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Chem. Eur. J. **2002**

Supporting Information for
An Efficient Synthesis of Liquid Crystalline Gigantocycles Combining Banana-Shaped and Rod-Like Mesogenic Units

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1. Preparation of starting materials

3-Tetrahydropyranyloxyprop-1-yne.[1] Dihydropyran (66.0 g, 784 mmol) is slowly added to a cooled (ice bath) solution of prop-2-ynol (30.0 g, 535 mmol) and toluenesulfonic acid monohydrate (4.8 g, 25 mmol) in diethyl ether (300 mL) (exothermic reaction!). After the addition was completed, the ice bath was removed and the reaction mixture was stirred for 4-5 h at room temperature. NaOH (2 N, 50 mL) and then water were added, and the aqueous phase was extracted with diethyl ether. The combined organic phases were washed with water and brine, dried ($MgSO_4$), and concentrated in vacuo. Fractional distillation (69-73 ^oC, 12 mm) of the residue gave 3-tetrahydropyranyloxyprop-1-yne (57 g, 76%) as a colorless liquid. Most often two distillations were needed to give sufficiently pure material.

2,6-Dimethyl-4-iodophenol.[2] To a solution of 2,6-dimethylphenol (20.0 g, 16.4 mmol) in acetic acid (100 mL) was added dropwise a solution of iodomonochloride (28 g, 17.2 mmol) in acetic acid (70 mL) at room temperature. After stirring overnight, the reaction mixture was decolorized with saturated aqueous Na_2SO_3 and the product was precipitated by the addition of water. It was filtered off and washed well with water. After recrystallizing twice from acetic acid/water [2:1; 1) 270 mL, 2) 120 mL], the crystals were dissolved in CH_2Cl_2. The solution was washed with saturated aqueous $NaHCO_3$, then with 2N HCl and dried ($MgSO_4$). Removal of the solvent in vacuo gave 2,6-dimethyl-4-iodophenol (10.2 g, 17 %) as a colorless solid. The repeated crystallization was necessary to get pure product (according to ^{1}H NMR).

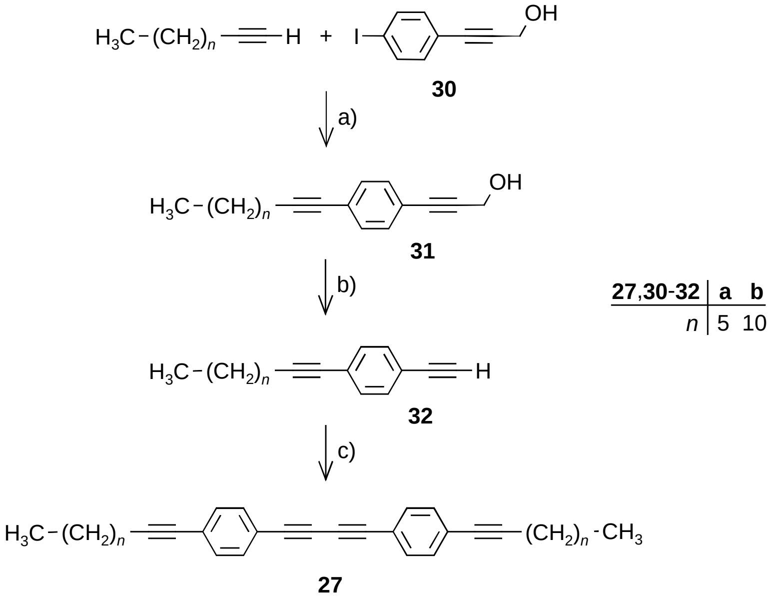
11-Bromoundecyltrimethylsilylether (10). A solution of 11-bromoundecanol (50.0 g, 199 mmol) in hexamethyldisilazane (100 mL) and trimethylsilylchloride (2 mL) was kept at 120 °C for 5.5 h. Excess of the reagents was distilled off at 9 mbar. The residue was dissolved in diethyl ether and water. The aqueous phase was extracted with diethyl ether. The combined organic phases were washed with water, dried (Na_2SO_4), and the solvent was removed in vacuo. Fractional distillation (120-122 °C, 0.01 mbar) using a Bösherz distillation column gave **10** (67 g, 88%) as a slightly yellow liquid. The other distillation fractions (70-119 °C, 0.01 mbar) contained olefinic material, most probably $H_2C{=}CH(CH_2)_9OTMS$. ^{1}H-NMR: δ = 3.43 (t, J = 6.5 Hz, 2 H, OCH_2), 3.24 (t, J = 6.9 Hz, 2 H, CH_2Br), 1.71 (m, 2 H, $OCH_2C\mathbf{H}_2$), 1.50–1.10 (m, 16 H, CH_2), 0.04 (s, 9 H, $SiCH_3$); ^{13}C-NMR: δ = 62.3 (OCH_2), 33.1, 32.7, 32.5, 29.4 - 28.0 (5 signals) and 25.6 (CH_2), -0.7 ($SiCH_3$); Elemental analysis (%) calcd for $C_{14}H_{31}BrOSi$ (323.397): C 51.99, H 9.66; found C 51.65, H 9.02.

Additional note: The product can also be used without distillation for the preparation of **11**.

1-Bromo-4-(triethylsilylethynyl)benzene (18c). To a cold (0 °C) solution of 4-bromo-1-iodobenzene (25.00 g, 88.37 mmol) in diethylamine (200 mL) was added triethylsilylethyne (17 ml, 95 mmol) followed by $PdCl_2(PPh_3)_2$ (620 mg, 0.88 mmol) and CuI (336 mg, 1.76 mmol). After 16 h at room temperature the solvent was removed in vacuo and the residue was dissolved in petroleum ether and 2N HCl (exothermic!). The aqueous phase was extracted with petroleum ether and the combined organic phases were washed with 2 N HCl and dried ($MgSO_4$). Distillation (99-103 °C, 10^{-2} mbar) gave **18c** (21.1 g, 81 %) as a pale yellow liquid. ^{1}H NMR: δ = 7.42 (half of AA'XX', 2 H, H-2, -6), 7.32 (half of AA'XX', 2 H, H-3, -5), 1.04 (t, J = 7.9 Hz, 9 H, CH_3), 0.67 (q, J = 7.9 Hz, 6 H, CH_2); ^{13}C NMR: δ = 133.4 (C-3,-5), 131.4 (C-2,-6), 122.6 and 122.3 (C-1,-4), 105.2 and 93.1 ($C{\equiv}C$), 7.4 (CH_3), 4.4 (CH_2); Elemental analysis (%) calcd for $C_{14}H_{19}SiBr$ (295.302): calcd C 56.94, H 6.49; found C 57.08, H 6.54. In several cases, the distilled product contained traces of 1,4-bis(triethylsilylethynyl)benzene (^{1}H NMR: δ = 7.38).

1-Iodo-4-(triethylsilylethynyl)benzene (19c). To a solution of **18c** (20.16 g, 68.27 mmol) in THF (200 mL) was added dropwise (ca. 20 min) 1.6 M *n*-BuLi in hexane (47 mL, 75.2 mmol) at -85 °C. After stirring the solution at -85 °C for 45 min, iodine (20.1 g, 79.20 mmol) was added as a solid. The cooling bath was removed and the reaction mixture was allowed to come to room temperature. Then, saturated aqueous $Na_2S_2O_3$ was added. The aqueous phase was extracted with petroleum ether, the organic phase was washed with saturated aqueous $Na_2S_2O_3$ and finally with brine, and dried ($MgSO_4$). Distillation (102-106 °C, $9 \cdot 10^{-3}$ mbar) gave iodo compound **19c** (20.5 g, 88%) as a reddish liquid. The product was once again dissolved in petroleum ether, washed with saturated aqueous $Na_2S_2O_3$, water, and brine, and dried ($MgSO_4$) to give a colorless oil (19.7 g, 84%). The product contained traces of the hydrolysis product (triethylsilylethynyl)benzene. M.p.: 28.5-29.2 °C; ^{1}H NMR: $\delta = 7.63$ (half of AA'XX', 2 H, H-2, -6), 7.18 (half of AA'XX', 2 H, H-3, -5), 1.03 (t, $J = 7.9$ Hz, 9 H, CH_3), 0.66 (q, $J = 7.9$ Hz, 6 H, CH_2); ^{13}C NMR: $\delta = 137.3$ (C-2,-6), 133.5 (C-3,-5), 122.9 (C-4), 105.2 (**C**≡CSi), 94.2 (C-1), 93.4 (C≡**C**Si), 7.4 (CH_3), 4.4 (CH_2); Elemental analysis (%) calcd for $C_{14}H_{19}ISi$ (342.297): C 49.13, H 5.60; found C 49.53, H 5.79.

2. Synthesis of the rodlike model compounds (Scheme 1)



27,30-32	**a**	**b**
n	5	10

Scheme 1. a) $Pd(PPh_3)_2Cl_2$, CuI, piperidine; b) MnO_2, powdered KOH, diethyl ether; c) $Pd(PPh_3)_2Cl_2$, CuI, piperidine, THF, air.

3-[4-(Oct-1-ynyl)phenyl]prop-2-yn-1-ol (31a). To a solution of 3-(4-iodophenyl)prop-2-yn-1-ol (**30**)[3] (1.75 g, 6.8 mmol) and 1-octyne (1.5 mL, 10 mmol) in piperidine (20 mL) were added $PdCl_2(PPh_3)_2$ (47 mg, 0.07 mmol) and CuI (26 mg, 0.14 mmol) at room temperature.

The reaction was slightly exothermic. After 19 h the reaction mixture was cooled (ice bath) diethyl ether and 5 N HCl were added. The organic phase was washed with 5 N HCl, dried ($MgSO_4$), and the solvent was removed. Flash chromatography (petroleum ether/diethyl ether 1:1 v/v) gave **31a** (670 mg, 41%) as a yellow-brownish solid ($R_f = 0.53$). The low yield is due to difficult separation from 3-[4-(Oct-1-ynyl)phenyl]undec-2-en-4-yn-1-ol ($R_f = 0.59$) which results from a competing carbometallation reaction. M.p.: 39.4-40.6 °C; ^{1}H NMR: $\delta = 7.32$ (singlet shaped, 4 H, ArH), 4.48 (s, 2 H, CH_2O), 2.39 (t, $J = 7.0$ Hz, 2 H, ArC**H**$_2$), 1.71 (br s, 1H, OH), 1.59 (m, 2 H, C**H**$_2$CH$_2$O), 1.5-1.2 (m, 6 H, CH_2), 0.89 (m, 3 H, CH_3); ^{13}C NMR: $\delta =$ 131.5 and 131.4 (CH), 124.4 and 121.5 (C-1,-4 of ArH), 92.7, 88.5, 85.5, and 80.2 (C≡C), 51.7 (CH_2O), 31.3, 28.64, 28.59, 22.5, and 19.5 (CH_2), 14.0 (CH_3); Elemental analysis (%) calcd for $C_{17}H_{20}O$ (240.346): C 84.96, H 8.39; found C 84.95, H 8.45.

3-[4-(Oct-1-ynyl)phenyl]prop-2-yne (32a). To a solution of **31a** (555 mg, 2.31 mmol) in diethyl ether (40 mL) were added a mixture of MnO_2 (activated MnO_2 from Aldrich company; 3.0 g, 34 mmol) and powdered KOH (969 mg, 17 mmol) in three portions within 4 h.[4-6] The reaction can be monitored by TLC (petroleum ether/diethyl ether 1:1 v/v). After the reaction was quantitative, the reaction mixture was applied to a column filled with silica gel and **32a** (398 mg, 82% was eluted with petroleum ether as a tawny colored liquid. ^{1}H NMR: $\delta = 7.40$ and 7.33 (AA'XX', 2 H each, ArH), 3.13 (s, 1 H, C≡CH), 2.40 (t, $J = 7.0$ Hz, 2 H, ArC**H**$_2$), 1.60 (m, 2 H, C**H**$_2$CH$_2$O), 1.5-1.2 (m, 6 H, CH_2), 0.90 (m, 3 H, CH_3); ^{13}C NMR: $\delta = 131.9$ and 131.4 (CH), 124.7 and 121.1 (C-1,-4 of ArH), 92.7, 83.4, 80.2, and 78.3 (C≡C), 31.3, 28.63, 28.59, 22.5, and 19.5 (CH_2), 14.0 (CH_3); Elemental analysis (%) calcd for $C_{16}H_{18}$ (210.320): C 91.37, H 8.63; found C 90.83, H 7.98.

4,4'-Bis-[4-(oct-1-ynyl)phenyl]butadiyne (27a). A solution of **32a** (447 mg, 2.12 mmol), $PdCl_2(PPh_3)_2$ (36 mg, 0.05 mmol) and CuI (19 mg, 0.10 mmol) in THF (15 mL) and piperidine (5 mL) was stirred at room temperature under air for 5 h. To the cooled (ice bath) reaction mixture were added 5N HCl and petroleum ether. The aqueous phase was extracted with petroleum ether. The combined organic phases were washed with 5N HCl, brine, and dried ($MgSO_4$). The solvent was removed in vacuo. Flash chromatography (petroleum ether/CH_2Cl_2 1:1 v/v) gave **27a** (382 mg, 86%) as a yellow-brown solid. M.p.: 141.0-142.8 °C; ^{1}H NMR: $\delta = 7.42$ and 7.33 (AA'XX', 4 H each, ArH), 2.41 (t, $J = 7.0$ Hz, 4 H, ArC**H**$_2$), 1.60 (m, 4 H, C**H**$_2$CH$_2$O), 1.5-1.2 (m, 12 H, CH_2), 0.90 (m, 6 H, CH_3); ^{13}C NMR: $\delta = 132.3$ and 131.5 (CH), 125.2 and 120.6 (C-1,-4 of ArH), 93.6 (CH$_2$**C**≡C), 82.0 (**C**≡C-C≡**C**), 80.3

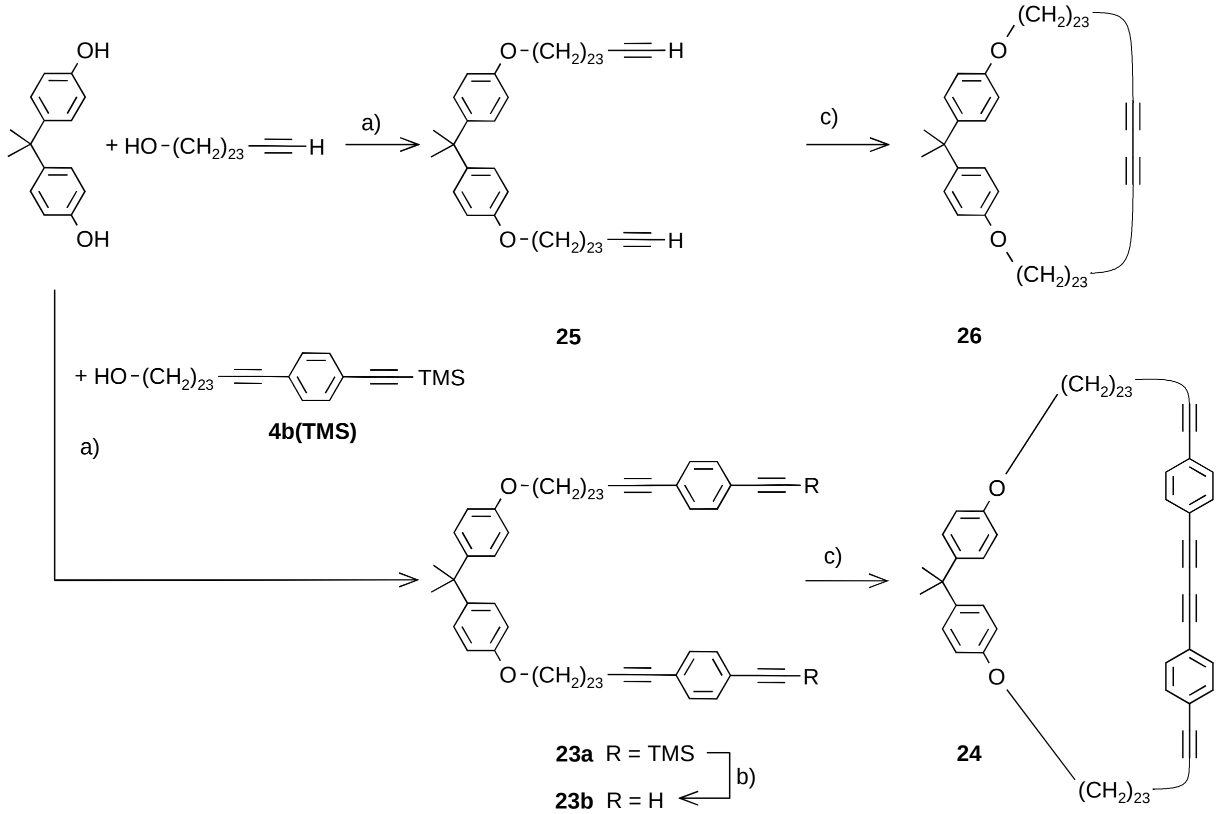
($CH_2C\equiv$**C**), 75.2 (C≡**C**-**C**≡C), 31.3, 28.6, 22.5, and 19.5 (CH_2), 14.0 (CH_3); Elemental analysis (%) calcd for $C_{32}H_{34}$ (418.624): C 91.81, H 8.19; found C 91.68, H 8.15.

3-[4-(Tridec-1-ynyl)phenyl]prop-2-yn-1-ol (31b). Following the procedure given for the preparation of **31a**, compound **31b** (941 mg, 52%; R_f = 0.57) was obtained as a red-brown solid starting from **30**[3] (1.49 g, 5.77 mmol), 1-tridecyne (2.0 mL, 8.7 mmol), $PdCl_2(PPh_3)_2$ (40 mg, 0.06 mmol) and CuI (22 mg, 0.11 mmol) in piperidine (20 mL). As in the case of **31a**, the accompanying carbometallation product 3-[4-(tridec-1-ynyl)phenyl]hexadec-2-en-4-yn-1-ol (R_f = 0.69) was formed as a side product; M.p.: 50.8-51.5 °C; ^1H NMR: δ = 7.32 (singlet shaped, 4 H, ArH), 4.48 (s, 2 H, CH_2O), 2.39 (t, J = 7.0 Hz, 2 H, ArC**H**$_2$), 1.74 (br s, 1H OH), 1.59 (m, 2 H, C**H**$_2$CH$_2$O), 1.5-1.2 (m, 16 H, CH_2), 0.89 (m, 3 H, CH_3); ^{13}C NMR: δ = 131.47 and 131.45 (CH), 124.4 and 121.5 (C-1,-4 of ArH), 92.7, 88.5, 85.5, and 80.2 (C≡C), 51.6 (CH_2O), 31.3 - 28.7 (7 signals), 22.7, and 19.5 (CH_2), 14.1 (CH_3); Elemental analysis (%) calcd for $C_{22}H_{30}O$ (310.481): C 85.11, H 9.74; found C 85.01, H 9.68.

3-[4-(Tridec-1-ynyl)phenyl]prop-2-yne (32b). Following the procedure given for the preparation of **32a**, compound **32b** (663 mg, 88%) was obtained as a tawny colored liquid starting from **31b** (830 mg, 2.67 mmol), MnO_2 (2.4 g, 27 mmol), and KOH (768 mg, 13 mmol) in diethyl ether (40 mL). ^1H NMR: δ = 7.40 and 7.33 (AA'XX', 2 H each, ArH), 3.12 (s, 1 H, C≡CH), 2.40 (t, J = 7.0 Hz, 2 H, ArC**H**$_2$), 1.60 (m, 2 H, C**H**$_2$CH$_2$O), 1.5-1.2 (m, 16 H, CH_2), 0.89 (m, 3 H, CH_3); ^{13}C NMR: δ = 131.9 and 131.4 (CH), 124.7 and 121.1 (C-1, -4 of ArH), 92.7, 83.4, 80.2, and 78.3 (C≡C), 31.9 - 28.7 (7 signals), 22.7, and 19.5 (CH_2), 14.0 (CH_3); Elemental analysis (%) calcd for $C_{21}H_{28}$ (280.455): C 89.94, H 10.06; found C 89.88, H 10.03.

4,4'-Bis-[4-(tridec-1-ynyl)phenyl]butadiyne (27b). Following the procedure given for the preparation of **27a**, compound **27b** (290 mg, 74%) was obtained as a yellow solid starting from **32b** (393 mg, 1.40 mmol), $PdCl_2(PPh_3)_2$ (21 mg, 0.03 mmol) and CuI (12 mg, 0.06 mmol) in THF (9 mL) and piperidine (3 mL). Diethyl ether was used for extraction. M.p.: 123.7-125.8 °C; ^1H NMR: δ = 7.42 and 7.33 (AA'XX', 4 H each, ArH), 2.40 (t, J = 7.0 Hz, 4 H, ArC**H**$_2$), 1.60 (m, 4 H, C**H**$_2$CH$_2$O), 1.5-1.2 (m, 32 H, CH_2), 0.88 (m, 6 H, CH_3); ^{13}C NMR: δ = 132.3 and 131.5 (CH), 125.2 and 120.6 (C-1,-4 of ArH), 93.6 (CH_2**C**≡C), 82.0 (**C**≡C-C≡**C**), 80.3 ($CH_2C\equiv$**C**), 75.2 (C≡**C**-**C**≡C), 31.9 - 28.64 (7 signals), 28.6, 22.7, and 19.5 (CH_2), 14.1 (CH_3); Elemental analysis (%) calcd for $C_{42}H_{54}$ (558.894): C 90.26, H 9.74; found C 89.83, H 9.86.

3. Preparation of the cyclic molecules 24 and 26 (Scheme 2)



Scheme 2. a) 4-iodophenol, diethyl azodicarboxylate, PPh_3, THF; b) n-Bu_4NF, THF; c) CuCl, $CuCl_2$, pyridine.

2,2-Bis[4-(pentacos-24-ynyloxy)phenyl]propane (25). To a suspension of pentacos-24-yn-1-ol (2.50 g, 6.84 mmol) and 2,2-bis-(4-hydroxyphenyl)propane (744 mg, 3.26 mmol) in THF (25 mL) were added PPh_3 (1.88 g, 7.17 mmol) and diethyl azodicarboxylate (1.13 mL, 7.18 mmol) at room temperature. Upon addition of diethyl azodicarboxylate the reaction mixture got warm and cleared up for a short time. The newly formed precipitate dissolved after some time. After stirring the clear, yellow solution for 20 h at room temperature, the cooled (ice bath) reaction mixture was quenched with water (125 mL) and the colorless precipitate was filtered off and washed with water. The solid was extracted with hot ethanol (first time 75 mL; second time 40 mL). Upon cooling to room temperature, a solid crystallized from the thus obtained ethanol solutions. These solids together with the residual solid from the extraction were recrystallized from ethanol (200 mL; filtration of the hot solution) to give **25** (1.2 g, 40%) as a colorless solid; M.p.: 69.7 °C; ^{1}H NMR: δ = 7.12, 6.78 (AA'XX', 4 H each H_{aryl}2,-6 and H_{aryl}-3,-5), 3.91 (t, J = 6.5 Hz, 4 H, OCH_2), 2.18 (dt, J =

2.6 Hz, *J* = 7.0 Hz, 4 H, C≡CCH$_2$), 1.93 (t, *J* = 2.6 Hz, 2 H, C≡CH), 1.75 (m, 4 H, OCH$_2$C**H**$_2$), 1.63 (s, 6 H, CH$_3$), 1.6 - 1.1 (m, 80 H, CH$_2$); ^{13}C NMR: δ = 157.0 (C$_{\text{aryl}}$-4), 142.9 (C$_{\text{aryl}}$-1), 127.6 (CH-2,-6), 113.8 (CH-3,-5), 84.8, 67.99 (**C**≡**C**), 67.92 (OCH$_2$), 41.6 (**C**Me$_2$), 31.1 (CH$_3$), 29.7 - 28.5 (8 signals, 26.1, and 18.4 (CH$_2$); Elemental analysis (%) calcd for $C_{65}H_{108}O_2$ (921.577): C 84.72, H 11.81; found C 84.72, H 11.97.

2,2-Bis-{4-[25-(4-(2-trimethylsilylethynyl)phenyl)pentacos-24-yn-1-yloxy]phenyl}-propane (23a). To a suspension of 25-[4-(2-trimethylsilylethynyl)phenyl]pentacos-24-yn-1-ol (**4b(TMS)**)[7] (300 mg, 0.57 mmol) and 2,2-bis-(4-hydroxyphenyl)propane (60 mg, 0.26 mmol) in THF (5 mL) were added PPh$_3$ (150 mg, 0.57 mmol) and diethyl azodicarboxylate (0.09 mL, 0.57 mmol) at room temperature. After stirring overnight, the reaction mixture was diluted with CH_2Cl_2 and washed with 2N HCl and brine, and dried (MgSO$_4$). Flash chromatography (petroleum ether/diethyl ether 2:1 v/v) gave **23a** (120 mg, 36%) as a colorless solid; ^{1}H-NMR: δ = 7.35, 7.29 (AA'XX', 4 H each, CH of C≡C-C$_6$H$_4$-C≡C), 7.11 (half of AA'XX', 4 H, H-2,-6 of ArO), 6.77 (half of AA'XX', 4 H, H-3,-5 of ArO), 3.90 (t, *J* = 6.5 Hz, 4 H, ArOC**H**$_2$), 2.38 (t, *J* = 7.1 Hz, 4 H, CH$_2$C≡C), 1.74 (m, 4 H, ArOCH$_2$C**H**$_2$), 1.61 (s, 6 H, CCH$_3$), 1.57 (m, 4 H, C**H**$_2$CH$_2$C≡C), 1.5-1.2 (m, 76 H, CH$_2$), 0.23 (s, 18 H, SiCH$_3$); ^{13}C-NMR: δ = 157.0, 143.0, 131.7, 131.3, 127.7, 124.3, 122.1, 113.8, 104.8, 95.6, 92.7, 80.3, 67.9, 41.6, 31.1, 29.7-28.7 (8 signals), 26.1, 19.5, -0.1; FD-MS: *m/z* = 1366.3 (6%, M$^+$ of a species elongated by a phenyleneethynylene moiety), 1266.3 (100%, M$^+$), 1193.3 (8%), 632.5 (12%, M^{2+}); calcd for $C_{87}H_{132}O_2Si_2$: 1266.183.

2,2-Bis-{4-[25-(4-ethynylphenyl)pentacos-24-yn-1-yloxy]phenyl}propane 23b.

To a solution of **23a** (150 mg, 0.12 mmol) in THF (5 mL) was added 1M *n*-Bu$_4$NF (0.36 mL, 0.36 mmol) in THF. After 3 h at room temperature, water was added and the aqueous phase was extracted with CH_2Cl_2. The combined organic phases were dried (MgSO$_4$) and the solvent was removed in vacuo. Recrystallization from ethanol gave ring precursor **23b** (127 mg, 97%) as a colorless solid. ^{1}H-NMR: δ = 7.38, 7.31 (AA'XX', 4 H each, CH of C≡C-C$_6$H$_4$-C≡C), 7.10 (half of AA'XX', 4 H, H-2,-6 of ArO), 6.76 (half of AA'XX', 4 H, H-3,-5 of ArO), 3.89 (t, *J* = 6.5 Hz, 4 H, ArOC**H**$_2$), 3.11 (s, 2 H, C≡CH), 2.38 (t, *J* = 7.1 Hz, 4 H, CH$_2$C≡C), 1.73 (m, 4 H, ArOCH$_2$C**H**$_2$), 1.61 (s, 6 H, CH$_3$), 1.55 (m, 4 H, C**H**$_2$CH$_2$C≡C), 1.5-1.2 (m, 76 H, CH$_2$); ^{13}C-NMR: δ = 157.0, 143.0, 131.9, 131.4, 127.7, 124.7, 122.2, 113.8, 92.8, 83.4, 80.3, 78.3, 67.9, 41.6, 31.1, 29.7-28.7 (6 signals), 26.1, 19.5; FD-MS: *m/z* = 1122.1 (100%, M$^+$), 561.2 (6%, M^{2+}); calcd for $C_{81}H_{116}O_2$: 1121.817.

Cyclic compound 24. A suspension of CuCl (882 mg, 8.91 mmol) and $CuCl_2$ (147 mg, 1.09 mmol) in pyridine (100 mL) was prepared as described in the procedure given for the preparation of **9**. To this suspension, the solution of ring precursor **23b** (100 mg, 0.09 mmol) in pyridine (10 mL) was added within 7 h at room temperature. After complete addition, the reaction mixture was stirred for 24 h. The reaction mixture was diluted with CH_2Cl_2, washed extensively with 2 N HCl, and dried ($MgSO_4$). Flash chromatography (petroleum ether/CH_2Cl_2 2:1 v/v) gave **24** (85 mg, 85%) as a slightly yellow colored solid. Mp.: 84.4 °C; ^{1}H-NMR: $\delta = 7.41$, 7.32 (AA'XX', 8 H, CH C≡C-C_6H_4-C≡C), 7.10 (half of AA'XX', 4 H, H-2,-6 of ArO), 6.77 (half of AA'XX', 4 H, H-3,-5 of ArO), 3.89 (t, $J = 6.5$ Hz, 4 H, ArOC**H**$_2$), 2.41 (t, $J = 6.6$ Hz, 4 H, CH_2C≡C), 1.74 (m, 4 H, ArOCH$_2$C**H**$_2$), 1.61 (s, 6 H, CCH_3), 1.57 (m, 4 H, C**H**$_2$CH$_2$C≡C), 1.5-1.2 (m, 76 H, CH_2); ^{13}C-NMR: $\delta = 157.0$, 143.0, 132.3, 131.5, 127.7, 125.2, 120.6, 113.8, 93.6, 82.0, 80.4, 75.2, 67.9, 41.6, 31.1, 29.6-28.4 (7 signals), 26.1, 19.5; Elemental analysis (%) calcd for $C_{81}H_{114}O_2$ (1119.801): C 86.87, H 10.27; found C 86.77, H 10.17; FD-MS: *m/z* = 1220 (5%, M^+ of a species elongated by a phenyleneethynylene moiety), 1118.9 (100%, M^+), 559.4 (23%, M^{2+}).

4. Preparation of the angular shaped model compound

Ethyl 3,5-Bis-{4-[2-(4-dodecyloxyphenyl)ethynyl]phenyl}-4-hydroxybenzoate (7c).

Following the procedure given for the preparation of **7b**, compound **7c** was obtained starting from **6** (1.00 g, 0.27 mmol), 1-iodo-4-dodecyloxybenzene (2.55 g, 0.66 mmol) $PdCl_2(PPh_3)_2$ (19 mg, 0.03 mmol) and CuI (11 mg, 0.06 mmol) in piperidine (50 mL). Aqueous work up with CH_2Cl_2 and 2N HCl followed by flash chromatography (petroleum ether/CH_2Cl_2 2:1 v/v) gave 7c (1.6 g, 66%) as a reddish-brown solid. M.p. determined with DSC (10K/min): 118 (114) °C upon first (second and third) heating scan; ^{1}H-NMR: $\delta = 7.99$ (s, 2 H, H_α), 7.62 and 7.54 (AA'XX', 4 H each, H_β), 7.74 (half of AA'XX', 4 H, H_γ-2,-6), 6.87 (half of AA'XX', 4 H, H_γ-3,-5), 5.85 (s, 1 H, OH), 4.37 (q, $J = 7.1$ Hz, 2 H, CO_2CH_2), 3.97 (t, $J = 6.6$ Hz, 4 H, ArOC**H**$_2$), 1.78 (m, 4 H, OCH$_2$C**H**$_2$), 1.38 (t, $J = 7.1$ Hz, 3 H, CH_3), 1.5 - 1.2 (m, 36 H, CH_2), 0.88 (m, 6 H, CH$_2$CH$_2$C**H**$_3$); ^{13}C-NMR: $\delta = 166.1$ (CO_2), 159.4 (C_γ-4), 153.3 (C_α-4), 135.9 (C_β-1), 133.1 (C_γ-2,-6), 131.9 (C_β-3,-5), 131.6 (C_α-2,-6), 129.3 (C_β-2,-6), 128.3 (C_α-3,-5), 123.6 (C_β-4), 123.3 (C_α-1), 114.9 (C_γ-1), 114.6 (C_γ-3,-5), 90.6 (C≡**C**Ar$_\gamma$), 87.6 (Ar$_\beta$**C**≡C), 68.1 (ArO**C**H$_2$), 60.9 (CO$_2$**C**H$_2$), 31.9 - 29.2 (8 signals), 26.0, and 22.7 (CH_2), 14.4 ($CH_2CH_2CH_3$), 14.1 (OCH$_2$**C**H$_3$); Elemental analysis (%) calcd for $C_{61}H_{74}O_5$ (887.258): C 82.58, H 8.41; found C 82.21, H 8.68.

4. References

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[7] 25-[4-(2-Trimethylsilylethynyl)phenyl]pentacos-24-yn-1-ol (**4b(TMS)**)was prepared in analogy to **4b** starting from pentacos-24-yn-1-ol and 1-iodo-4-(trimethylsilylethynyl)benzene (**19b**). The latter was prepared in analogy to **19c**.