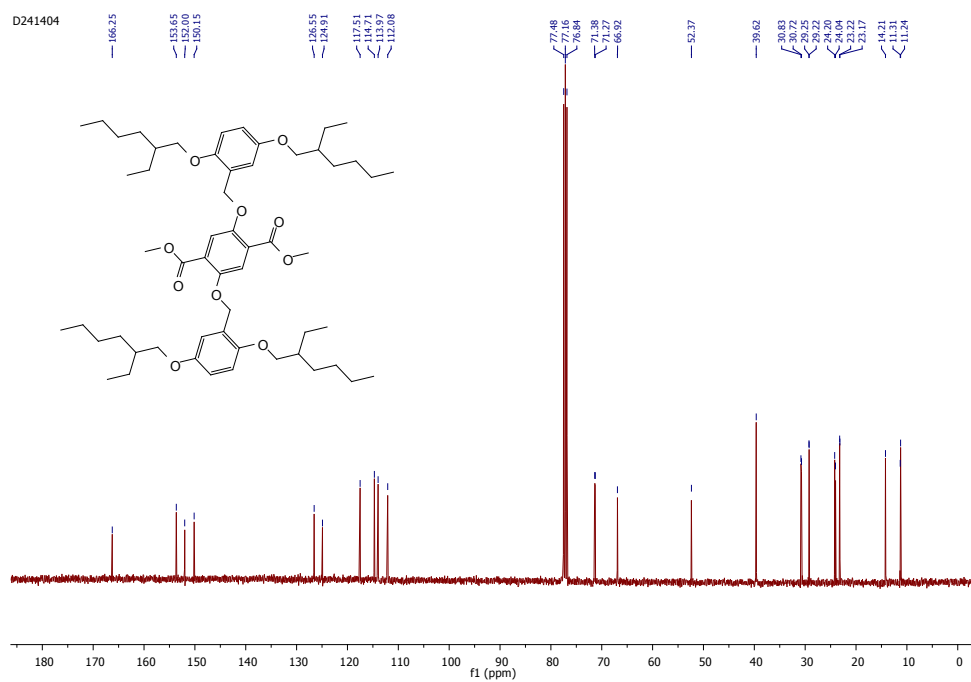


Figure S17. ^{13}C NMR spectrum of compound 6.

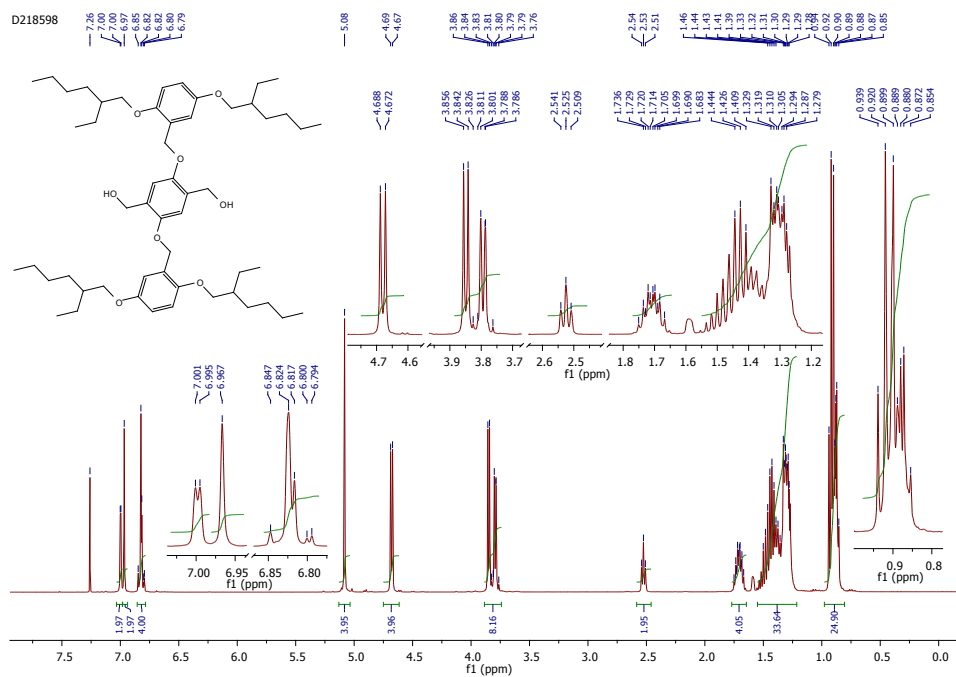


Figure S18. ^1H NMR spectrum of compound 7.

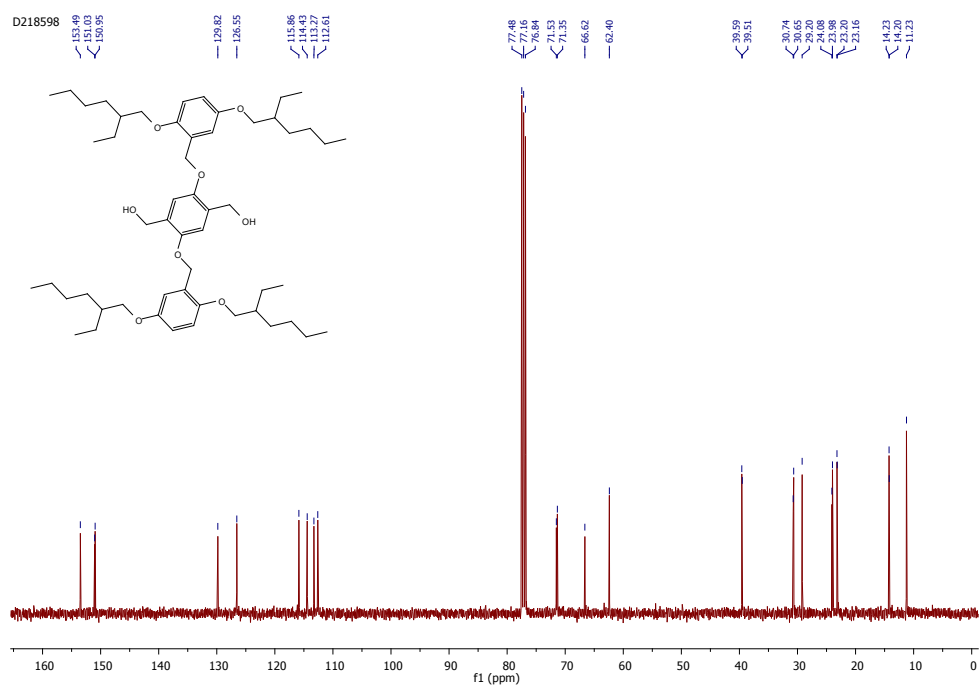


Figure S19. ^{13}C NMR spectrum of compound 7.

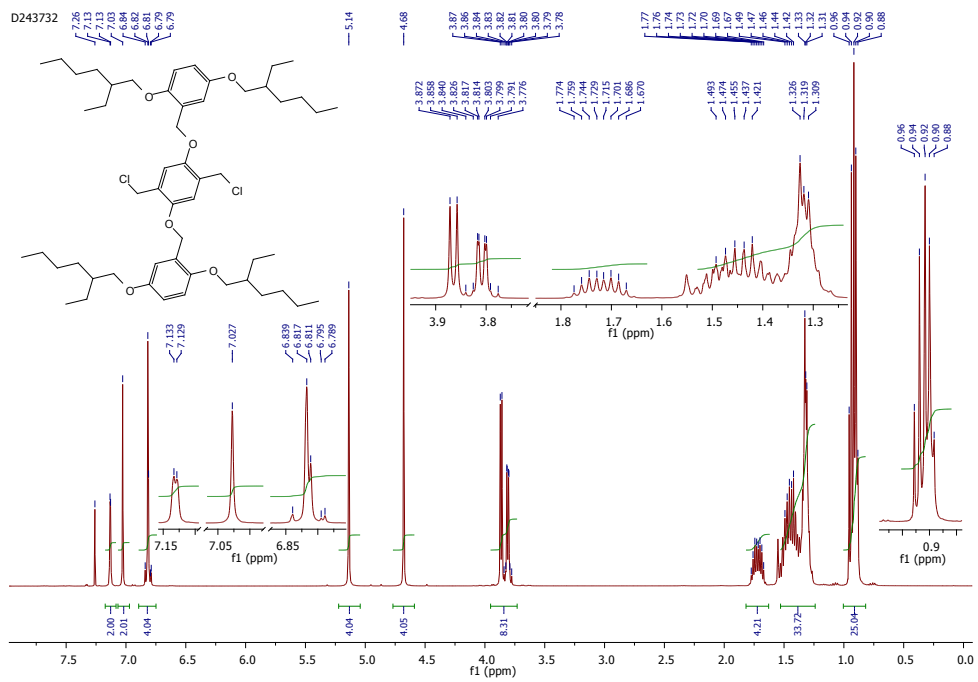


Figure S20. ^1H NMR spectrum of compound 8.

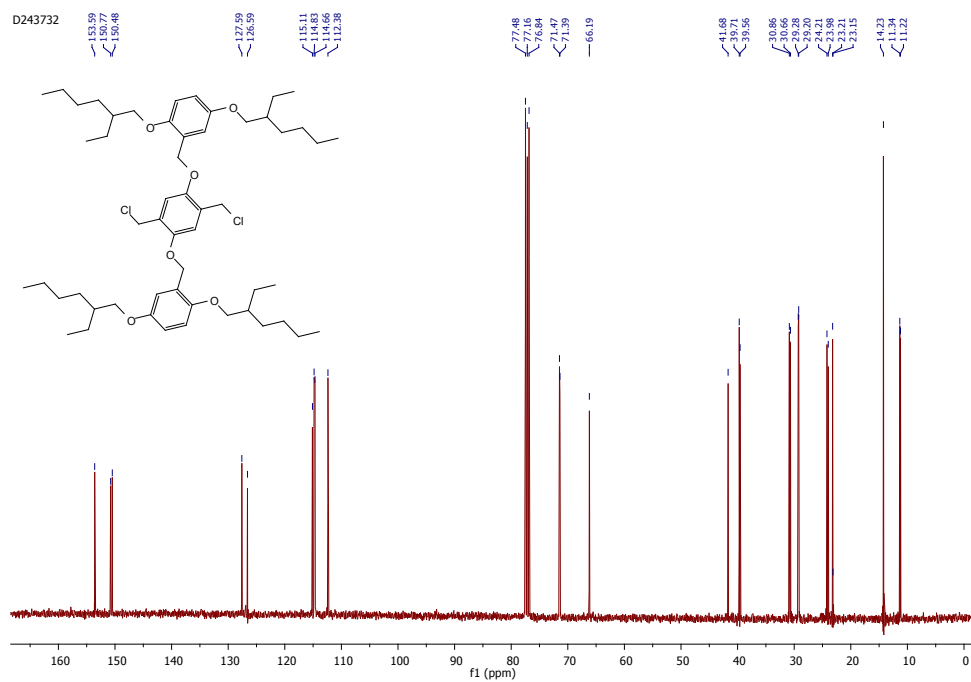


Figure S21. ^{13}C NMR spectrum of compound 8.

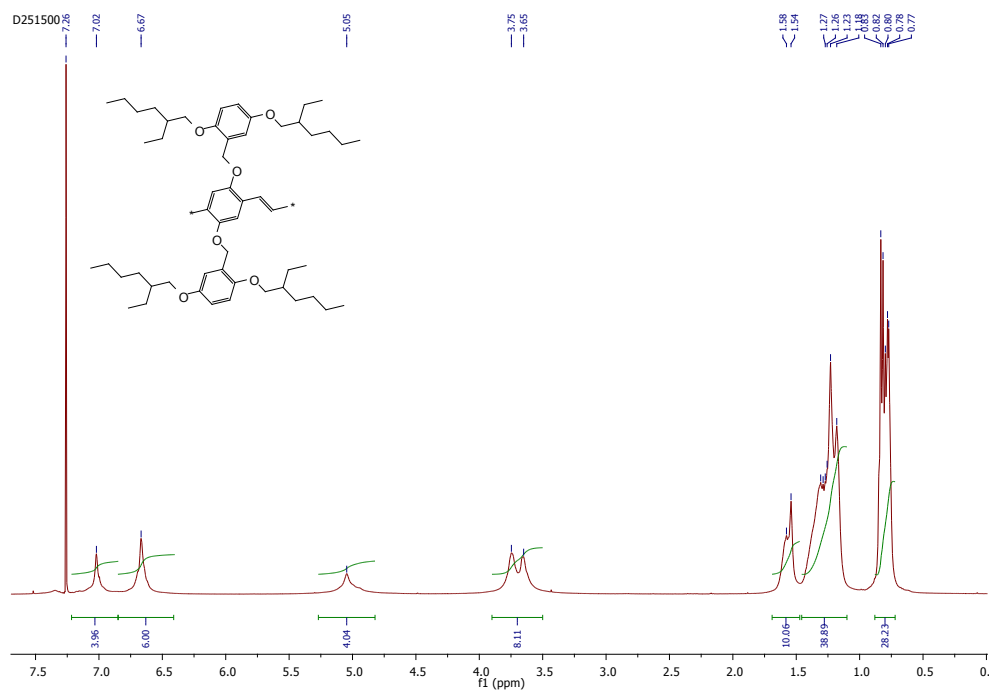


Figure S22. ¹H NMR spectrum of polymer 9.