

Supporting Information

Odd-Even Effects and the Influence of Length and Specific Positioning of Alkoxy Side Chains on the Optical Properties of PPE-PPV Polymers

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EXPERIMENTALS

Instrumentation: ¹H NMR and ¹³C NMR spectra were obtained in deuterated chloroform using a Bruker DRX 400 and a Bruker AC 250. Elemental Analysis was measured on a CHNS-932 Automat Leco. Infrared spectroscopy was recorded on a Nicolet Impact 400. Gel-permeation chromatography (GPC) was performed on a set of Knauer using THF as eluent and polystyrene as a standard. The absorption spectra were recorded in dilute chloroform solution (10⁻⁵- 10⁻⁶ M) on a Perkin Elmer UV /VIS-NIR Spectrometer Lambda 19. Quantum-corrected emission spectra were measured in dilute chloroform solution (10⁻⁶ M) with a LS 50 luminescence spectrometer (Perkin Elmer). The fluorescence quantum yields (error < ± 10%) were calculated relative quinine sulfate; used as standard ($\Phi_f = 55\%$). The absorbance at the excitation wavelength was kept below 0.05 for the samples and the reference. Thin film samples of 100 –150 nm thickness were cast from chlorobenzene on the thin glass substrate. The quantum yield of the thin films was determined against a CF₃P-PPV (poly{1,4-

phenylene-[1-(4-trifluoromethyl)phenyl-vinylene]-2,5-dimethoxy-1,4-phenylene-[2-(4-trifluoromethyl)phenyl-vinylene]]) copolymer reference that has been measured by integrating sphere as 0.43.¹

The kinetics of fluorescence was investigated with a CD900 time correlating single photon counting spectrometer (Edinburgh Instruments). The excitation source was a hydrogen filled nanosecond flash lamp which yielded an instrument response pulse of 1.3 ns FWHM.

Decay curves were accumulated until 2000 counts in the maximum with at least 10^3 occupied channels. The channel width corresponded to 25 ps.

Picosecond fluorescence kinetics was measured with an apparatus consisting of a picosecond laser diode (PicoQuant, pulse width 60 ps, repetition rate 40 MHz, emission wavelength 408 nm) as the excitation source and a Hamamatsu microchannel plate photomultiplier (MCP-PMT R3809U-50) and a SPC-430 single photon counting board (Becker & Hickl, Berlin) as the detecting unit. Decay curves were accumulated until 10^4 counts in the maximum with at least 3000 occupied channels. The channel width corresponded to 1.52 ps. The instrument response has a pulse width (FWHM) of 85 ps.

In order to calculate the fluorescence lifetime, the LEVEL 1 (up to 4 exponentials) package implemented in the Edinburgh Instruments software were used. (The analysis makes use of the iterative reconvolution technique and the Marquardt fitting algorithm.) Plots of weighted residuals and of the autocorrelation function and values of reduced residuals χ^2 were used to judge the quality of the fit.

Diffuse reflection curves of the bulk polymers **Pn+10/n** were obtained with the help of a “Praying Mantis” (PrM) accessory of a CARY 5000 Spectrophotometer (VARIAN). The maximum of the first derivative of the diffuse reflection curve was taken as a measure of the absorption edge.

An internal integrating sphere was additionally used for comparison. The absorption edges found with the help of this technique coincided with those of the PrM within the

reproducibility of about ± 2 nm. Because the PrM technique is more convenient and since it needs significantly less material the majority bulk measurements were performed with the help of the PrM.

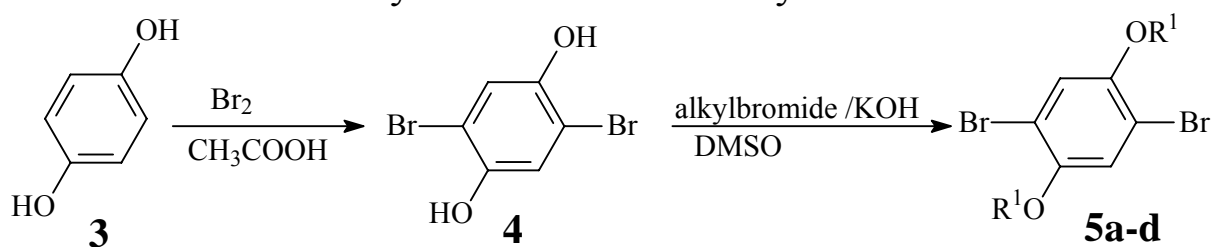
Thermal Behavior and Crystalline Morphologies: A home-made apparatus served for the thermogravimetric measurements. Differential Scanning Calorimetry (DSC) experiments were conducted with cooling and heating rates of 10 K/min using a Mettler 30 calorimeter with a cell purged with nitrogen. Calibration for the temperature and enthalpy changes was performed using Indium as a standard.

Polarized Optical Microscopy (POM) observations were performed using a Zeiss microscope (D-7082) equipped with a temperature controlled stage (Linkam TMS91/THM600) and a colour digital camera (Hitachi KPD50).

Light Emitting Diodes Preparation and Characterization: Diodes of the configuration ITO/PEDOT:PSS/polymer/Ca/Al were prepared in similar manner as described elsewhere by us.¹ The electroluminescence spectra were acquired using a calibrated Ocean Optics HR2000 High-resolution Miniature Fiber Optic Spectrometer. The luminance and the color coordinates were measured with a Minolta CS-100 Chromameter. The I(V) characteristics of the devices were recorded with a Keithley 2400 Source/Measure Unit.

Materials. All starting materials were purchased from commercial suppliers (Fluka, Merck and Aldrich). Toluene, THF, diethyl ether, DMSO and diisopropylamine were dried prior to use.

Synthesis of the dialdehydes



a: $\text{R}^1 = \text{hexadecyl}$; **b:** $\text{R}^1 = \text{heptadecyl}$; **c:** $\text{R}^1 = \text{octadecyl}$; **d:** $\text{R}^1 = \text{nonadecyl}$.

1,4-Dibromohydroquinone (**4**)²

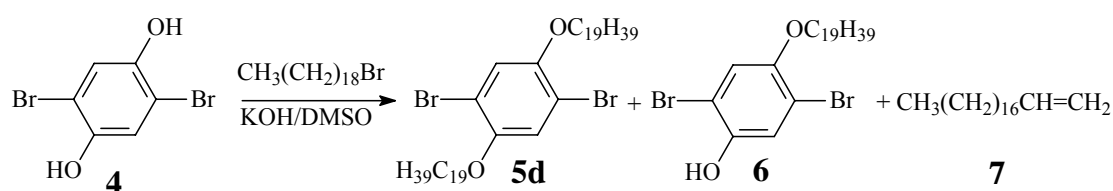
A solution of bromine (46.6 ml, 145.4 g, 0.91 mol) in glacial acetic acid (200 ml) was added dropwise to a vigorously stirred suspension of hydroquinone (**3**) (50 g, 0.454 mol) in glacial acetic acid (240 ml) while keeping the temperature between 10 and 15°C. After standing 12 h at room temperature pale crystals precipitated and were filtered off. The filtrate was reduced to the minimum under vacuum and further solid material was obtained. The crude product was recrystallized several times from methanol giving the title compound as white crystals (49.0 g, 182 mmol). Yield: 40%; m.p. 182°C. $^1\text{H-NMR}$ (250 MHz, acetone- d_6 , 298 K):

$\delta/\text{ppm} = 7.17$ (s, $\text{C}_{\text{aryl}}\text{-H}$), 8.70 (s, $\text{C}_{\text{aryl}}\text{-OH}$). $^{13}\text{C-NMR}$ (63 MHz, acetone- d_6 , 295 K): $\delta/\text{ppm} = 109.52$ ($\text{C}_{\text{aryl}}\text{-Br}$), 120.67 ($\text{C}_{\text{aryl}}\text{-H}$), 148.61 ($\text{C}_{\text{aryl}}\text{-OH}$). Anal. Calcd for $\text{C}_6\text{H}_4\text{O}_2\text{Br}_2$ (267.91): C, 26.90; H, 1.50; Br 59.65. Found: C, 27.18; H, 1.51; Br, 59.83.

1,4-Dibromo-2,5-diheptadecyloxy-benzene (**5b**)

A suspension of KOH powder (2.7 g, 48.12 mmol) in dry DMSO (150 ml) was degassed under vigorous stirring for 1 h. 1,4-Dibromohydroquinone (**4**) (1.225 g, 4.56 mmol) and 1-bromoheptadecane (3.03 g, 9.49 mmol) were then added to it. The solution was stirred for 8 h at room temperature under argon. The reaction mixture was poured into ice water; the obtained precipitate was filtered off, washed with distilled water, dried and subsequently recrystallized in a 1 to 1 mixture of acetone and toluene. 2.43 g (3.26 mmol) of a white substance were obtained. Yield: 72%. M.p. 82-83°C. $^1\text{H-NMR}$ (250 MHz, CDCl_3 , 298 K): δ

/ppm = 0.81 (6H, t, $^3J = 6.59$ Hz, $-\text{CH}_3$), 1.18 → 1.41 (m, $-(\text{CH}_2)_{14}-$), 1.73 (4H, q, $^3J \approx 6.92$ Hz, $-\text{O}-\text{CH}_2-\text{CH}_2-$), 3.87 (4H, t, $^3J = 6.49$ Hz, $-\text{O}-\text{CH}_2-$), 7.01 (2H, s, $\text{C}_{\text{aryl}}-\text{H}$). ^{13}C -NMR (63 MHz, CDCl_3 , 298 K): δ /ppm = 14.14 ($-\text{CH}_3$), 22.70, 25.93, 29.12, 29.31, 29.38, 29.56, 29.59, 29.67, 29.71, 31.94 ($-(\text{CH}_2)_{15}-$), 70.31 ($-\text{CH}_2\text{O}-$), 111.12 ($\text{C}_{\text{aryl}}-\text{Br}$), 118.46 ($\text{C}_{\text{aryl}}-\text{H}$), 150.08 ($\text{C}_{\text{aryl}}-\text{OR}$). Anal. Calcd for $\text{C}_{40}\text{H}_{72}\text{Br}_2\text{O}_2$ (744.82): C, 64.50; H, 9.74; Br, 21.46. Found: C, 64.79; H, 9.46; Br, 21.48.



1,4-Dibromo-2,5-dinonadecyloxy-benzene (5d), *1-Hydroxy-2,5-dibromo-4-nonadecyloxy-benzene (6)* and *1-Nonadecene (7)*.

1-Bromononadecane (3.00 g, 8.64 mmol) and **4** (1.13 g, 4.22 mmol) were added to a degassed suspension of KOH powder (2.6 g, 46.35 mmol) in dry DMSO (150 ml). The suspension was stirred vigorously under argon for 16 h at room temperature and then further 20 h at 50°C.

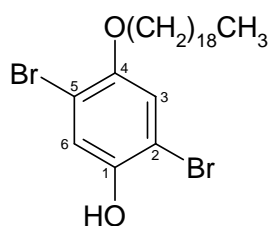
After this time the reaction mixture was poured into ice water; the precipitate was filtered off, washed with distilled water, dried and chromatographed on a silica gel column with toluene as the eluent. **5d** (2.4 g, 3mmol) was obtained in a mixture with small amount of **7** at $R_f = 0.97$ (2.4 g, 3mmol). **7** was easily removable by sublimation. **6** was obtained at $R_f = 0.53$ (0.24 g, 0.45 mmol). Yield: 10.6%; m.p. 83°C.

5d: Yield: 71%. M.p. 80-86°C. ^1H NMR (250 MHz, CDCl_3 , 298 K): δ /ppm = 0.81 (6H, t, $^3J = 6.25$ Hz, $-\text{CH}_3$), 1.08 → 1.53 (m, $-(\text{CH}_2)_{14}-$), 1.73 (4H, "q", $^3J \approx 6.88$ Hz, $-\text{O}-\text{CH}_2-\text{CH}_2-$), 3.87 (4H, t, $^3J = 7.50$ Hz, $-\text{O}-\text{CH}_2-$), 7.01 (2H, s, $\text{C}_{\text{aryl}}-\text{H}$). ^{13}C NMR (63 MHz, CDCl_3 , 298

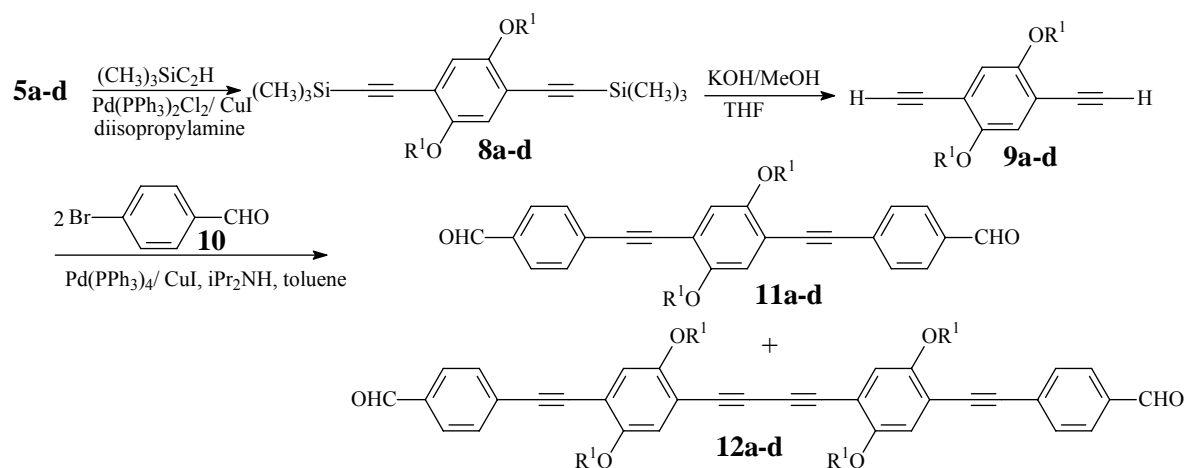
K): δ /ppm = 14.15 ($-\text{CH}_3$), 22.71, 25.94, 29.12, 29.31, 29.39, 29.56, 29.60, 29.68, 29.72, 31.94 ($-(\text{CH}_2)_{15}-$), 70.29 ($-\text{CH}_2\text{O}-$), 111.11 ($\text{C}_{\text{aryl}}\text{-Br}$), 118.42 ($\text{C}_{\text{aryl}}\text{-H}$), 150.06 ($\text{C}_{\text{aryl}}\text{-OR}$).

Anal. Calcd for $\text{C}_{44}\text{H}_{80}\text{O}_2\text{Br}_2$ (800.93): C, 65.98; H, 10.07; Br, 19.95. Found: C, 67.66; H, 10.7; Br, 18.67.

6: Yield: 10.6%. M.p. 83°C . $^1\text{H-NMR}$ (250 MHz, CDCl_3 , 298 K): δ /ppm = 0.88 (3H, t, $^3J = 6.6$ Hz, $-\text{CH}_3$), ca.1.18 \rightarrow 1.60 (32H, m, $-(\text{CH}_2)_{16}-$), 1.81 (2H, pq, $^3J \approx 6.91$ Hz, $-\text{O}-\text{CH}_2-\text{CH}_2-$), 3.93 (2H, t, $^3J = 6.48$ Hz, $-\text{O}-\text{CH}_2-$), 5.13 (1H, s, $-\text{OH}$), 6.98 (1H, s, $\text{C}_{\text{aryl},3}\text{-H}$), 7.24 (1H, s, $\text{C}_{\text{aryl},6}\text{-H}$). $^{13}\text{C-NMR}$ (63 MHz, CDCl_3 , 298 K): δ /ppm = 14.10 ($-\text{CH}_3$), 22.67, 25.91, 29.06, 29.27, 29.34, 29.52, 29.56, 29.64, 29.68, 31.91 ($-(\text{CH}_2)_{16}-$), 70.35 ($-\text{CH}_2\text{O}-$), 108.33 ($\text{C}_{\text{aryl},5}\text{-Br}$), 112.46 ($\text{C}_{\text{aryl},2}\text{-Br}$), 116.59 ($\text{C}_{\text{aryl},3}\text{-H}$), 120.24 ($\text{C}_{\text{aryl},6}\text{-H}$), 146.73 ($\text{C}_{\text{aryl},1}\text{-OH}$), 150.06 ($\text{C}_{\text{aryl},4}\text{-OR}$). Anal. Calcd for $\text{C}_{25}\text{H}_{42}\text{Br}_2\text{O}_2$ (534.42): C, 56.19; H, 7.92; Br, 29.90. Found: C, 56.73; H, 8.23; Br, 29.33.



7: $^1\text{H-NMR}$ (250 MHz, CDCl_3 , 298 K): δ /ppm = 0.91 (t, $^3J = 6.61$ Hz, $-\text{CH}_3$), 1.20 \rightarrow 1.70 (m, $-(\text{CH}_2)_{15}-$), 2.07 ("q""t"; "q": $^3J \approx 6.99$ Hz, "t": $^4J \approx 1.25$ Hz; $\text{H}_2\text{C}=\text{CH}-\text{CH}_2-\text{CH}_2-$), 4.96 (1H, ddt; d: $^2J = 2.38$ Hz, d: $^3J = 10.00$ Hz, t: $^4J = 1.19$ Hz; $\text{H}_{\text{cis}}\text{-HC}=\text{CH}-\text{CH}_2-$), 5.02 (1H, ddt; d: $^2J = 2.19$ Hz, d: $^3J = 16.95$ Hz, t: $^4J = 1.50$ Hz; $\text{H}_{\text{trans}}\text{-HC}=\text{CH}-\text{CH}_2-$), 5.847 (1H, ddt; d: $^3J_{\text{cis}} = 10.32$ Hz, d: $^3J_{\text{trans}} = 17.20$ Hz, t: $^3J = 6.72$ Hz; $\text{H}_2\text{C}=\text{CH}-\text{CH}_2-$). $^{13}\text{C-NMR}$ (63 MHz, CDCl_3 , 298 K): δ /ppm = 14.11 ($-\text{CH}_3$), 22.69 \rightarrow 34.02 ($-(\text{CH}_2)_{16}-$), 114.06 ($\text{H}_2\text{C}=\text{C}$), 139.27 ($=\text{CH}-\text{CH}_2-$).



a: R¹ = hexadecyl, **b:** R¹ = heptadecyl, **c:** R¹ = octadecyl, **d:** R¹ = nonadecyl.

1,4-Diheptadecyloxy-2,5-bis(trimethylsilyl)ethynyl-benzene (**8b**)

5b (2.25 g, 3.02 mmol), Pd(PPh₃)₂Cl₂ (105 mg, 0.15 mmol) and CuI (29 mg, 0.15 mmol) were given to dried and degassed diisopropylamine (40 ml). 800 mg (8.14 mmol) trimethylsilylacetylene was added over a period of 12 min to the vigorously stirred solution. The reaction mixture was then stirred at reflux under argon for 5 h. After cooling, toluene (35 ml) was added and the ammonium bromide precipitate was filtered off. The solvent was removed on a rotary evaporator; the remaining dark solid was dissolved in toluene and passed through a 6 cm plug of silica gel. The evaporation of the solvent led to a brown oil which crystallized upon standing. Recrystallization (twice) from ethanol/chloroform (v/v:5/3) yielded 1.88 g (2.41 mmol) of pale yellow material. Yield: 80%. M.p. 69-71°C. ¹H NMR (200 MHz, CDCl₃, 298 K): δ/ppm = 0.23 (18H, s, -Si(CH₃)₃), 0.85 (6H, t, ³J = 6.50 Hz, -CH₃), 1.13 → 1.53 (m, -(CH₂)₁₄-), 1.75 (4H, "q", ³J ≈ 6.85 Hz, -O-CH₂-CH₂-), 3.91 (4H, t, ³J = 6.30 Hz, -O-CH₂-), 6.85 (2H, s, C_{aryl}-H). ¹³C NMR (50 MHz, CDCl₃): δ/ppm = -0.075 (-Si(CH₃)₃), 14.06 (-CH₃), 22.66, 26.00, 29.33, 29.41, 29.66, 31.90 (-(CH₂)₁₇-), 69.49 (-CH₂O-), 100.02 (≡C-Si(CH₃)₃), 101.08 (C_{aryl}-C≡), 114.01 (C_{aryl}-C≡C-), 117.29 (C_{aryl}-H), 154.03 (C_{aryl}-OR). Calcd for C₅₀H₉₀O₂Si₂ (779.4344 g/mol): C, 77.05; H, 11.64. Found C, 76.76; H, 11.78.

1,4-Dinonadecyloxy-2,5-bis(trimethylsilylethynyl)-benzene (8d)

The same method as above was used for the preparation of this compound. **5d** (2.2 g, 2.747 mmol), Pd(PPh₃)₂Cl₂ (115 mg, 0.164 mmol), CuI (50 mg, 0.26 mmol) and trimethylsilylacetylene (700 mg, 7.13 mmol) were given to diisopropylamine (44 ml). The reaction time was 5.5 h. After work up 1.83 g (2.2 mmol) of pale, rod-shaped crystals were obtained. Yield: 80%. M.p. 72-73°C. ¹H NMR (200 MHz, CDCl₃): δ/ppm = 0.26 (18H, s, –Si(CH₃)₃), 0.88 (6H, t, ³J = 6.40 Hz, –CH₃), 1.17 → 1.57 (m, –(CH₂)₁₆–), 1.79 (4H, "q", ³J ≈ 6.75 Hz, –O–CH₂–CH₂–), 3.94 (4H, t, ³J = 6.30 Hz, –O–CH₂–), 6.89 (2H, s, C_{aryl}–H). ¹³C NMR (50 MHz, CDCl₃): δ/ppm = -0.059 (–Si(CH₃)₃), 14.08 (–CH₃), 22.67, 26.02, 29.35, 29.43, 29.69, 31.92 (–(CH₂)₁₇–), 69.51 (–CH₂O–), 100.03 (≡C–Si(CH₃)₃), 101.10 (C_{aryl}–C≡), 114.04 (C_{aryl}–C≡C–), 117.31 (C_{aryl}–H), 154.05 (C_{aryl}–OR). Anal. Calcd for C₅₄H₉₈O₂Si₂ (835.54): C, 77.63; H, 11.82. Found: C, 77.49; H, 11.90.

1,4-Diethynyl-2,5-diheptadecyloxy-benzene (9b)

A mixture of methanol (20 ml) and aqueous KOH (1.4 ml, 20%) was added at room temperature to a stirred solution of **8b** (1.71 g, 2.194 mmol) in THF (40 ml). After stirring for 3.5 h under light exclusion distilled water (30 ml) was added and the product precipitate was filtered off, dried and recrystallized from hexane with charcoal (twice). 860 mg (1.35 mmol) of pale yellow crystals were obtained. Yield: 62%. M.p. 84-86°C. ¹H-NMR (400 MHz, CDCl₃, 298 K): δ/ppm = 0.86 (6H, t, ³J = 6.80 Hz, –CH₃), 1.21 → 1.48 (m, –(CH₂)₁₄–), 1.77 (4H, "q", ³J ≈ 7.00 Hz, –O–CH₂–CH₂–), 3.30 (2H, s, ≡C–H), 3.95 (4H, t, ³J = 6.60 Hz, –O–CH₂–), 6.93 (2H, s, C_{aryl}–H). ¹³C NMR (100 MHz, CDCl₃, 298 K): δ/ppm = 14.11 (–CH₃), 22.69, 25.90, 29.13, 29.36, 29.58, 29.70 31.93 (–(CH₂)₁₅–), 69.68 (–CH₂O–), 79.79 (C_{aryl}–C≡), 82.37 (≡C–H), 113.27 (C_{aryl}–C≡C–), 117.76 (C_{aryl}–H), 153.99 (C_{aryl}–OR). Anal. Calcd for C₄₄H₇₄O₂ (635.07): C, 83.22; H, 11.74. Found: C, 82.95; H, 12.03.

1,4-Diethynyl-2,5-dinonadecyloxybenzene (9d)

The same method as described above for **9b** was used here. Methanol (19 ml) and aqueous KOH (1.3 ml, 20%) were added to a solution of **8d** (1.72 g, 2.06 mmol) in THF (40 ml). After stirring for 2.5 h water (40 ml) was added and the substance precipitate was filtered off and recrystallized to give 935 mg (1.35 mmol) of white crystals. Yield: 66%. M.p. 87-89°C. ¹H NMR (200 MHz, CDCl₃, 298 K): δ /ppm = 0.88 (6H, t, ³J = 6.50 Hz, -CH₃), 1.20 → 1.49 (64H, m, -(CH₂)₁₄-), 1.80 (4H, "q", ³J ≈ 6.85 Hz, -O-CH₂-CH₂-), 3.33 (2H, s, ≡C-H), 3.97 (4H, t, ³J = 6.60 Hz, -O-CH₂-), 6.95 (2H, s, C_{aryl}-H). ¹³C NMR (100 MHz, CDCl₃, 298 K): δ /ppm = 14.07 (-CH₃), 22.66, 25.88, 29.12, 29.32, 29.56, 29.67 31.90 (-(CH₂)₁₇-), 69.70 (-CH₂O-), 79.78 (C_{aryl}-C≡), 82.33 (≡C-H), 113.30 (C_{aryl}-C≡C-), 117.81 (C_{aryl}-H), 154.00 (C_{aryl}-OR). Anal. Calcd for C₄₈H₈₂O₂ (691.18): C, 83.41; H, 11.96. Found: C, 83.13; H 11.85.

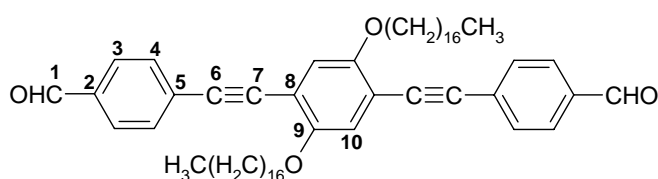
1,4-Bis(4-formylphenyl-1-ethynyl)-2,5-diheptadecyloxybenzene (11b) and

1,4-Bis[4-formylphenyl-(2,5-diheptadecyloxyphenyl)]-but-1,3-diyne (12b)

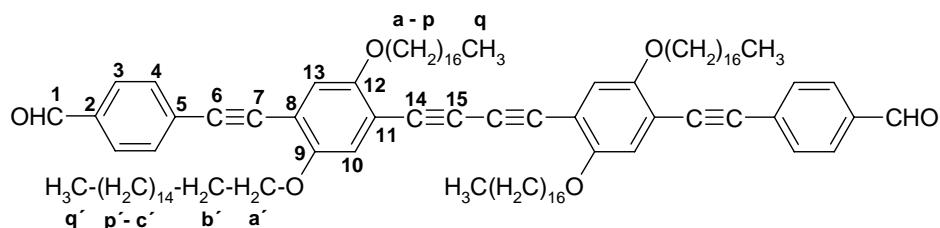
Route1: Diethynyl derivative **9b** (810 mg, 1.28 mmol), 4-bromobenzaldehyde (**10**) (840 mg, 4.97 mmol), Pd(PPh₃)₄ (59 mg, 0.051 mmol, 4 mol%) and CuI (10 mg, 0.053 mmol, 4 mol%) were added to a degassed mixture of toluene (38 ml). The reaction mixture was heated at 60-80°C for 36 h under argon. After cooling to room temperature, it was added dropwise into 250 ml of vigorously stirred methanol to give bright yellow suspension. The precipitate was collected (after 1h stirring) and chromatographed on a silica gel column with toluene as eluent. **11b** was obtained at *R_f* = 0.52 (890 mg, 1.06 mmol) as a bright yellow substance. **12b** was obtained at *R_f* = 0.80 (24 mg, 0.016 mmol) also as a bright yellow powder.

11b: Yield: 82.4%. M.p. 102°C. ¹H NMR (250 MHz, CDCl₃, 298 K): δ /ppm = 0.80 (6H, t, ³J = 6.59 Hz, -CH₃), 1.12 → 1.50 (m, -(CH₂)₁₄-), 1.79 (4H, "q", ³J ≈ 6.87 Hz, -O-CH₂-CH₂-), 3.97 (4H, t, ³J = 6.39 Hz, -O-CH₂-), 6.97 (2H, s, C_{aryl,10}-H), 7.60 (4H, d, ³J = 8.21 Hz, C_{aryl,4}-H), 7.80 (4H, d, ³J = 8.43 Hz, C_{aryl,3}-H), 9.95 (2H, s, -CHO). ¹³C NMR (63 MHz,

CDCl₃, 298 K): δ /ppm = 14.10 (–CH₃), 22.67, 26.06, 29.28, 29.34, 29.38, 29.60, 29.64, 29.68, 31.90 (–(CH₂)₁₅–), 69.57 (–CH₂O–), 90.00 (–C≡C₇–), 94.24 (–C₆≡C–), 113.88 (C_{aryl,8}–C≡C–), 116.80 (C_{aryl,10}), 129.56 (C_{aryl,3}), 129.65 (C_{aryl,5}–C≡C–), 132.02 (C_{aryl,4}), 135.41 (C_{aryl,2}–CHO), 153.84 (C_{aryl,9}–OR), 191.31 (–C₁HO). IR(KBr): 2916 and 2850 (vs, –CH₂– and CH₃–), 2725 (w, –CHO), 2206 (m, disubst. –C≡C–), 1699 (s, –CHO), 1284 (m, C_{aryl}–OR)cm^{–1}. UV-Vis (CHCl₃): λ_{\max} /nm (ϵ /(L·mol^{–1}·cm^{–1})) 396 (38900). Anal. Calcd for C₅₈H₈₂O₄ (843.29): C, 82.61; H, 9.80. Found: C, 82.66; H, 9.62.



12b: Yield: 2.54%. ¹H NMR (400 MHz, CDCl₃): δ /ppm = 0.85/0.86 (12H, 2t, ³J = 6.80/6.80 Hz, –C_qH₃/–C_qH₃), 1.12 → 1.56 (m, –(CH₂)₁₄–), 1.82 (8H, "q", ³J ≈ 6.90 Hz, –O–CH₂–CH₂–), 3.99/4.00 (8H, 2t (superposed), ³J = 6.40/6.40 Hz, –O–C_aH₂–/–O–C_aH₂–), 6.98 (4H, s, C_{aryl,10/13}–H), 7.65 (4H, d, ³J = 8.41 Hz, C_{aryl,4}–H), 7.85 (4H, d, ³J = 8.41 Hz, C_{aryl,3}–H), 10.00 (2H, s, –CHO). ¹³C NMR (100 MHz, CDCl₃): δ /ppm = 14.10 (–CH₃), 22.68, 25.95, 26.08, 29.75, 29.29, 29.37, 29.41, 29.70, 29.72, 31.92 (–(CH₂)₁₅–), 69.58/69.87 (–C_aH₂O–/–C_aH₂O–), 79.59/79.64 (–C₁₄≡C–/–C≡C₁₅–), 90.03 (–C≡C₇–), 94.47 (–C₆≡C–), 113.47/114.23 (C_{aryl,8}–C≡C–/ C_{aryl,11}–C≡C–), 117.03/117.59 (C_{aryl,10}/C_{aryl,13}), 129.56 (C_{aryl,3}), 129.67 (C_{aryl,5}–C≡C–), 132.05 (C_{aryl,4}), 135.47 (C_{aryl,2}–CHO), 153.78/154.99 (C_{aryl,12}–OR/C_{aryl,9}–OR), 191.27 (–C₁HO).

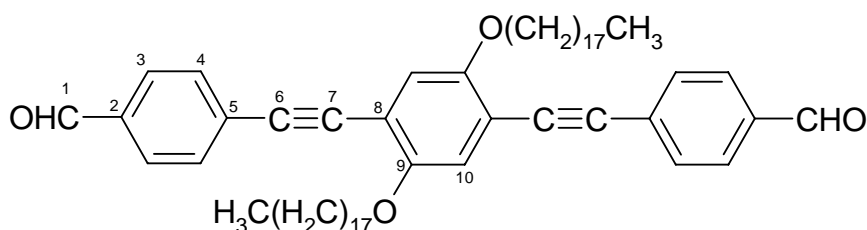


1,4-Bis(4-formylphenyl-1-ethynyl)-2,5-dioctadecyloxybenzene (11c) and

*1,4-Bis[4-formylphenylethynyl-(2,5-dioctadecyloxyphenyl)]-but-1,3-diyne (12c)*⁴

Same synthetic procedure was used as described above for **11b**. Diethynyl derivative **9c** (2.6 g, 3.92 mmol), 4-bromobenzaldehyde (**6**) (2.5 g, 13.51 mmol), Pd(PPh₃)₄ (217 mg, 0.19 mmol, 5 mol%) and CuI (38 mg, 0.2 mmol, 5 mol%) were added to a degassed mixture of toluene (110 ml) and diisopropylamine (60 ml). The reaction time was 26h.

11c: $R_f = 0.34$. 2.33 g (2.67 mmol, yield: 68.2%). M.p. 99-100°C. ¹H NMR (250 MHz, CDCl₃, 298 K): δ /ppm = 0.90 (6H, t, $3J = 6.63$ Hz, $-\text{CH}_3$), 1.21 \rightarrow 1.61 (60H, $-(\text{CH}_2)_{15}-$), 1.90 (4H, "qui", $3J \approx 6.88$ Hz, $-\text{O}-\text{CH}_2-\text{CH}_2-$), 4.075 (4H, t, $3J = 6.25$ Hz, $-\text{O}-\text{CH}_2-$), 7.07 (2H, s, $\text{C}_{\text{aryl},10}-\text{H}$), 7.70 (4H, d, $3J = 8.25$ Hz, $\text{C}_{\text{aryl},4}-\text{H}$), 7.90 (4H, d, $3J = 8.5$ Hz, $\text{C}_{\text{aryl},3}-\text{H}$), 10.05 (2H, s, $-\text{C}_1\text{HO}$). ¹³C NMR (63 MHz, CDCl₃, 298 K): δ /ppm = 14.14 ($-\text{CH}_3$), 22.70, 26.09, 29.31, 29.37, 29.42, 29.64, 29.67, 29.71, 31.93 ($-(\text{CH}_2)_{16}-$), 69.58 ($-\text{CH}_2\text{O}-$), 90.03 ($-\text{C}_7\equiv\text{C}-$), 94.27 ($-\text{C}\equiv\text{C}_6-$), 113.89 ($\text{C}_{\text{aryl},8}-\text{C}\equiv\text{C}-$), 116.80 ($\text{C}_{\text{aryl},9}$), 129.59 ($\text{C}_{\text{aryl},5}-\text{C}\equiv\text{C}-$), 129.67 ($\text{C}_{\text{aryl},3}$), 132.05 ($\text{C}_{\text{aryl},4}$), 135.43 ($\text{C}_{\text{aryl},2}-\text{CHO}$), 153.85 ($\text{C}_{\text{aryl},9}-\text{OR}$), 191.35 ($-\text{C}_1\text{HO}$). IR(KBr): 2916 and 2850 (vs, $-\text{CH}_2-$ and CH_3-), 2721 (w, $-\text{CHO}$), 2206 (m, disubst. $-\text{C}\equiv\text{C}-$), 1700 (s, $-\text{CHO}$), 1283 (m, $\text{C}_{\text{aryl}}-\text{OR}$) cm^{-1} . UV-Vis (CHCl₃): $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/(\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1})$) 396 (40100). Anal. Calcd for C₆₀H₈₆O₄ (871.34): C, 82.71; H, 9.95. Found: C, 82.67; H, 9.51.



12c: $R_f = 0.64$. 49 mg (0.032 mmol, yield: 1.63%).⁴

1,4-Bis(4-formylphenyl-1-ethynyl)-2,5-dihexadecyloxybenzene (11a) and

1,4-bis[4-formylphenylethynyl-(2,5-dihexadecyloxyphenyl)]-but-1,3-diyne (12a)

Same synthetic procedure was used as described above for **11b**. 1,4-diethynyl-2,5-dihexadecyloxybenzene **9a** (1.51 g, 2.48 mmol), 4-bromobenzaldehyde (**6**) (1.61 g, 8.68 mmol), Pd(PPh₃)₄ (114.3 mg, 0.10 mmol, 4 mol%) and CuI (20.6 mg, 0.10 mmol, 4 mol%) were added to a degassed mixture of toluene (66 ml) and diisopropylamine (33 ml). The reaction time was 24h.

11a: $R_f = 0.45$. 0.9 g (2.67 mmol, yield: 45 %). M.p. 99°C. ¹H NMR (250 MHz, CDCl₃, 298 K): δ /ppm = 0.90 (6H, t, $3J = 6.25$ Hz, -CH₃), 1.21 → 1.81 (56H, m, -(CH₂)₁₄-), 3.98 (4H, t, $3J = 6.25$ Hz, -O-CH₂-), 7.07 (2H, s, C_{aryl}-H), 7.70 (4H, d, $^3J = 7.50$ Hz, C_{aryl}-H), 7.90 (4H, d, $^3J = 7.50$ Hz, C_{aryl}-H), 9.95 (2H, s, -CHO). ¹³C NMR (63 MHz, CDCl₃, 298 K): δ /ppm = 14.13 (-CH₃), 22.70, 26.08, 29.31, 29.37, 29.41, 29.63, 29.70, 31.93 (-(CH₂)₁₄-), 69.60 (-CH₂O-), 90.02, 94.27 (-C≡C-), 113.90, 116.80, 129.59, 129.67, 132.05, 135.43, 153.85 (C_{aryl} 's), 191.35 (-CHO). Anal. Calcd for C₅₆H₇₈O₄ (815.23): C, 82.51; H, 9.64. Found: C, 82.19; H, 9.71.

12a: $R_f = 0.60$. Yield: 0.3g (8.5 %). ¹H NMR (250 MHz, CDCl₃, 298 K): δ /ppm = 0.76→1.80 (124H, m, CH₃(CH₂)₁₄-), 3.98 (8H, t, $^3J = 6.50$ Hz, -O-CH₂-), 6.93 (4H, s, C_{aryl}-H), 7.60 (4H, d, $^3J = 8.21$ Hz, C_{aryl}-H), 7.80 (4H, d, $^3J = 8.46$ Hz, C_{aryl}-H), 9.95 (2H, s, -CHO). ¹³C NMR (63 MHz, CDCl₃, 298 K): δ /ppm = 14.12 (-CH₃), 22.69, 25.94, 26.08, 29.13, 29.37, 29.70, 29.73, 31.93 (-(CH₂)₁₄-), 69.53 (-CH₂O-), 79.62 (-C≡C-C≡C-) 90.01, 94.48 (-C≡C-), 113.39, 114.16, 116.93, 129.57, 129.65, 132.05, 135.43 153.74, 154.95 (C_{aryl} 's), 191.34 (-CHO).

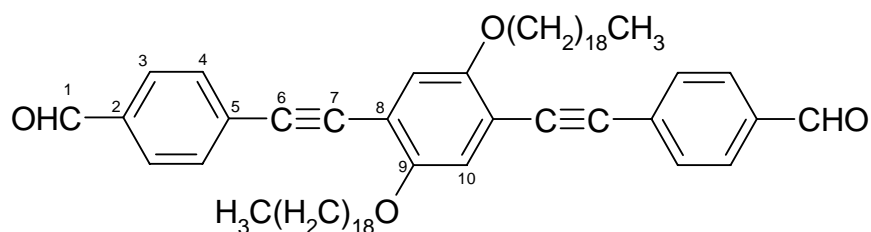
1,4-Bis(4-formylphenyl-1-ethynyl)-2,5-dinonadecyloxybenzene (11d) and

1,4-bis[4-formylphenylethynyl-(2,5-dinonadecyloxyphenyl)]-but-1,3-diyne (12d)

Same synthetic procedure as described above for **11b**. Diethynyl derivative **5d** (845 mg, 1.22 mmol), 4-bromobenzaldehyde (**6**, 795 mg, 4.7 mmol) and Pd(PPh₃)₄ (69 mg, 0.06 mmol, 5

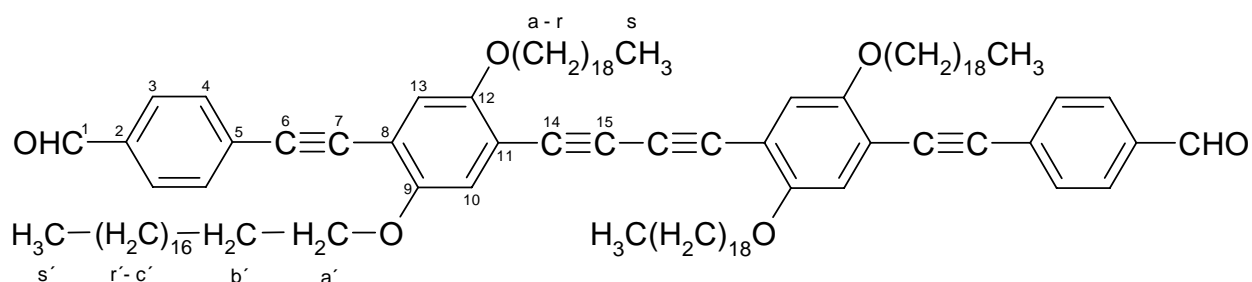
mol%). and CuI (11 mg, 0.058 mmol, 5 mol%) were added to a degassed mixture of toluene (35 ml) and diisopropylamine (18 ml) The reaction time amounted to 26 h.

11d: $R_f = 0.49$. 731 mg (0.81 mmol, yield: 66.6%). M.p. 105-107°C. $^1\text{H NMR}$ (200 MHz, CDCl_3 , 298 K): $\delta/\text{ppm} = 0.86$ (6H, t, $^3J = 6.50$ Hz, $-\text{CH}_3$), 1.12 \rightarrow 1.55 (m, $-(\text{CH}_2)_{16}-$), 1.84 (4H, "q", $^3J \approx 6.85$ Hz, $-\text{O}-\text{CH}_2-\text{CH}_2-$), 4.03 (4H, t, $^3J = 6.40$ Hz, $-\text{O}-\text{CH}_2-$), 7.01 (2H, s, $\text{C}_{\text{aryl},10}-\text{H}$), 7.65 (4H, d, $^3J = 8.21$ Hz, $\text{C}_{\text{aryl},4}-\text{H}$), 7.85 (4H, d, $^3J = 8.41$ Hz, $\text{C}_{\text{aryl},3}-\text{H}$), 10.00 (2H, s, $-\text{CHO}$). $^{13}\text{C NMR}$ (50 MHz, CDCl_3 , 298 K): $\delta/\text{ppm} = 14.09$ ($-\text{CH}_3$), 22.68, 22.98, 26.09, 28.94, 29.35, 29.40, 29.69, 30.40, 31.92 ($-(\text{CH}_2)_{17}-$), 69.69 ($-\text{CH}_2\text{O}-$), 90.05 ($-\text{C}\equiv\text{C}-$), 94.26 ($-\text{C}_6\equiv\text{C}-$), 114.02 ($\text{C}_{\text{aryl},8}-\text{C}\equiv\text{C}-$), 116.96 ($\text{C}_{\text{aryl},10}$), 129.56 ($\text{C}_{\text{aryl},3}$), 129.70 ($\text{C}_{\text{aryl},5}-\text{C}\equiv\text{C}-$), 132.05 ($\text{C}_{\text{aryl},4}$), 135.49 ($\text{C}_{\text{aryl},2}-\text{CHO}$), 153.93 ($\text{C}_{\text{aryl},9}-\text{OR}$), 191.24 ($-\text{C}_1\text{HO}$). IR(KBr): 2918 and 2850 (vs, $-\text{CH}_2-$ and CH_3-), 2721 (w, $-\text{CHO}$), 2207 (m, disubst. $-\text{C}\equiv\text{C}-$), 1701 (s, $-\text{CHO}$), 1284 (m, $\text{C}_{\text{aryl}}-\text{OR}$) cm^{-1} . UV-Vis (CHCl_3): $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/(\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1})$) 397 (41500). Anal. Calcd for $\text{C}_{62}\text{H}_{90}\text{O}_4$ (899.39): C, 82.80; H, 10.09. Found: C, 82.66; H, 10.69.

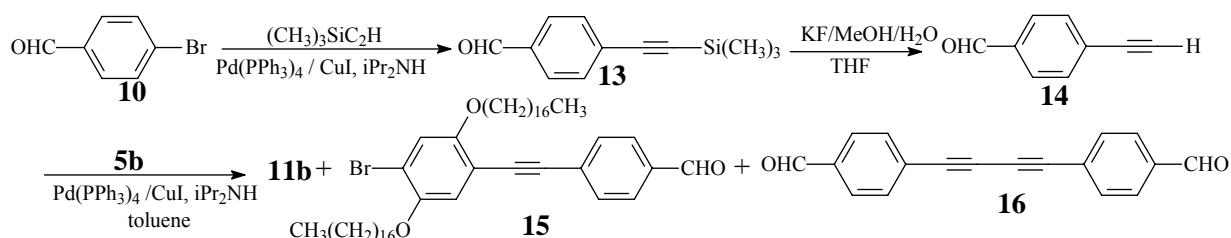


12d: $R_f = 0.78$. 66 mg (0.042 mmol, yield 6.81%). $^1\text{H NMR}$ (400 MHz, CDCl_3 , 313 K): $\delta/\text{ppm} = 0.87$ (12H, t, $^3J = 7.00$ Hz, $-\text{CH}_3$), 1.18 \rightarrow 1.58 (m, $-(\text{CH}_2)_{16}-$), 1.83 (8H, "q", $^3J \approx 7.00$ Hz, $-\text{O}-\text{CH}_2-\text{CH}_2-$), 4.00/4.02 (8H, 2t (superposed), $^3J = 6.20/6.40$ Hz, $-\text{O}-\text{C}_a\text{H}_2-/-\text{O}-\text{C}_a\text{H}_2-$), 6.99 (4H, s, $\text{C}_{\text{aryl},10/13}-\text{H}$), 7.65 (4H, d, $^3J = 8.41$ Hz, $\text{C}_{\text{aryl},4}-\text{H}$), 7.85 (4H, d, $^3J = 8.41$ Hz, $\text{C}_{\text{aryl},3}-\text{H}$), 10.01 (2H, s, $-\text{CHO}$). $^{13}\text{C NMR}$ (100 MHz, CDCl_3 , 313 K): $\delta/\text{ppm} = 14.03$ ($-\text{CH}_3$), 22.66, 25.98, 26.10, 29.204, 29.34, 29.41, 29.69, 30.83, 31.92 ($-(\text{CH}_2)_{15}-$), 69.73/70.03 ($-\text{C}_a\text{H}_2\text{O}-/-\text{C}_a\text{H}_2\text{O}-$), 79.62/79.68 ($-\text{C}_{14}\equiv\text{C}-/-\text{C}\equiv\text{C}_{15}-$), 90.07 ($-\text{C}\equiv\text{C}_7-$), 94.46 ($-\text{C}_6\equiv\text{C}-$), 113.67/114.42 ($\text{C}_{\text{aryl},8}-\text{C}\equiv\text{C}-/ \text{C}_{\text{aryl},11}-\text{C}\equiv\text{C}-$), 117.27/117.80 ($\text{C}_{\text{aryl},10}/\text{C}_{\text{aryl},13}$), 129.51 ($\text{C}_{\text{aryl},3}$),

129.72 ($C_{\text{aryl},5}-C\equiv C-$), 132.05 ($C_{\text{aryl},4}$), 135.58 ($C_{\text{aryl},2}-CHO$), 153.90/155.10 ($C_{\text{aryl},12}-OR/C_{\text{aryl},9}-OR$), 191.09 ($-C_1HO$).



Route 2

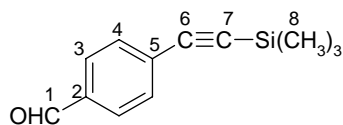


4-(Trimethylsilylethynyl)-benzaldehyde (**13**)³

CuI (196 mg, 1.03 mmol) and Pd(PPh₃)₂Cl₂ (700 mg, 1 mmol) were given to a degassed solution of 4-bromobenzaldehyde (**10**) (10 g, 54.05 mmol) in a mixture of toluene (50 ml) and diisopropylamine (210 ml). Under vigorous stirring 6.9 g (70.74 mmol) of trimethylsilylacetylene were added in small portions over a period of 1 h. After further 4.5 h stirring at reflux under argon more toluene (100 ml) was given to it and the ammonium bromide precipitate was filtered off. The solvents were removed on rotary evaporator; the remaining dark oil was dissolved in toluene and passed through a column of 350 g silica gel.

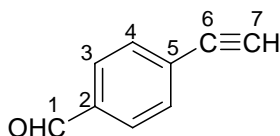
The crude product was recrystallized from hexane (3 times) to give 7.6 g (37.6 mmol) pale brown needles. Yield: 69.5%. M.p. 67-68°C. ¹H NMR (250 MHz, CDCl₃): δ /ppm = 0.24 (9H, s, $-CH_3$), 7.57 (2H, d, ³J = 8.25 Hz, $C_{\text{aryl},4}-H$), 7.79 (2H, d, ³J = 8.5 Hz, $C_{\text{aryl},3}-H$), 9.97 (1H, s, $-CHO$). ¹³C NMR (63 MHz, CDCl₃): δ /ppm = 0.00 ($-Si-CH_3$), 99.24 ($-C\equiv C_7-Si$),

104.04 ($C_{\text{aryl}}-C_6\equiv C-$), 129.56 ($C_{\text{aryl},5}-C\equiv C-$), 129.65 ($C_{\text{aryl},3}$), 132.69 ($C_{\text{aryl},4}$) 135.79 ($C_{\text{aryl},2}-CHO$), 191.64 ($-C_1HO$). Anal. Calcd for $C_{12}H_{14}OSi$ (202.33): C, 71.24; H, 6.97. Found: C, 71.24; H, 6.94.



4-Ethynyl-benzaldehyde (**13**)^{3a}

A mixture of methanol (16 ml), H_2O (2 ml) and KF (1.3 g, 22.4 mmol) was added to a solution of **13** (3 g, 14.83 mmol) in THF (16 ml). After 12 h stirring at room temperature and under light exclusion the reaction solution was concentrated by under vacuum. Dichloromethane (80 ml) was added. The mixture was filtered; the filtrate was washed three times with dilute aqueous Na_2CO_3 solution. After drying the organic phase over $MgSO_4$, the solvent was removed on rotary evaporator; the remaining tawny powder was dried to give 1.78 g of crude product. 0.75 g of this was further purified by sublimation ($3.8 \cdot 10^{-2}$ Torr, the temperature was slowly enhanced to $60^\circ C$) to give 700 mg of small, white crystals for analytical purpose. Yield: 86.1%. M.p. $92^\circ C$. 1H NMR (250 MHz, $CDCl_3$, 298 K): $\delta/ppm = 3.30$ (s, $\equiv C-H$), 7.64 (2H, d, $^3J = 8.30$ Hz, $C_{\text{aryl},4}-H$), 7.84 (2H, d, $^3J = 8.50$ Hz, $C_{\text{aryl},3}-H$), 10.01 (1H, s, $-CHO$). ^{13}C NMR (63 MHz, $CDCl_3$, 298 K): $\delta/ppm = 81.04$ ($H-C_7\equiv C-$), 82.59 ($-C\equiv C_6-C_{\text{aryl}}$), 128.26 ($C_{\text{aryl},5}-C\equiv C-$), 129.45 ($C_{\text{aryl},3}$), 132.67 ($C_{\text{aryl},4}$) 135.90 ($C_{\text{aryl},2}-CHO$), 191.35 ($-C_1HO$). Anal. Calcd for C_9H_6O (130.15): Calcd. C, 83.06; H, 4.65. Found: C, 83.23, H, 4.61.



1,4-Bis(4-formylphenyl)-1-ethynyl)-2,5-diheptadecyloxybenzene (**11b**),

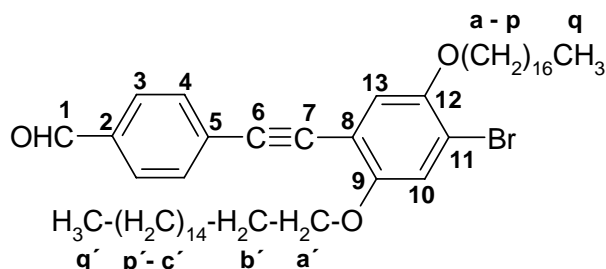
4-Brom-1-(4-formylphenylethynyl)-2,5-bis(heptadecyloxy)-benzene (15) and
1,4-Bis-(4-formylphenyl)-but-1,3-diyne (16).

Route 2: Dibromo derivative **5b** (1.016 g, 1.36 mmol), sublimated 4-ethynylbenzaldehyde (**14**) (365 mg, 2.8 mmol), Pd(PPh₃)₄ (81 mg, 0.07 mmol 5 mol%) and CuI (20 mg, 0.11 mmol, 8 mol%) were added to a degassed mixture of toluene (48 ml) and diisopropylamine (30 ml). The reaction mixture was heated at 60-80°C for 24 h under argon. After cooling to room temperature, it was given dropwise into 300 ml of vigorously stirred methanol. The greenish yellow precipitate was filtered off after 1h stirring, dried to 0.83 g and chromatographed on a silica gel column (68 cm, 300 g) with toluene as eluent. **11b** was obtained at $R_f = 0.36$ (220 mg, 0.26 mmol, yield: 19.2%). The monoaldehyde **15** was obtained at $R_f = 0.78$ as a pale green powder (140 mg 0.18 mmol, yield: 13%). The diyne-containing dialdehyde **16** was obtained at $R_f = 0.15$ and further purified by recrystallization from chloroform to give pale gray needles (24 mg, 0.093 mmol, yield: 6.6%). Some of the starting material **3b** was also regained ($R_f = 0.98$, ~300 mg).

For the analytical data of **11b** see above.

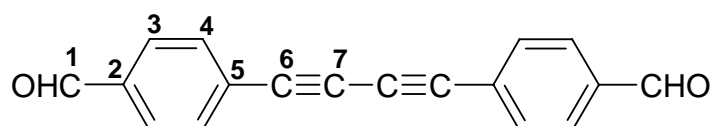
15: M.p. 67°C. ¹H NMR (250 MHz, CDCl₃, 298 K): δ /ppm = 0.88 (6H, t, ³ $J = 6.50$ Hz, –CH₃), 1.22 → 1.58 (m, –(CH₂)₁₄–), 1.79 (4H, m, –O–CH₂–CH₂–), 3.99/4.00 (4H, 2t, ³ $J = 6.38/6.50$ Hz, –O–CH₂–), 7.02 (1H, s, C_{aryl,10}–H), 7.12 (1H, s, C_{aryl,13}–H), 7.66 (2H, d, ³ $J = 8.20$ Hz, C_{aryl,4}–H), 7.86 (2H, d, ³ $J = 8.43$ Hz, C_{aryl,3}–H), 10.02 (1H, s, –CHO). ¹³C NMR (63 MHz, CDCl₃): δ /ppm = 14.10 (–CH₃), 22.67, 25.95, 26.01, 29.15, 29.22, 29.31, 29.34, 29.55, 29.58, 29.64, 29.68 31.91 (–(CH₂)₁₅–), 69.76/70.12 (–CH₂O–), 89.65 (–C≡C₇–), 93.04 (–C₆≡C–), 111.67 (C_{aryl,11}–Br), 114.31 (C_{aryl,10}–H), 117.49 (C_{aryl,8}–C≡), 117.90 (C_{aryl,5}–C≡), 129.54 (C_{aryl,3}–H), 129.75 (C_{aryl,13}–H), 131.94 (C_{aryl,4}–H), 135.33 (C_{aryl,2}–CHO), 149.46 (C_{aryl,12}–OR), 154.38 (C_{aryl,9}–OR), 191.32 (–C₁HO). IR (KBr): 2916 and 2850 (vs, –CH₂– and CH₃–), 2727 (w, –CHO), 2208 (m, disubst.–C≡C–), 1702 (s, –CHO),

1266 (m, C_{aryl}-OR) cm⁻¹. UV-Vis (CHCl₃): λ_{max}/nm (ε/(L·mol⁻¹·cm⁻¹)) 359 (23300). Anal. Calcd for C₄₉H₇₇O₃Br (794.05): C, 74.12; H, 9.77; Br, 10.06. Found: C, 74.35; H, 10.00; Br, 9.80.

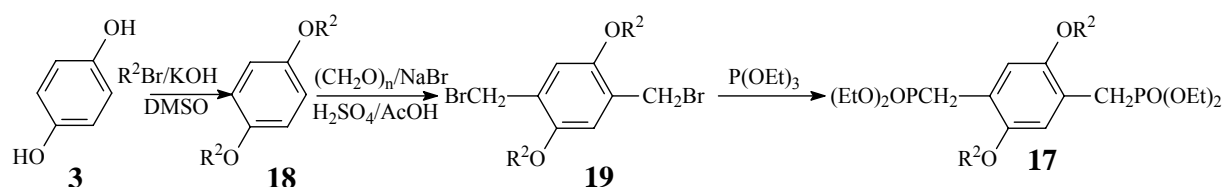


16: M.p. 259-265°C (decomposes). ¹H-NMR (200 MHz, CDCl₃, 298 K): δ/ppm = 7.67 (4H, d, ³J = 8.21 Hz, C_{aryl,4}-**H**), 7.86 (4H, d, ³J = 8.41 Hz, C_{aryl,3}-**H**), 10.02 (2H, s, -CHO).

¹³C NMR (50 MHz, CDCl₃, 298 K): δ/ppm = 82.14 (-C≡C-), 127.57 (C_{aryl,5}-C≡C-), 129.58 (C_{aryl,3}), 133.12 (C_{aryl,4}), 136.33 (C_{aryl,2}-CHO), 191.09 (-C₁HO). Anal. Calcd for C₄₉H₇₇O₃Br (794.05): C, 83.71; H, 3.90. Found: C, 83.05; H, 4.01.



Synthesis of bisphosphonates



1,4-Diheptyloxy-benzene (18b)

A suspension of KOH-powder (8.5 g, 151.5 mmol) in dried DMSO (130 ml) was degassed under vigorous stirring for 1 h. Hydroquinone (**1**) (2.2 g, 20 mmol) and 1-bromoheptane (7.52 g, 42 mmol) were then added to it. It was stirred for 5.5 h at room temperature under argon. The reaction mixture was then poured into ice water (~400 ml); the precipitate was filtered off, washed with distilled water, dried and subsequently recrystallized from a 1:1 mixture of acetone and toluene to give colourless crystals (5.51 g, 18 mmol). Yield: 90%. M.p. 57°C. ¹H NMR (250 MHz, CDCl₃, 298 K): δ /ppm = 0.90 (6H, t, ³J = 6.72 Hz, -CH₃), 1.25 → 1.58 (16H, m, -(CH₂)₄-), 1.76 (4H, "q", ³J ≈ 6.94 Hz, -O-CH₂-CH₂-), 3.90 (4H, t, ³J = 6.58 Hz, -O-CH₂-), 6.83 (4H, s, C_{aryl}-H). ¹³C NMR (63 MHz, CDCl₃, 298 K): δ /ppm = 14.07 (-CH₃), 22.60, 26.01, 29.07, 29.39, 31.78 (-(CH₂)₆-), 68.63 (-CH₂O-), 115.36 (C_{aryl}-H), 153.18 (C_{aryl}-OR). Anal. Calcd for C₂₀H₃₄O₂ (306,49): C, 78.38; H, 11.18. Found: C, 78.60; H 10.94.

1,4-Dioctyloxy-benzene (18c)

This compound was prepared under the same reaction conditions as described for **18b**.

Hydroquinone (**3**) (2.2 g, 20 mmol) and 1-bromooctane (8.2 g, 42.5 mmol) were added to a degassed suspension of KOH-powder (8.7 g, 155 mmol) in dried DMSO (130 ml). After a reaction time of 5 h the reaction mixture was poured in ice water (~350 ml). The subsequent work up resulted in 5.85 g (17.5 mmol) of colourless crystals. Yield: 87.5%. M.p. 54°C.

¹H NMR (250 MHz, CDCl₃, 298 K): δ /ppm = 0.89 (6H, t, 3J = 6.70 Hz, -CH₃), 1.22 → 1.48 (20H, m, -(CH₂)₅-), 1.76 (4H, "q", ³J ≈ 6.95 Hz, -O-CH₂-CH₂-), 3.90 (4H, t, ³J = 6.58 Hz, -O-CH₂-), 6.82 (4H, s, C_{aryl}-H). ¹³C NMR (63 MHz, CDCl₃, 298 K): δ /ppm = 14.08 (-CH₃), 22.64, 26.05, 29.23, 29.37, 29.38, 31.80 (-(CH₂)₇-), 68.64 (-CH₂O-), 115.36 (C_{aryl}-H), 153.17 (C_{aryl}-OR). Anal. Calcd for C₂₂H₃₈O₂ (334,54): C, 78.99; H, 11.45. Found: C, 79.15; H, 11.41.

1,4-Dinonyloxy-benzene (18d)

This compound was prepared under the same reaction conditions as described for **18b**. Hydroquinone (**3**) (2 g, 18.2 mmol) and 1-bromnonane (8.3 g, 40.1 mmol) were added to a degassed suspension of KOH-powder (8.2 g, 146 mmol) and DMSO (150 ml). After 4.5 h stirring at room temperature the mixture was poured in ice water. 5.55 g (15.3 mmol) of colourless crystals were obtained after workup. Yield: 84.1%. M.p. 66°C. ¹H NMR (250 MHz, CDCl₃, 298 K): δ /ppm = 0.92 (6H, t, ³J = 6.55 Hz, -CH₃), 1.26 → 1.51 (24H, m, -(CH₂)₆-), 1.78 (4H, "qui", ³J ≈ 6.94 Hz, -O-CH₂-CH₂-), 3.93 (4H, t, ³J = 6.57 Hz, -O-CH₂-), 6.85 (4H, s, C_{aryl}-H). ¹³C NMR (63 MHz, CDCl₃): δ /ppm = 14.11 (-CH₃), 22.68, 26.07, 29.27, 29.41, 29.43, 29.55, 31.89 (-(CH₂)₇-), 68.66 (-CH₂O-), 115.38 (C_{aryl}-H), 153.20 (C_{aryl}-OR). Anal. Calcd for C₂₄H₄₂O₂ (362,60): C, 79.5; H, 11.68. Found C, 79.31; H 11.07.

1,4-Bis(bromomethyl)-2,5-diheptyloxybenzene (19b)

A suspension of **18b** (4.04 g, 13.18 mmol), paraformaldehyde (5.6 g, 186.5 mmol, (CH₂O)_n) and NaBr (7.1 g, 69 mmol) in glacial acetic acid (90 ml) was heated to 60°C. A 1:1 mixture of conc. sulfuric acid (14 g) and glacial acetic acid (14 g) was added dropwise, and the reaction mixture was stirred for 4 h at 70°C. After cooling at 0°C, the precipitate was filtered off, washed with much water, dried and recrystallized from hexane giving 4.7 g (9.55 mmol) of white crystals. Yield: 72.4%. M.p. 90°C. ¹H NMR (250 MHz, CDCl₃, 298 K): δ /ppm = 0.90 (6H, t, ³J = 6.63 Hz, -CH₃), 1.25 → 1.55 (16H, m, -(CH₂)₆-), 1.82 (4H, "q", ³J ≈ 6.89 Hz, -O-CH₂-CH₂-), 3.99 (4H, t, ³J = 6.41 Hz, -O-CH₂-), 4.53 (4H, s, -CH₂Br), 6.86 (2H, s, C_{aryl}-H). ¹³C NMR (63 MHz, CDCl₃, 298 K): δ /ppm = 14.09 (-CH₃), 22.60, 26.03, 29.02, 29.32, 31.78 (-(CH₂)₅-), 28.74 (-CH₂Br), 68.99 (-CH₂O-), 114.62 (C_{aryl}-H), 127.49 (C_{aryl}-CH₂Br), 150.64 (C_{aryl}-OR). Anal. Calcd for C₂₂H₃₆Br₂O₂ (492.33): C, 53.67; H, 7.37; Br 32.46. Found: C, 54.01; H, 7.39; Br, 32.29.

1,4-Bis(brommethyl)-2,5-dioctyloxy-benzol (19c)

The synthesis of this compound was carried out in the same way as described for **19b**.

To a suspension of **18c** (4.4 g, 13.15 mmol), paraformaldehyde (5.53 g, 154.42 mmol) and NaBr (6.77 g, 65.76 mmol) in glacial acetic acid (90 ml), heated at 60°C, was added dropwise a 1:1 mixture of conc. sulfuric acid (12.31 g) and glacial acetic acid (12.31 g). The reaction mixture was stirred 4 h at 70°C. After work up 4.8 g (9.22 mmol) of a white substance were obtained. Yield: 70.1%. M.p. 88°C. ¹H NMR (250 MHz, CDCl₃, 298 K): δ/ppm = 0.90 (6H, t, ³J = 6.67 Hz, -CH₃), 1.25 → 1.55 (20H, -(CH₂)₅-), 1.82 (4H, "q", ³J ≈ 6.90 Hz, -O-CH₂-CH₂-), 3.99 (4H, t, ³J = 6.41 Hz, -O-CH₂-), 4.53 (4H, s, -CH₂Br), 6.86 (2H, s, C_{aryl}-H).

¹³C NMR (63 MHz, CDCl₃, 298 K): δ/ppm = 14.10 (-CH₃), 22.65, 26.06, 29.23, 29.30, 31.80 (-(CH₂)₆-), 28.74 (-CH₂Br), 68.99 (-CH₂O-), 114.63 (C_{aryl}-H), 127.49 (C_{aryl}-CH₂Br), 150.64 (C_{aryl}-OR). Anal. Calcd for C₂₄H₄₀Br₂O₂ (520.39): C, 55.39; H, 7.75; Br, 30.71. Found C, 55.79; H, 7.69; Br, 30.38.

1,4-Bis(brommethyl)-2,5-dinonyloxybenzene (19d)

The same method as for **19b** was used to synthesise this compound.

18d (4.0 g, 11.03 mmol), paraformaldehyde (4.64 g, 154.42 mmol), NaBr (5.7 g, 55.15 mmol) and glacial acetic acid (95 ml) were mixed and heated at 60°C. A mixture of sulfuric acid (10.3 g) and glacial acetic acid (10.3 g) were added dropwise to the suspension within 80 min. Afterward the stirred mixture was heated at 70°C for 4.5 h. The work up brought 4.8 g (8.75 mmol) of white material. Yield: 79.3%. M.p. 90-92°C. ¹H-NMR (250 MHz, CDCl₃, 298 K): δ/ppm = 0.92 (6H, t, ³J = 6.65 Hz, -CH₃), 1.25 → 1.58 (24H, -(CH₂)₆-), 1.84 (4H, "qui", ³J ≈ 6.88 Hz, -O-CH₂-CH₂-), 4.01 (4H, t, ³J = 6.41 Hz, -O-CH₂-), 4.56 (4H, s, -CH₂Br), 6.88 (2H, s, C_{aryl}-H). ¹³C-NMR (63 MHz, CDCl₃, 298 K): δ/ppm = 14.12 (-CH₃), 22.69, 26.08, 29.27, 29.34, 29.37, 29.55, 31.89 (-(CH₂)₇-), 28.77 (-CH₂Br), 69.01 (-CH₂O-), 114.65

(C_{aryl}-H), 127.51 (C_{aryl}-CH₂Br), 150.67 (C_{aryl}-OR). Anal. Calcd for C₂₆H₄₄O₂Br₂ (548.44): C, 56.94; H, 8.09; Br, 29.14. Found: C, 57.51; H, 7.99; Br, 28.65.

2,5-Diheptyloxy-*p*-xylene-bis(diethylphosphonate) (**17b**)

A mixture of **19b** (4.4 g, 8.94 mmol) and an excess of triethylphosphite (4.46 g, 26.81 mmol) was heated slowly to 150°C, and the evolving ethyl bromide was distilled off simultaneously. After 4.5 h, vacuum was applied for 45 min at 170°C to distill off the excess of triethylphosphite. The remaining oil was allowed to cool to room temperature to form a pale solid, which was recrystallized from diethyl ether giving 5.24 g (8.64 mmol) of a white substance. Yield 96.6%. M.p. 61°C. ¹H NMR (250 MHz, CDCl₃, 298 K): δ/ppm = 0.91 (6H, t, ³J = 6.72 Hz, -O-(CH₂)₆-CH₃), 1.25 (12H, t, ³J = 7.04 Hz, -P(O)-(O-CH₂-CH₃)₂), 1.29 → 1.52 (m, 16H, -(CH₂)₄-), 1.79 (4H, "q", ³J ≈ 6.88 Hz, -O-CH₂-CH₂-), 3.24 (4H, d, ²J_{(H-C-P)} = 20.13 Hz, C_{aryl}-CH₂-P(O)-) 3.93 (4H, t, ³J = 6.53 Hz, -O-CH₂-), 4.03 (8H, "q", ³J_{(H-C-C-H, H-C-O-P)} ≈ 7.18 Hz, -(O)P-(O-CH₂-CH₃)₂), 6.93 (2H, d, ⁴J_{H-C-C-C-P} = 1.57, C_{aryl}-H). ¹³C NMR (63 MHz, CDCl₃, 298 K): δ/ppm = 14.07 (-O-(CH₂)₈-CH₃), 16.29, 16.34, 16.39 (-O)P-O-CH₂-CH₃), 22.59, 26.08, 29.09, 29.47, 31.79 (-(CH₂)₅-, C_{aryl}-CH₂-P(O)-), 61.78, 61.83, 61.88 (-P(O)-O-CH₂-CH₃), 68.99 (-O-CH₂-(CH₂)₇-CH₃), 114.92 (C_{aryl}-CH₂-P(O)-), 119.45 (C_{aryl}-H), 150.37 (C_{aryl}-OR). Anal. Calcd for C₃₀H₅₆P₂O₈ (606.72): C, 59.39; H, 9.30; Found: C, 59.80; H, 9.37.}}}

2,5-Dioctyloxy-*p*-xylene-bis(diethylphosphonate) (**17c**)

This compound was prepared under the same reaction conditions as described for **17b**.

19d (4.35 g, 8.36 mmol) and triethylphosphite (4.3 g, 25.9 mmol) were heated at 150°C for 4.25 h. Afterward the temperature was enhanced up to 170°C and the pressure reduced by using a membrane pump. After recrystallisation from diethyl ether a white material (4.25 g, 6.7 mmol) was obtained. Yield: 80.1%. M.p. 50°C. ¹H NMR (250 MHz, CDCl₃, 298 K): δ /ppm = 0.91 (6H, t, ³J = 6.68 Hz, -O-(CH₂)₇-CH₃), 1.26 (12H, t, ³J = 7.07 Hz, -P(O)-(O-

CH₂-CH₃)₂), 1.29 → 1.52 (m, 20H, -(CH₂)₅-), 1.78 (4H, "qui", ³J ≈ 6.92 Hz, -O-CH₂-CH₂-), 3.24 (4H, d, ²J_(H-C-P) = 20.12 Hz, C_{aryl}-CH₂-P(O)-), 3.94 (4H, t, ³J = 6.53 Hz, -O-CH₂-), 4.04 (8H, "q", ³J_(H-C-C-H, H-C-O-P) ≈ 7.19 Hz, -(O)P-(O-CH₂-CH₃)₂), 6.93 (2H, d, ⁴J_{H-C-C-C-P} = 1.52, C_{aryl}-H). ¹³C-NMR (63 MHz, CDCl₃, 298 K): δ/ppm = 14.08 (-O-(CH₂)₈-CH₃), 16.30, 16.35, 16.40 (-O)P-O-CH₂-CH₃), 22.65, 25.15, 26.13, 27.36, 29.25, 29.39, 29.47, 31.79 (-O-CH₂-CH₃), 61.79, 61.84, 61.89 (-P(O)-O-CH₂-CH₃), 69.00 (-O-CH₂-CH₂-CH₃), 114.92 (d, ²J_{C-C-P} = 1.26 Hz, C_{aryl}-CH₂-P(O)-), 119.52 (C_{aryl}-H), 150.37 (C_{aryl}-OR). Anal. Calcd for C₃₂H₆₀P₂O₈ (634.77): C, 60.55; H 9.53. Found: C, 60.70; H, 9.52.

2,5-Dinonyloxy-p-xylene-bis(diethylphosphonate) (17d)

This compound was prepared under the same conditions as described above for **17b**.

19d (3.0 g, 5.47 mmol) and triethylphosphite (2.82g, 24.24 mmol) were stirred at 150°C for 4 h. Afterward the mixture was heated to 180°C and vacuum was applied to remove the excess of triethylphosphite. The residue was worked up to give 2.86 g (4.31 mmol) of a white substance. Yield: 79%. M.p. 54-56°C. ¹H NMR (250 MHz, CDCl₃, 298 K): δ/ppm = 0.88 (6H, t, ³J = 6.60 Hz, -O-(CH₂)₈-CH₃), 1.23 (12H, t, ³J = 7.07 Hz, (-P(O)-(O-CH₂-CH₃)₂), 1.26 → 1.52 (24H, -(CH₂)₆-), 1.75 (4H, "q", ³J ≈ 6.90 Hz, -O-CH₂-CH₂-), 3.21 (4H, d, ²J_(H-C-P) = 20.14 Hz, C_{aryl}-CH₂-P(O)-) 3.91 (4H, t, ³J = 6.53 Hz, -O-CH₂-), 4.01 (8H, "q", ³J_(H-C-C-H, H-C-O-P) ≈ 7.18 Hz, -(O)P-(O-CH₂-CH₃)₂), 6.91 (2H, s, C_{aryl}-H). ¹³C NMR (63 MHz, CDCl₃, 298 K): δ/ppm = 14.07 (-O-(CH₂)₈-CH₃), 16.28, 16.32, 16.37 (-O)P-O-CH₂-CH₃), 22.63, 25.11, 26.10, 29.23, 29.41, 29.45, 29.53, 31.85 (-O-CH₂-CH₃), 61.76, 61.81, 61.86 (-P(O)-O-CH₂-CH₃), 68.97 (-O-CH₂-(CH₂)₇-CH₃), 114.88 (C_{aryl}-CH₂-P(O)-), 119.40 (C_{aryl}-H), 150.37 (C_{aryl}-OR). Anal. Calcd for C₃₄H₆₄O₈P₂ (662.82): C, 61.61; H 9.73. Found: C, 62.04; H 9.48.

Polycondensation

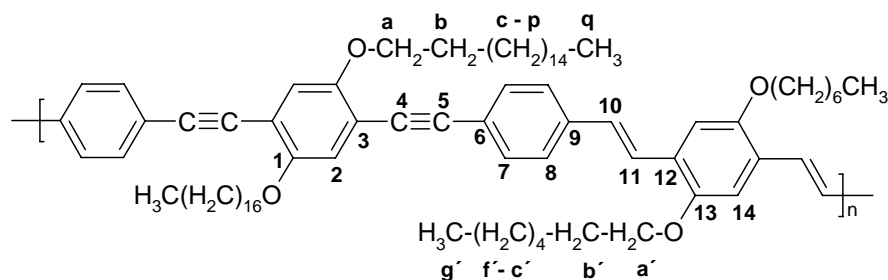
Poly[1,4-phenylenethynylene-1,4-(2,5-dihexadecyloxyphenylene)-1,4-phenylenethene-1,2-diyl-1,4-(2,5-dihexyloxyphenylene)ethene-1,2-diyl] (**P16/6**)

Dialdehyde **11a** (100 mg, 0.123 mmol) and **15a** (71 mg, 0.123 mmol) were dissolved in dried toluene (5ml) while stirring vigorously under argon and heating under reflux. The polycondensations was started by adding potassium-*tert*-butoxide (43 mg, 0.383 mmol). In spite of the rapidly increasing viscosity, the reaction solution was held mixable by adding further dried toluene in small portion ($\Sigma \sim 3$ ml) over the time of reaction. After 25 min benzaldehyde (0.4 ml, 0.42 g, 4 mmol) was added. Toluene (40 ml) and an excess of dilute HCl were mixed in, 2 minutes later. The organic layer was separated and extracted several times with distilled water until the water phase became neutral (pH = 6 – 7). A Dean-Stark apparatus was used to dry the organic layer. The hot (50-60°C) toluene solution was filtered, the filtrate was concentrated to the minimum by using a rotary evaporator and then precipitated in vigorously stirred acetone (300 ml). The polymer was extracted (soxlett extractor) 12 h with methanol, dissolved once more in a small amount of toluene, reprecipitated in acetone and dried under vacuum. 96 mg (0.0884 mmol, pertaining of the repeating unit) of orange red polymer were obtained. Yield: 72%. GPC (THF, polystyrene): $\bar{M}_w = 44\ 600$ g/mol, $\bar{M}_n = 16\ 900$ g/mol, PDI = 2.64. IR (KBr): 3050 (w, $-\text{C}_{\text{aryl}}-\text{H}$), 2923 and 2852 (vs, $-\text{CH}_2-$ and CH_3-), 2202 (w, disubst. $-\text{C}\equiv\text{C}-$), 1625 (w, $-\text{CH}=\text{CH}-$), 1211 (s, $\text{C}_{\text{aryl}}-\text{OR}$), 964 (m, trans $-\text{CH}=\text{CH}-$) cm^{-1} . UV-Vis (CHCl_3): $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/(\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1})$) 448 (77600). Anal. Calcd for $(\text{C}_{76}\text{H}_{108}\text{O}_4)_n$ ($(1085.69)_n$): C, 84.08; H, 10.03. Found: C, 79.55; H, 10.03.

Poly[1,4-phenylenethynylene-1,4-(2,5-diheptadecyloxyphenylene)-1,4-phenylenethene-1,2-diyl-1,4-(2,5-diheptyloxyphenylene)ethene-1,2-diyl] (**P17/7**)

This polymer was prepared under similar reaction conditions as described for **P16/6**.

Dialdehyde **11b** (500 mg, 0.593 mmol) and **17b** (360 mg, 0.593 mmol) were dissolved in dried toluene (20 ml) while stirring vigorously under argon and heating under reflux. Potassium-*tert*-butoxide (210 mg, 1.87 mmol) was added; and the reaction mixture was heated at reflux for 36 min. Within this time, additional toluene (55 ml) was added in small portions due to the fast increase of viscosity of the reaction mixture. Further potassium-*tert*-butoxide (90 mg 0.8 mmol) were added after 30 min reaction. The polycondensations was quenched by adding of benzaldehyde (0.75 ml, 7.4 mmol), and dilute HCl (80 ml) The organic layer was separated, extracted with distilled water, dried, filtrated at room temperature, concentrated and precipitated in acetone (450 ml). The polymer was extracted with methanol for 18 h, dissolved and reprecipitated. The resulting yellow polymer was dried to 372 mg (0.326 mmol). Yield: 55%. GPC (THF, Polystyrene): $\bar{M}_w = 95\ 400$ g/mol, $\bar{M}_n = 28\ 600$ g/mol, PDI = 3.33. ^1H NMR (200 MHz, CDCl_3 , 298 K): $\delta/\text{ppm} = 0.84$ und 0.89 ($-\text{CH}_3$), $1.10 \rightarrow 1.52$ ($-(\text{CH}_2)_4-$ and $-(\text{CH}_2)_{14}-$), 1.83 ($-\text{O}-\text{CH}_2-\text{CH}_2-$), 4.04 ($-\text{O}-\text{CH}_2-$), $6.99 \rightarrow 7.6$ (aromatic – and vinylene H's). ^{13}C NMR (50 MHz, CDCl_3 , 298 K): $\delta/\text{ppm} = 14.05$ ($-\text{CH}_3$), 22.57 , 22.64 , 26.05 , 26.22 , 29.07 , 29.32 , 29.40 , 29.48 , 29.68 , 31.81 , 31.89 ($-(\text{CH}_2)_5-$, $-(\text{CH}_2)_{15}-$), 69.54 ($-\text{CH}_2\text{O}-$), 87.01 ($-\text{C}\equiv\text{C}_4-$), 95.21 ($-\text{C}_5\equiv\text{C}-$), 110.68 ($\text{C}_{\text{aryl},14}-\text{H}$), 114.11 ($-\text{C}_{\text{aryl},3}-\text{C}\equiv$), 117.00 ($\text{C}_{\text{aryl},2}-\text{H}$), 124.27 ($\text{C}_{\text{aryl},12}$), 126.36 ($-\text{C}_{10}=\text{C}_{11}-$), 128.20 ($\text{C}_{\text{aryl},6}-\text{C}\equiv$), 131.84 ($\text{C}_{\text{aryl},7,8}$), 137.94 ($\text{C}_{\text{aryl},9}-\text{C}=\text{}$), 151.22 ($\text{C}_{\text{aryl},13}-\text{OR}^2$), 153.67 ($\text{C}_{\text{aryl},1}-\text{OR}^1$). IR (KBr): 3052 (w, $-\text{C}_{\text{aryl}}-\text{H}$), 2923 und 2851 (vs, $-\text{CH}_2-$ and CH_3-), 2201 (w, disubst.- $\text{C}\equiv\text{C}-$), 1625 (m, $-\text{CH}=\text{CH}-$), 1211 (m, $\text{C}_{\text{aryl}}-\text{OR}$), 965 (m, trans $-\text{CH}=\text{CH}-$) cm^{-1} . UV-Vis (CHCl_3): $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/(\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1})$) 450 (101300). Anal. Calcd for $(\text{C}_{80}\text{H}_{116}\text{O}_4)_n$ ($(1141,8)_n$): C, 84.15; H, 10.24. Found: C, 83.61; H, 10.36.



Poly[1,4-phenylenethynylene-1,4-(2,5-dioctadecyloxyphenylene)-1,4-phenylenethene-1,2-diyl-1,4-(2,5-dioctyloxyphenylene)ethene-1,2-diyl] (P18/8)

Dialdehyde **11c** (600 mg, 0.69 mmol), **17c** (438 mg, 0.69 mmol), dried toluene (25 ml) and potassium-*tert*-butoxide (240 mg, 2.14 mmol) were mixed under argon and heating under reflux. From time to time small toluene ($\Sigma \sim 55$ ml) portions were added to regulate the viscosity of the reaction mixture. After 25 min further potassium-*tert*-butoxide (100 mg, 0.89 mmol), after 37 min benzaldehyde (1 ml, 10 mmol) and after 46 min toluene (50 ml) and dilute hydrochloric acid were added. The organic layer was washed with water, dried, filtered (55°C), concentrated and precipitated. The polymer was extracted for 20 h, dissolved, reprecipitated and dried to give 686 mg (0.57 mmol) of orange red polymer. Yield: 83%. GPC (THF, Polystyrene): $\bar{M}_w = 115\,600$ g/mol, $\bar{M}_n = 30\,600$ g/mol, PDI = 3.77. ^1H NMR (200 MHz, CDCl_3 , 298 K): δ /ppm = 0.85 und 0.89 ($-\text{CH}_3$), 1.10 \rightarrow 1.52 (m, $-(\text{CH}_2)_5-$ and $-(\text{CH}_2)_{15}-$), 1.85 ($-\text{O}-\text{CH}_2-\text{CH}_2-$), 4.06 ($-\text{O}-\text{CH}_2-$), 7.00 \rightarrow 7.60 (aromatic $-$ und vinylene H's). ^{13}C -NMR (50 MHz, CDCl_3 , 298 K): δ /ppm = 14.08 ($-\text{CH}_3$), 22.67, 26.08, 26.30, 29.35, 29.41, 29.70, 31.82, 31.91 ($-(\text{CH}_2)_5-$, $-(\text{CH}_2)_{15}-$), 69.60 ($-\text{CH}_2\text{O}-$), 110.74 ($\text{C}_{\text{aryl},14}-\text{H}$), 117.05 ($\text{C}_{\text{aryl},2}-\text{H}$), 126.40 ($-\text{C}_{10}=\text{C}_{11}-$), 131.87 ($\text{C}_{\text{aryl},7,8}$), 151.26 ($\text{C}_{\text{aryl},13}-\text{OR}^2$), 153.70 ($\text{C}_{\text{aryl},1}-\text{OR}^1$). IR (KBr): 3052 (w, $-\text{C}_{\text{aryl}}-\text{H}$), 2923 und 2851 (vs, $-\text{CH}_2-$ und CH_3-), 2201 (w, disubst.- $\text{C}\equiv\text{C}-$), 1628 (m, $-\text{CH}=\text{CH}-$), 1212 (m, $\text{C}_{\text{aryl}}-\text{OR}$), 965 (m, trans $-\text{CH}=\text{CH}-$) cm^{-1} .

UV-Vis (CHCl₃): λ_{\max}/nm ($\epsilon/(\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1})$) 450 (102600). Anal. Calcd for (C₈₄H₁₂₄O₄)_n ((1197.92)_n): C, 84.22; H, 10.44. Found: C 83.76, H 10.80.

Poly[1,4-phenylenethinylene-1,4-(2,5-dinonadecyloxyphenylene)-1,4-phenylenethen-1,2-diyl-1,4-(2,5-dinonyloxyphenylene)ethen-1,2-diyl] (**P19/9**)

Dialdehyde 11d (500 mg, 0.56 mmol), **17d** (369 mg, 0.56 mmol) and potassium-*tert*-butoxide (196 mg, 1.75 mmol) were given to 20 ml toluene (20 ml). Further 55 ml toluene were added in small portions during the 37 min reaction time. 7min before the end of the reaction further potassium-*tert*-butoxide (100 mg, 0.89 mmol) and benzaldehyde (1.0 ml, 10 mmol) were added. The work up was carried as described above. 625 mg (0.498 mmol) of a yellow polymer were obtained. Yield: 89%. GPC (THF, Polystyrene): $\bar{M}_w = 171\,900$ g/mol, $\bar{M}_n = 45\,700$ g/mol, PDI = 3.76. ¹H NMR (200 MHz, CDCl₃, 298 K): $\delta/\text{ppm} = 0.86$ und 0.88 (–CH₃), 1.10 → 1.65 (m, –(CH₂)₆– and –(CH₂)₁₆–), 1.85 (–O–CH₂–CH₂–), 4.05 (–O–CH₂–), 6.97→7.70 (aromatic – and vinylene H's). ¹³C-NMR (50 MHz, CDCl₃, 298 K): $\delta/\text{ppm} = 14.09$ (–CH₃), 22.68, 26.09, 26.31, 29.29, 29.36, 29.47, 29.72, 31.92 (–(CH₂)₆–, –(CH₂)₁₆–), 69.60 (–CH₂O–), 110.77 (C_{aryl,14}–H), 114.17 (–C_{aryl,3}–C≡), 117.02 (C_{aryl,2}–H), 124.47 (C_{aryl,12}), 126.40 (–C₁₀=C₁₁–), 128.26 (C_{aryl,6}–C≡), 131.87 (C_{aryl,7,8}), 137.87 (C_{aryl,9}–C=), 151.27 (C_{aryl,13}–OR²), 153.70 (C_{aryl,1}–OR¹). IR (KBr): 3054 (w, –C_{aryl}–H), 2922 und 2851 (vs, –CH₂– und CH₃–), 2201 (w, disubst. –C≡C–), 1624 (m, –CH=CH–), 1213 (m, C_{aryl}–OR), 965 (m, trans –CH=CH–) cm⁻¹. UV-Vis (CHCl₃): λ_{\max}/nm 447. Anal. Calcd for (C₈₈H₁₃₂O₄)_n ((1254.01)_n): C, 84.29; H, 10.61. Found: C, 83.61; H, 10.90.

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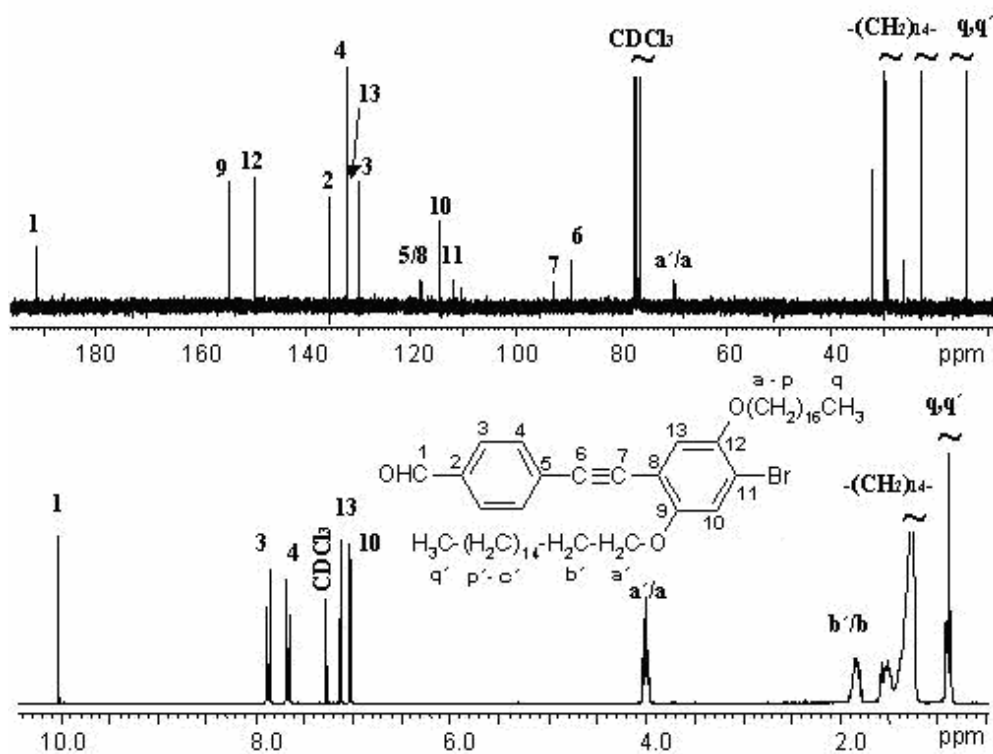


Figure S1: ^1H and ^{13}C NMR spectra of monoaldehyde **15** in CDCl_3 .

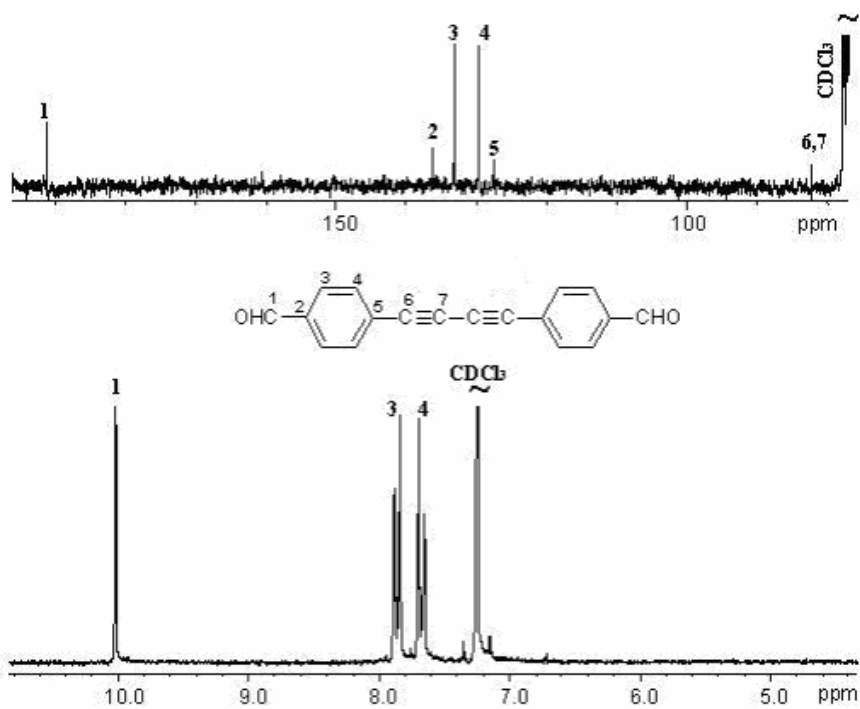


Figure S2: ^1H and ^{13}C NMR spectra of dialdehyde **16** in CDCl_3 .