

## 5 Experimental Part

### 5.1 General

**General Methods.** Catalyst Pd(PPh<sub>3</sub>)<sub>4</sub> was freshly prepared according to literature,<sup>[1]</sup> starting materials were commercial and used as received. 3,5-Diiodobenzoic acid, DPTS, and chiral alcohol (*S*)-2,5,8,11-tetraoxatetradecan-13-ol were synthesized and kindly provided by Christian Kaiser. Hexane, heptane, toluene, and THF were distilled prior to use under nitrogen or argon atmosphere over sodium/benzophenone or sodium tetraethylaluminum. Acetonitrile and dichloromethane were distilled prior to use under nitrogen or argon over calcium hydride. Triethylamine and diethylamine were distilled prior to use under nitrogen or argon atmosphere over potassium hydroxide. Benzyl alcohol was stirred under argon atmosphere over CaH<sub>2</sub> powder at rt overnight. The suspension was refluxed for few hours, and then distilled at 150 °C/30 mbar.

Propylene oxide (racemic PO or *S*-(-)-PO) was stirred under argon atmosphere over CaH<sub>2</sub> powder at rt overnight. The suspension was refluxed for few hours, then distilled at 50 °C, stirred for 1h over NaAlEt<sub>4</sub> and again distilled prior to use.

Microwave-assisted polycondensations were performed in a CEM-Discover monomode microwave reactor having a continuous microwave power delivery system from 0 to 300 W. The reactions were carried out in 10-mL sealed glass vials. The temperature was monitored by an IR sensor on the outer surface of the reaction vessel. All the reactions were performed with 50 W at 50 - 55°C. Column chromatography was carried out with 130-400 mesh silica gel.

#### **Analytic methods.**

**NMR** (<sup>1</sup>H and <sup>13</sup>C, respectively) were recorded on Bruker AB 250 (250.1 and 62.9 MHz for <sup>1</sup>H and <sup>13</sup>C, respectively), Bruker DPX 300 (300.1 and 75 MHz for <sup>1</sup>H and <sup>13</sup>C, respectively), Bruker AV400 (400.1 and 100.6 MHz for <sup>1</sup>H and <sup>13</sup>C, respectively) and AC500 (500 and 126 MHz for <sup>1</sup>H and <sup>13</sup>C, respectively) spectrometers at 23 ± 2 °C using residual protonated solvent signal as internal standard (<sup>1</sup>H: δ(CHCl<sub>3</sub>) = 7.24 ppm, δ(DMSO) = 2.49 ppm, and <sup>13</sup>C (CHCl<sub>3</sub>) = 77.0 ppm, δ(DMSO) = 39.7 ppm).

**Mass spectrometry** was performed on Perkin-Elmer Varian Type MAT 771 and CH6 (EI) or Type CH5DF (FAB) instruments.

**GPC** measurements in THF as the mobile phase were performed on a Waters 515 HPLC pump-GPC system equipped with a Waters 2487 UV detector (254 nm detection wavelength) at 40 °C using a flow rate of 1 mL/min. The samples were separated through Waters Styragel HR1 or HR3 columns with 5 μm bead sizes, which were calibrated with several narrow

polydispersity polystyrene samples using an internal toluene standard. GPC measurements were performed on an Agilent 1100 series HPLC system equipped with three 300 x 8 mm SDV columns (1,000,000 Å, 100,000 Å, 1000 Å) and one 50 x 8 mm SDV column (100 Å) using both UV (230 nm and 280 nm) and RI detection. The measurements were performed in THF at 30 °C using a flow rate of 1 mL/min. The columns were calibrated with several narrow polydispersity polystyrene samples. The HPLC system consisted of a Knauer Eurosphere 7µm C18, 4·120 mm silica gel column and UV-detection at 254 nm with an eluent flow of 1 mL/min.

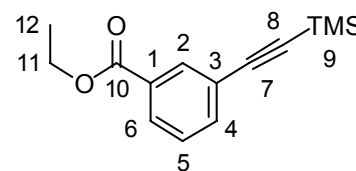
**Optical spectroscopy.** UV/visible absorption and emission spectra were recorded in spectroscopic grade solvents, using quartz cuvettes of 1 cm path length on a Cary 50 Spectrophotometer and a Cary Eclipse Fluorescence Spectrophotometer, respectively, both equipped with a Peltier thermostated cell holder ( $T = 25 \pm 0.05$  °C). The fluorescence samples were excited at the absorbance maximum wavelength, slit widths were set to 5 nm bandpass for excitation and emission. Fluorescence spectra were corrected for variations in photomultiplier response over wavelength using correction curves generated on the instrument. The corrected fluorescence spectra were normalized by the exact optical density (OD) from the corresponding absorbance spectra. For UV-visible absorption  $OD(\lambda_{\max}) \approx 1.0$  and for fluorescence measurements  $OD(\lambda_{\max}) \approx 0.1$  were used. Circular dichroism spectra were recorded on a JASCO 700 spectrometer using quartz cuvettes of 1 cm path length at 20 °C. In some cases circular dichroism spectra recorded as  $\theta$  in millidegrees, were converted to  $\Delta\epsilon$  using the equation  $\Delta\epsilon = \theta / (33982 \cdot c \cdot l)$ , where  $\Delta\epsilon$  is the difference in the molar absorptivity for oppositely polarized light in  $M^{-1}cm^{-1}$ ,  $c$  is concentration in mol/L, and  $l$  is the path length.

## 5.2 *ortho*- and *ortho-Alternating-para-Phenylene Ethynylenes*

*Iterative divergent/convergent approach.*

### Ethyl 3-(TMS-ethynyl)benzoate **12**

a) Ethyl 3-iodobenzoate **11a** (5.0 mL, 30.1 mmol),  $Pd(PPh_3)_4$  (1.74 g, 1.5 mmol), CuI (0.29 g, 1.5 mmol), and TMS-acetylene (5.1 mL, 36.1 mmol) were added to 30 mL of dried  $Et_3N$  under nitrogen



atmosphere. The apparatus is subjected to two Freeze-Pump-Thaw cycles and the yellow suspension first stirred at rt for 24 h, then at 70 °C for 2 h. The reaction mixture is cooled down to rt and filtrated. The red filtrate is concentrated, the oil redissolved in toluene, filtrated, and solvent removed. Purification by column chromatography (hexane:ethyl acetate = 20:1) yielded desired product as clear, light yellow oil (68 %).

b) Ethyl 3-bromobenzoate **11b** (1.62 mL, 10.1 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (1.14 g, 0.99 mmol), and CuI (0.19 g, 0.97 mmol) were transferred to a flame-dried flask under argon. A mixture of dry and degassed THF (6 mL), Et<sub>3</sub>N (6 mL), and MeCN (0.2 mL) was added, followed by TMS-acetylene (2.11 mL, 14.85 mmol). The brown suspension was once more FPTed, and then stirred overnight at 55 °C. Filtration through silica gel, (eluent Hex:EE=10:1) yielded a red filtrate, that was concentrated, redissolved in EE and washed subsequently with aq. sat. NH<sub>4</sub>Cl, aq. sat. NaHCO<sub>3</sub>, and aq. sat. NaCl. The organic phase was dried over MgSO<sub>4</sub>, filtered, and concentrated. Purification by column chromatography (silica gel, hexane:EE=50:1) yielded desired product as pale yellow oil (quantitative).

<sup>1</sup>H-NMR (250 MHz, CDCl<sub>3</sub>): δ(ppm) = 8.11 (t, <sup>4</sup>J(H,H) = 1.8 Hz, 1H, H-2), 7.95 (dd, <sup>3</sup>J(H,H) = 9.1 Hz, <sup>4</sup>J(H,H) = 1.8 Hz, 1H, H-6), 7.60 (dd, <sup>3</sup>J(H,H) = 9.1 Hz, <sup>4</sup>J(H,H) = 1.8 Hz, 1H, H-4), 7.35 (t, <sup>3</sup>J(H,H) = 7.7 Hz, 1H, H-5), 4.35 (q, <sup>3</sup>J(H,H) = 7.0 Hz, 2H, H-11), 1.37 (t, <sup>3</sup>J(H,H) = 7.3 Hz, 3H, H-12), 0.23 (s, 9H, H-9).

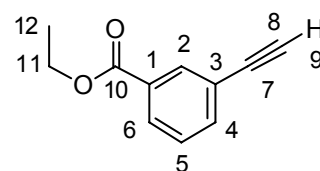
<sup>13</sup>C-NMR (63 MHz, CDCl<sub>3</sub>): δ(ppm) = 165.8 (C-10), 135.9 (C-4), 133.0 (C-2), 130.7 (C-1), 129.4 (C-6), 128.3 (C-5), 123.5 (C-3), 103.9 (C-7), 95.3 (C-8), 61.1 (C-11), 14.3 (C-12), -0.1 (C-9).

EI-MS (40 °C): *m/z* = 246, 231 (calcd 246 for C<sub>14</sub>H<sub>18</sub>O<sub>2</sub>Si<sup>+</sup>).

GC: 98.2 %

### Ethyl 3-ethynylbenzoate **13**

a) Ethyl (TMS-ethynyl)benzoate **12** (0.42 g, 1.2 mmol) and potassium carbonate (0.50 g, 3.6 mmol) were dissolved under nitrogen atmosphere in a solvent mixture of 5 mL ethanol and 5 mL THF. The solution was stirred at 50 °C for 6 h, and an excess



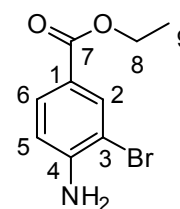
of ethyl acetate and water was added to achieve phase separation; the organic phase was separated, washed with aq. sat. NH<sub>4</sub>Cl, and the aq. phases washed once with ethyl acetate. The combined org. phases were dried over MgSO<sub>4</sub>, the solvent removed, and the obtained yellow powder dried in vacuo (83 %).

<sup>1</sup>H-NMR (250 MHz, CDCl<sub>3</sub>): δ(ppm) = 8.14 (t, <sup>4</sup>J(H,H) = 1.8 Hz, 1H, H-2), 8.00 (dd, <sup>3</sup>J(H,H) = 6.4 Hz, <sup>4</sup>J(H,H) = 1.8 Hz, 1H, H-6), 7.64 (dd, <sup>3</sup>J(H,H) = 9.1 Hz, <sup>4</sup>J(H,H) = 1.8 Hz, 1H, H-4), 7.38 (t, <sup>3</sup>J(H,H) = 7.7 Hz, 1H, H-5), 4.36 (q, <sup>3</sup>J(H,H) = 7.0, 2H, H-11), 3.10 (s, 1H, H-9), 1.38 (t, <sup>3</sup>J(H,H) = 6.8 Hz, 3H, H-12).

<sup>13</sup>C-NMR (126 MHz, CDCl<sub>3</sub>): δ(ppm) = 165.7 (C-10), 136.1 (C-4), 133.2 (C-2), 130.8 (C-1), 129.8 (C-6), 128.4 (C-5), 122.5 (C-3), 82.6 (C-7), 78.0 (C-8), 61.2 (C-11), 14.3 (C-12).

**Ethyl 4-amino-3-bromobenzoate 2**

Ethyl 4-aminobenzoate **1** (28.93 g, 175.1 mmol) was dissolved in 350 mL CH<sub>2</sub>Cl<sub>2</sub> and the solution cooled down to 0 °C and isolated from light. Under vigorous stirring, NBS (31.17 g, 175.1 mmol) was added in small portions and the reaction mixture left over night to warm up to rt. The white precipitate was filtered off, and the filtrate concentrated. Two times recrystallization in ethanol yielded desired product as white-beige crystals (68 %).



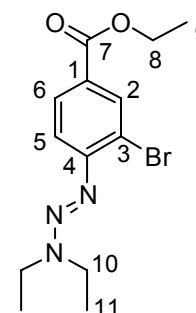
<sup>1</sup>H-NMR (250 MHz, CDCl<sub>3</sub>): δ(ppm) = 8.09 (d, <sup>4</sup>J(H,H) = 2.2 Hz, 1H, H-2), 7.77 (dd, <sup>3</sup>J(H,H) = 8.1 Hz, <sup>4</sup>J(H,H) = 1.5 Hz, 1H, H-6), 6.73 (d, <sup>3</sup>J(H,H) = 8.1 Hz, 1H, H-5), 4.50 (b, 2H, NH<sub>2</sub>), 4.29 (q, <sup>3</sup>J(H,H) = 7.1 Hz, 2H, H-8), 1.34 (t, <sup>3</sup>J(H,H) = 7.4 Hz, 3H, H-9).

<sup>13</sup>C-NMR (63 MHz, CDCl<sub>3</sub>): δ(ppm) = 151.7 (C-7), 148.0 (C-4), 134.4 (C-2), 130.2 (C-6), 114.2 (C-5), 107.9 (C-1), 60.6 (C-8), 14.4 (C-9).

EI-MS (60 °C): *m/z* = 243 (calcd 243 for C<sub>9</sub>H<sub>10</sub>BrNO<sub>2</sub><sup>+</sup>).

**Ethyl 3-bromo-4-(diethyltriazenyl)benzoate 3a**

Ethyl 4-amino-3-bromobenzoate **2** (28.01 g, 125.0 mmol) was added to a solution of 40 mL aq. 37%-HCl, 900 mL water, and 50 mL acetonitrile at 0 °C. To this yellow suspension, NaNO<sub>2</sub> (9.49 g, 137.5 mmol) was added in small portions, turning the rc mixture to a dark green solution. After stirring for 30 min, an ice-cooled solution of KOH (28.05 g, 500.0 mmol) and diethylamine (20.9 mL, 200.0 mmol) in 500 mL water was added and the solution stirred for another 30 min. The product was extracted several times with diethyl ether, the combined org. phases washed with aq. sat. NaCl, dried over MgSO<sub>4</sub>, and the solvent removed, and the obtained dark red oil purified by column chromatography (hexane:ethyl acetate = 6:1) yielding desired product as light orange oil (55 %).



<sup>1</sup>H-NMR (250 MHz, CDCl<sub>3</sub>): δ(ppm) = 8.23 (d, <sup>4</sup>J(H,H) = 2.2 Hz, 1H, H-2), 7.87 (dd, <sup>3</sup>J(H,H) = 8.8 Hz, <sup>4</sup>J(H,H) = 2.2 Hz, 1H, H-6), 7.41 (d, <sup>3</sup>J(H,H) = 8.8 Hz, 1H, H-5), 4.33 (q, <sup>3</sup>J(H,H) = 7.4 Hz, 2H, H-8), 3.81 (q, <sup>3</sup>J(H,H) = 7.4 Hz, 4H, H-10), 1.37 (t, <sup>3</sup>J(H,H) = 7.0 Hz, 3H, H-9), 1.31 (b, 6H, H-11).

<sup>13</sup>C-NMR (126 MHz, CDCl<sub>3</sub>): δ(ppm) = 165.6 (C-7), 152.0 (C-4), 134.5 (C-2), 129.1 (C-6), 127.6 (C-1), 119.3 (C-3), 117.7 (C-5), 61.0 (C-8), 49.6 (C-10), 42.4 (C-10'), 14.3 (C-9), 10.7 (C-11).

EI-MS (80 °C): *m/z* = 327, 282, 255, 227, 199 (calcd 327 for C<sub>13</sub>H<sub>18</sub>BrN<sub>3</sub>O<sub>3</sub><sup>+</sup>).

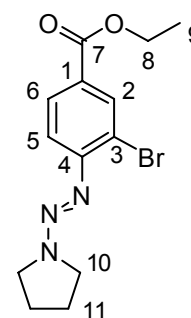
**Ethyl 3-bromo-4-(pyrrolidinyltriazenyl)benzoate 3b**

The procedure was analogous to the synthesis of ethyl 3-bromo-4-(diethyltriazenyl)benzoate using pyrrolidine as amine for quenching the diazonium salt (75%).

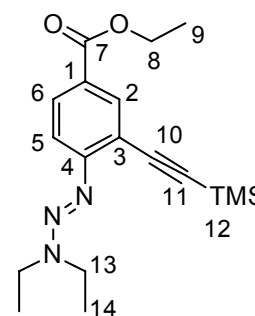
$^1\text{H-NMR}$  (250 MHz,  $\text{CDCl}_3$ ):  $\delta(\text{ppm}) = 8.23$  (d,  $^4\text{J}(\text{H,H}) = 1.5$  Hz, 1H, H-2), 7.87 (dd,  $^3\text{J}(\text{H,H}) = 8.8$  Hz,  $^4\text{J}(\text{H,H}) = 2.2$  Hz, 1H, H-6), 7.43 (d,  $^3\text{J}(\text{H,H}) = 8.8$  Hz, 1H, H-5), 4.33 (q,  $^3\text{J}(\text{H,H}) = 7.4$  Hz, 2H, H-8), 3.95 (t,  $^3\text{J}(\text{H,H}) = 5.9$  Hz, 2H, H-10), 3.74 (t,  $^3\text{J}(\text{H,H}) = 5.2$  Hz, 2H, H-10'), 2.05 (b, 4H, H-11), 1.37 (t,  $^3\text{J}(\text{H,H}) = 6.6$  Hz, 3H, H-9).

$^{13}\text{C-NMR}$  (63 MHz,  $\text{CDCl}_3$ ):  $\delta(\text{ppm}) = 165.5$  (C-7), 152.1 (C-4), 134.6 (C-2), 129.1 (C-6), 119.0 (C-1), 117.7 (C-5), 60.9 (C-8), 51.4 (C-10), 47.2 (C-10), 23.9 (C-11), 23.5 (C-11), 14.3 (C-9).

EI-MS (90 °C):  $m/z = 325, 255, 227, 199$  (calcd 325 for  $\text{C}_{13}\text{H}_{16}\text{BrN}_3\text{O}_2^+$ ).

**Ethyl 4-diethyltriazenyl-3-(TMS-ethynyl)benzoate 4a**

Ethyl 3-bromo-4-(diethyltriazenyl)benzoate **3a** (22.32 g, 68.0 mmol),  $\text{Pd}(\text{PPh}_3)_4$  (7.86 g, 6.8 mmol),  $\text{CuI}$  (1.30 g, 6.8 mmol), and TMS-acetylene (18.4 mL, 129.2 mmol) were added to a solvent mixture of 100 mL dry THF and 100 mL dry  $\text{Et}_3\text{N}$  under a nitrogen atmosphere. The red rc solution was subjected to two Freeze-pump-thaw cycles, followed by stirring at 90°C for 18 hours. The reaction mixture was



filtrated and the filtrate concentrated, redissolved in toluene, filtrated, and the filtrate again concentrated. Purification by column chromatography (hexane:ethyl acetate = 10:1) yielded desired product as a yellow solid (67 %).

$^1\text{H-NMR}$  (500 MHz,  $\text{CDCl}_3$ ):  $\delta(\text{ppm}) = 8.13$  (d,  $^4\text{J}(\text{H,H}) = 1.9$  Hz, 1H, H-2), 7.88 (dd,  $^3\text{J}(\text{H,H}) = 8.5$  Hz,  $^4\text{J}(\text{H,H}) = 2.1$  Hz, 1H, H-6), 7.42 (d,  $^3\text{J}(\text{H,H}) = 8.7$  Hz, 1H, H-5), 4.33 (q,  $^3\text{J}(\text{H,H}) = 7.1$  Hz, 2H, H-8), 3.81 (q,  $^3\text{J}(\text{H,H}) = 7.2$  Hz, 4H, H-13), 1.37 (t,  $^3\text{J}(\text{H,H}) = 7.1$  Hz, 3H, H-9), 1.34 (t,  $^3\text{J}(\text{H,H}) = 7.2$  Hz, 3H, H-14), 1.28 (t,  $^3\text{J}(\text{H,H}) = 6.7$  Hz, 3H, H-14'), 0.22 (s, 9H, H-12).

$^{13}\text{C-NMR}$  (126 MHz,  $\text{CDCl}_3$ ):  $\delta(\text{ppm}) = 166.1$  (C-7), 156.0 (C-4), 135.0 (C-2), 130.3 (C-6), 126.3 (C-1), 117.9 (C-5), 116.4 (C-3), 102.6 (C-10), 98.6 (C-11), 60.8 (C-8), 49.5 (C-13), 42.2 (C-13'), 14.4 (C-9), 10.9 (C-14), 0.0 (C-12).

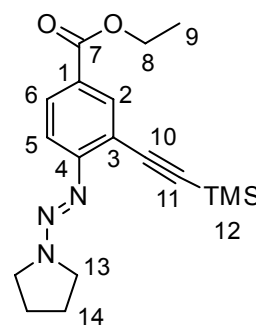
EI-MS (70 °C):  $m/z = 345, 300$  (calcd 345 for  $\text{C}_{18}\text{H}_{27}\text{N}_3\text{O}_2\text{Si}^+$ ).

**Ethyl 4-pyrrolidinyltriazenyl-3-(TMS-ethynyl)benzoate 4b**

The procedure was analogous to the synthesis of ethyl 4-diethyltriazenyl-3-(TMS-ethynyl)benzoate using ethyl 3-bromo-4-(pyrrolidinyltriazenyl)-benzoate **3b** as starting material (56 %).

<sup>1</sup>H-NMR (250 MHz, CDCl<sub>3</sub>): δ(ppm) = 8.14 (d, <sup>4</sup>J(H,H) = 1.5 Hz, 1H, H-2), 7.88 (dd, <sup>3</sup>J(H,H) = 8.8 Hz, <sup>4</sup>J(H,H) = 2.2 Hz, 1H, H-6), 7.45 (d, <sup>3</sup>J(H,H) = 8.8 Hz, 1H, H-5), 4.33 (q, <sup>3</sup>J(H,H) = 7.1 Hz, 2H, H-8), 3.95 (b, 2H, H-13), 3.73 (b, 2H, H-13'), 2.04 (b, 4H, H-14), 1.37 (t, <sup>3</sup>J(H,H) = 7.0 Hz, 3H, H-9), 0.24 (s, 9H, H-12).

<sup>13</sup>C-NMR (63 MHz, CDCl<sub>3</sub>): δ(ppm) = 166.0 (C-7), 156.1 (C-4), 135.0 (C-2), 130.3 (C-6), 126.3 (C-1), 117.6 (C-5), 116.5 (C-3), 102.5 (C-10), 86.8 (C-11), 60.8 (C-8), 51.2 (C-13), 46.9 (C-13'), 23.9 (C-14), 23.5 (C-14'), 14.3 (C-9), 0.1 (C-12).

**Ethyl 4-diethyltriazenyl-3-ethynylbenzoate 6a**

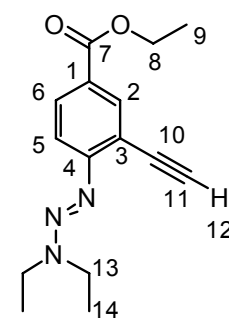
Ethyl 4-diethyltriazenyl-3-(TMS-ethynyl)benzoate **4a** (3.80 g, 11.0 mmol) and potassium carbonate (3.80 g, 27.5 mmol) were dissolved under nitrogen atmosphere in a solvent mixture of 50 mL ethanol, 20 mL THF, and 10 mL water. The solution was stirred at 50 °C for 3 h, and an excess of ethyl acetate and water was added to achieve phase separation; the organic phase was separated, washed with aq. sat. NH<sub>4</sub>Cl, and the aq.

phases washed once with ethyl acetate. The combined org. phases were dried over MgSO<sub>4</sub>, the solvent removed, and the obtained red solid dried in vacuo (93 %).

<sup>1</sup>H-NMR (250 MHz, CDCl<sub>3</sub>): δ(ppm) = 8.16 (d, <sup>4</sup>J(H,H) = 1.8 Hz, 1H, H-2), 7.91 (dd, <sup>3</sup>J(H,H) = 8.2 Hz, <sup>4</sup>J(H,H) = 1.8 Hz, 1H, H-6), 7.43 (d, <sup>3</sup>J(H,H) = 8.2 Hz, 1H, H-5), 4.33 (q, <sup>3</sup>J(H,H) = 7.3 Hz, 2H, H-8), 3.81 (q, <sup>3</sup>J(H,H) = 7.3 Hz, 4H, H-13), 3.24 (s, 1H, H-12), 1.37 (t, <sup>3</sup>J(H,H) = 6.8 Hz, 3H, H-9), 1.30 (b, 6H, H-14).

<sup>13</sup>C-NMR (63 MHz, CDCl<sub>3</sub>): δ(ppm) = 165.9 (C-7), 156.3 (C-4), 135.3 (C-2), 130.5 (C-6), 126.4 (C-1), 116.9 (C-3), 116.7 (C-5), 81.3 (C-10), 81.2 (C-11), 60.8 (C-8), 49.4 (C-13), 42.2 (C-13'), 14.3 (C-9), 10.8 (C-14).

EI-MS (50 °C): *m/z* = 273, 228 (calcd 273 for C<sub>15</sub>H<sub>19</sub>N<sub>3</sub>O<sub>2</sub><sup>+</sup>).

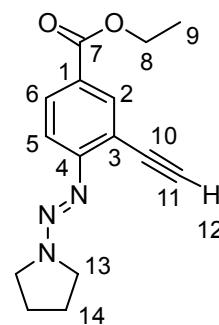
**Ethyl 3-ethynyl-4-(pyrrolidinyltriazenyl)benzoate 6b**

The procedure was analogous to the synthesis of ethyl 3-ethynyl-4-diethyltriazenylbenzoate using ethyl 3-(TMS-ethynyl)-4-(pyrrolidinyltriazenyl)benzoate **4b** as starting material (97 %).

$^1\text{H-NMR}$  (250 MHz,  $\text{CDCl}_3$ ):  $\delta(\text{ppm}) = 8.17$  (d,  $^4\text{J}(\text{H,H}) = 2.2$  Hz, 1H, H-2), 7.91 (dd,  $^3\text{J}(\text{H,H}) = 8.8$  Hz,  $^4\text{J}(\text{H,H}) = 2.2$  Hz, 1H, H-6), 7.46 (d,  $^3\text{J}(\text{H,H}) = 8.8$  Hz, 1H, H-5), 4.33 (q,  $^3\text{J}(\text{H,H}) = 7.1$  Hz, 2H, H-8), 3.95 (b, 2H, H-13), 3.74 (b, 2H, H-13'), 3.28 (s, 1H, H-12), 2.04 (b, 4H, H-14), 1.36 (t,  $^3\text{J}(\text{H,H}) = 7.0$  Hz, 3H, H-9).

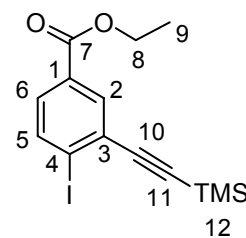
$^{13}\text{C-NMR}$  (63 MHz,  $\text{CDCl}_3$ ):  $\delta(\text{ppm}) = 165.9$  (C-7), 156.3 (C-4), 135.4 (C-2), 130.6 (C-6), 126.5 (C-1), 118.0 (C-3), 116.7 (C-5), 81.4 (C-11), 81.2 (C-10), 60.8 (C-8), 51.3 (C-13), 47.0 (C-13'), 23.7 (C-14), 14.3 (C-9).

EI-MS (80eV, 3kV, 60 °C):  $m/z = 271, 242, 226, 201, 173, 145$  (calcd 271 for  $\text{C}_{15}\text{H}_{17}\text{N}_3\text{O}_2^+$ ).



### Ethyl 3-(TMS-ethynyl)-4-iodobenzoate **5**

a) Ethyl 4-diethyltriazenyl-3-(TMS-ethynyl)benzoate **4a** (3.11 g, 9.0 mmol) was dissolved in 3 mL MeI in a presurable vessel. The red-brown solution was subjected to 2x Freeze-Pump-Thaw cycles and heated to 110-120 °C for 2 d under pressure. The black mixture was diluted with diethyl ether, the black precipitate filtered off over celite, and the red filtrate concentrated. Purification by column chromatography (hexane:ethyl acetate = 10:1) yielded desired product as yellow-orange crystalline solid (96 %).



b) In an analogous procedure ethyl 4-(pyrrolidinyltriazenyl)-3-(TMS-ethynyl)benzoate **4b** was used as starting material (91 %).

$^1\text{H-NMR}$  (250 MHz,  $\text{CDCl}_3$ ):  $\delta(\text{ppm}) = 8.06$  (d,  $^4\text{J}(\text{H,H}) = 1.8$  Hz, 1H, H-2), 7.90 (d,  $^3\text{J}(\text{H,H}) = 8.2$  Hz, H-5), 7.59 (dd,  $^3\text{J}(\text{H,H}) = 8.2$  Hz,  $^4\text{J}(\text{H,H}) = 1.8$  Hz, 1H, H-6), 4.34 (q,  $^3\text{J}(\text{H,H}) = 7.0$  Hz, 2H, H-8), 1.37 (t,  $^3\text{J}(\text{H,H}) = 7.3$  Hz, H-9), 0.27 (s, 9H, H-12).

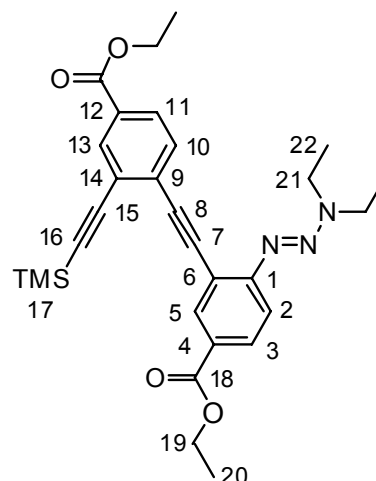
$^{13}\text{C-NMR}$  (63 MHz,  $\text{CDCl}_3$ ):  $\delta(\text{ppm}) = 165.5$  (C-7), 139.0 (C-5), 133.3 (C-2), 130.5 (C-6), 130.2 (C-3), 129.9 (C-1), 107.1 (C-4), 105.7 (C-10), 100.0 (C-11), 61.4 (C-8), 14.3 (C-9), -0.3 (C-12).

EI-MS (30 °C):  $m/z = 372, 357$  (calcd 372 for  $\text{C}_{14}\text{H}_{17}\text{IO}_2\text{Si}^+$ ).

HPLC (MeOH): 1.82 min (96 %).

### Diethyl TMS-ethynyl-(oPE-dimer)-diethyltriazenyl **8a**

Ethyl 3-(TMS-ethynyl)-4-iodobenzoate **5** (3.09 g, 8.3 mmol), ethyl 4-diethyltriazenyl-3-ethynylbenzoate **6a** (2.27 g, 8.3 mmol),  $\text{Pd}(\text{PPh}_3)_4$  (0.96 g, 0.8 mmol), and  $\text{CuI}$  (0.19 g, 1.0 mmol) were added to a solvent mixture of 55 mL dry  $\text{Et}_3\text{N}$ , 35 mL dry THF, and 5 mL dry MeCN under a nitrogen



atmosphere. The red reaction solution was subjected to two Freeze-pump-thaw cycles, followed by stirring at 70°C for 18 hours. The reaction mixture was diluted with CH<sub>2</sub>Cl<sub>2</sub>, filtrated and the red filtrate concentrated. Purification by column chromatography (hexane:ethyl acetate = 10:1 and CH<sub>2</sub>Cl<sub>2</sub>:MeOH = 200:1) yielded desired product as a yellow solid (36 %).

<sup>1</sup>H-NMR (250 MHz, CDCl<sub>3</sub>): δ(ppm) = 8.23 (d, <sup>4</sup>J(H,H) = 2.2 Hz, 1H, H-5), 8.15 (d, <sup>4</sup>J(H,H) = 1.5 Hz, 1H, H-13), 7.95 (dd, <sup>3</sup>J(H,H) = 8,8 Hz, <sup>4</sup>J(H,H) = 2.2 Hz, 1H, H-11), 7.91 (dd, <sup>3</sup>J(H,H) = 8.1 Hz, <sup>4</sup>J(H,H) = 1.5 Hz, 1H, H-3), 7.50 (d, <sup>3</sup>J(H,H) = 8.1 Hz, 2H, H-2, H-10), 4.36 (q, <sup>3</sup>J(H,H) = 7.1 Hz, 2H, H-19), 4.35 (q, <sup>3</sup>J(H,H) = 7.1 Hz, 2H, H-19), 3.84 (q, <sup>3</sup>J(H,H) = 7.1 Hz, 4H, H-21), 1.38 (m, 12H, H-20, H-22), 0.26 (s, 9H, H-17).

<sup>13</sup>C-NMR (62.9 MHz, CDCl<sub>3</sub>): δ(ppm) = 165.9 (C-18), 165.5 (C-18), 155.7 (C-1), 134.6 (C-5), 133.2 (C-13), 131.5 (C-10), 130.8 (C-9), 130.7 (C-3), 129.4 (C-12), 128.8 (C-11), 126.4 (C-4), 125.6 (C-14), 117.6 (C-2), 116.6 (C-6), 102.6 (C-15), 99.7 (C-16), 94.6 (C-8), 91.8 (C-7), 61.2 (C-19), 60.8 (C-19), 49.6 (C-21), 42.3 (C-21), 14.4 (C-20), 14.3 (C-20), 10.9 (C-22), -0.1 (C-17).

FAB-MS (MNBA): *m/z* = 518 (calcd 518 for C<sub>29</sub>H<sub>36</sub>N<sub>3</sub>O<sub>4</sub>Si<sup>+</sup>).

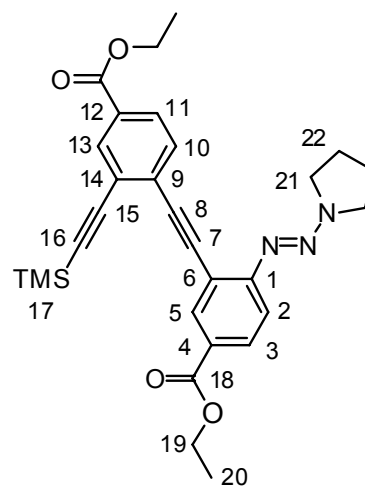
HPLC (MeOH): 3.13 min (97%).

### Diethyl TMS-ethynyl-(*o*PE-dimer)-pyrrolidinyltriazenyl **8b**

The procedure was analogous to the synthesis of TMS-ethynyl-(*o*PE-dimer)-diethyltriazenyl using ethyl 3-ethynyl-4-(pyrrolidinyltriazenyl)benzoate **6b** as starting material (29 %).

<sup>1</sup>H-NMR (250 MHz, CDCl<sub>3</sub>): δ(ppm) = 8.22 (d, <sup>4</sup>J(H,H) = 1.8 Hz, 1H, H-5), 8.14 (d, <sup>4</sup>J(H,H) = 1.8 Hz, 1H, H-13), 7.95 (dd, <sup>3</sup>J(H,H) = 9.1 Hz, <sup>4</sup>J(H,H) = 1.8 Hz, 1H, H-11), 7.91 (dd, <sup>3</sup>J(H,H) = 8.2 Hz, <sup>4</sup>J(H,H) = 1.8 Hz, 1H, H-3), 7.52 (d, <sup>3</sup>J(H,H) = 8.2 Hz, 1H, H-2), 7.50 (d, <sup>3</sup>J(H,H) = 9.1 Hz, 1H, H-10), 4.36 (q, <sup>3</sup>J(H,H) = 7.3 Hz, 2H, H-19), 4.34 (q, <sup>3</sup>J(H,H) = 7.3 Hz, 2H, H-19'), 3.97 (t, <sup>3</sup>J(H,H) = 6.4 Hz, 2H, H-21), 3.78 (t, <sup>3</sup>J(H,H) = 5.5 Hz, 2H, H-21'), 2.05 (b, 4H, H-22), 1.38 (t, <sup>3</sup>J(H,H) = 7.3 Hz, 3H, H-20), 1.36 (t, <sup>3</sup>J(H,H) = 7.3 Hz, 3H, H-20'), 0.25 (s, 9H, H-17).

<sup>13</sup>C-NMR (126 MHz, CDCl<sub>3</sub>): δ(ppm) = 165.9 (C-18), 165.5 (C-18'), 155.8 (C-1), 134.8 (C-5), 133.3 (C-13), 131.7 (C-10), 130.9 (C-9), 130.8 (C-3), 129.4 (C-12), 128.8 (C-11), 126.5 (C-4), 125.6 (C-14), 117.3 (C-6), 116.7 (C-2), 102.6 (C-8), 99.7 (C-7), 94.5 (C-16), 92.1 (C-





15), 61.3 (C-19), 60.8 (C-19'), 51.3 (C-21), 47.0 (C-21'), 24.0 (C-22), 23.5 (C-22'), 14.4 (C-20), 14.3 (C-20'), -0.1 (C-17).

### Diethyl ethynyl-(*o*PE-dimer)-diethyltriazenyl **7a**

TMS-ethynyl-(*o*PE-dimer)-diethyltriazenyl **8a** (0.748 g, 1.5 mmol) and potassium carbonate (0.50 g, 3.6 mmol) were dissolved under nitrogen atmosphere in a solvent mixture of 10 mL ethanol, 4 mL THF, and 2 mL water. The solution was stirred at 50 °C for 3 h, and an excess of ethyl acetate and water was added to achieve phase separation; the organic phase was separated, washed with aq. sat. NH<sub>4</sub>Cl, and the aq. phases washed once with ethyl acetate. The combined org. phases were dried over MgSO<sub>4</sub>, the solvent removed, and the obtained light yellow solid dried in vacuo (93 %).

<sup>1</sup>H-NMR (250 MHz, CDCl<sub>3</sub>): δ(ppm) = 8.24 (d, <sup>4</sup>J(H,H) = 2.2 Hz, 1H, H-5), 8.21 (d, <sup>4</sup>J(H,H) = 1.5 Hz, 1H, H-13), 7.95 (dd, <sup>3</sup>J(H,H) = 8.1 Hz, <sup>4</sup>J(H,H) = 1.5 Hz, 1H, H-11), 7.93 (dd, <sup>3</sup>J(H,H) = 8.1 Hz, <sup>4</sup>J(H,H) = 2.2 Hz, H-3), 7.54 (d, <sup>3</sup>J(H,H) = 8.1 Hz, 1H, H-10), 7.48 (d, <sup>3</sup>J(H,H) = 8.8 Hz, 1H, H-2), 4.36 (q, <sup>3</sup>J(H,H) = 7.1 Hz, 2H, H-19), 4.35 (q, <sup>3</sup>J(H,H) = 7.1 Hz, 2H, H-19'), 3.84 (t, <sup>3</sup>J(H,H) = 5.2 Hz, 4H, H-21), 3.36 (s, 1H, H-17), 1.38 (t, <sup>3</sup>J(H,H) = 7.4 Hz, 6H, H-20), 1.31 (t, <sup>3</sup>J(H,H) = 8.1 Hz, 6H, H-22).

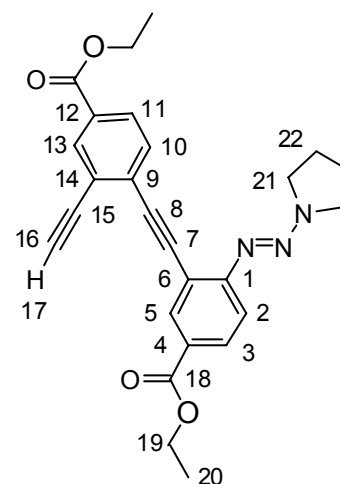
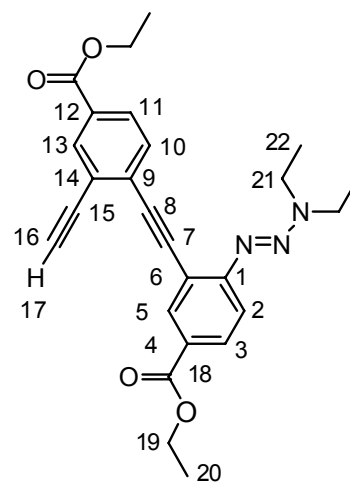
<sup>13</sup>C-NMR (63 MHz, CDCl<sub>3</sub>): δ(ppm) = 166.0, 165.4 (C-18), 155.8 (C-1), 135.1, 133.7, 131.8, 131.1, 130.7, 129.6, 129.2, 126.5, 124.6, 117.5, 116.8, 94.8, 91.6, 81.8, 81.6, 61.3 (C-19), 60.9 (C-19'), 49.5 (C-21), 42.3 (C-21'), 14.3 (C-20), 11.1 (C-22)

FAB-MS (MNBA): *m/z* = 468 (M+Na), 446, 400, 345, 300, 272, 244 (calcd 446 for C<sub>26</sub>H<sub>28</sub>N<sub>3</sub>O<sub>4</sub><sup>+</sup>).

### Diethyl ethynyl-(*o*PE-dimer)-pyrrolidinyltriazenyl **7b**

The procedure was analogous to the synthesis of ethynyl(dimer)diethyltriazenyl using TMS-ethynyl-(*o*PE-dimer)-pyrrolidinyltriazenyl **8b** as starting material (72 %).

<sup>1</sup>H-NMR (250 MHz, CDCl<sub>3</sub>): δ(ppm) = 8.24 (d, <sup>4</sup>J(H,H) = 2.2 Hz, 1H, H-), 8.17 (d, <sup>4</sup>J(H,H) = 2.2 Hz, 1H, H-), 7.95 (dd, <sup>3</sup>J(H,H) = 8.1 Hz, <sup>4</sup>J(H,H) = 1.5 Hz, 1H, H-), 7.93 (dd, <sup>3</sup>J(H,H) = 8.8 Hz, <sup>4</sup>J(H,H) = 1.5 Hz, 1H, H-), 7.57 (d, <sup>3</sup>J(H,H) = 8.1 Hz, 1H, H-), 7.49 (d, <sup>3</sup>J(H,H) = 8.8 Hz, 1H, H-), 4.36 (q, <sup>3</sup>J(H,H) = 7.4 Hz, 2H, H-19), 4.35 (q, <sup>3</sup>J(H,H) = 7.1 Hz, 2H, H-19'), 3.97



(t,  $^3J(\text{H,H}) = 5.9$  Hz, 2H, H-21), 3.79 (t,  $^3J(\text{H,H}) = 5.9$  Hz, 2H, H-21'), 3.34 (s, 1H, H-17), 2.05 (b, 4H, H-22), 1.38 (t,  $^3J(\text{H,H}) = 7.0$  Hz, 6H, H-20).

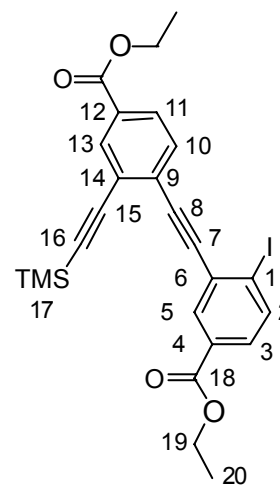
$^{13}\text{C-NMR}$  (126 MHz,  $\text{CDCl}_3$ ):  $\delta(\text{ppm}) = 166.0$  (C-18), 165.4 (C-18'), 155.9 (C-1), 135.2 (C-5), 133.8 (C-13), 132.0 (C-10), 131.0 (C-9), 130.8 (C-3), 129.6 (C-12), 129.2 (C-11), 126.5 (C-4), 124.5 (C-14), 117.2 (C-6), 116.9 (C-2), 94.7 (C-8), 91.7 (C-7), 81.8 (C-16), 81.6 (C-15), 61.3 (C-19), 60.9 (C-19'), 51.4 (C-21), 47.1 (C-21'), 24.0 (C-22), 23.5 (C-22'), 14.4 (C-20), 14.3 (C-20').

EI-MS (150-180 °C):  $m/z = 443, 428, 414, 398, 374$  (calcd 443 for  $\text{C}_{26}\text{H}_{25}\text{N}_3\text{O}_4^+$ ).

### Diethyl TMS-ethynyl(dimer)iodide **9**

a) TMS-ethynyl-(*o*PE-dimer)-diethyltriazenyl **8a** (0.36 g, 0.7 mmol) was dissolved in 5 mL MeI in a pressurable vessel. The yellow solution was subjected to 2x Freeze-Pump-Thaw cycles and heated to 110 °C for 16 h under pressure. The black mixture was diluted with diethyl ether, the black precipitate filtered off over celite, and the red filtrate concentrated. Purification by column chromatography (hexane:ethyl acetate = 10:1) yielded desired product as intense yellow solid (80 %).

b) In an analogous procedure (120 °C, 24 h) ethyl TMS-ethynyl-(*o*PE-dimer)-pyrrolidinyltriazenyl **8b** (0.67 g, 1.3 mmol) was used as starting material (79 %).



$^1\text{H-NMR}$  (250 MHz,  $\text{CDCl}_3$ ):  $\delta(\text{ppm}) = 8.16$  (s, 2H, H-5, H-13), 7.97 (d,  $^3J(\text{H,H}) = 8.2$  Hz, 1H, H-11), 7.95 (dd,  $^3J(\text{H,H}) = 8.2$  Hz,  $^4J(\text{H,H}) = 1.8$  Hz, 1H, H-3), 7.66 (d,  $^3J(\text{H,H}) = 8.2$  Hz, 2H, H-2, H-10), 4.37 (q,  $^3J(\text{H,H}) = 7.0$  Hz, 2H, H-19), 4.36 (q,  $^3J(\text{H,H}) = 7.3$  Hz, 2H, H-19'), 1.39 (t,  $^3J(\text{H,H}) = 7.3$  Hz, 3H, H-20), 1.37 (t,  $^3J(\text{H,H}) = 7.3$  Hz, 3H, H-20'), 0.27 (s, 9H, H-17).

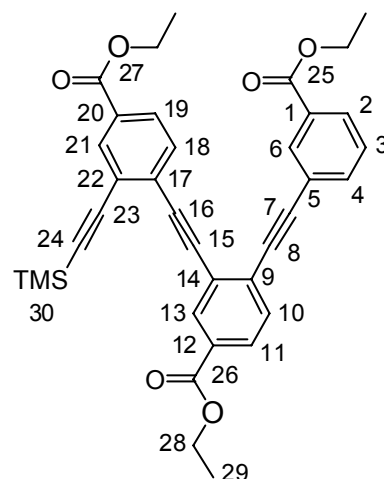
$^{13}\text{C-NMR}$  (126 MHz,  $\text{CDCl}_3$ ):  $\delta(\text{ppm}) = 165.4, 165.3$  (C-18), 139.1 (C-2), 133.5 (C-5), 133.4 (C-13), 132.1 (C-10), 130.6 (C-3), 130.4 (C-6), 130.3 (C-9), 129.9 (C-12), 129.3 (C-4), 128.9 (C-11), 125.8 (C-14), 106.8 (C-15), 102.3 (C-1), 100.2 (C-16), 96.9 (C-7), 91.7 (C-8), 61.4 (C-19), 14.3 (C-20), -0.1 (C-17).

EI-MS (80eV, 8kV, 140 °C):  $m/z = 544, 529$  (calcd 544 for  $\text{C}_{25}\text{H}_{25}\text{IO}_4\text{Si}^+$ ).

HPLC (MeOH): 3.98 min (98 %).

**Triethyl TMS-ethynyl-(*o*PE-trimer) 22**

TMS-ethynyl-(*o*PE-dimer)-iodide **9** (0.56 g, 1.0 mmol), ethyl 3-ethynylbenzoate **13** (0.27 g, 1.5 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (0.24 g, 0.2 mmol), and CuI (0.04 g, 0.2 mmol) were added to a solvent mixture of 5 mL dry Et(*i*Pr)<sub>2</sub>N, 5 mL dry THF, and 1 mL dry MeCN under a nitrogen atmosphere. The reaction solution was subjected to two Freeze-Pump-Thaw cycles, followed by stirring at 70°C for 18 hours. The reaction mixture was filtered, the filtrate concentrated, the obtained oil redissolved with toluene, filtrated, and the red filtrate concentrated. Purification by column chromatography (CH<sub>2</sub>Cl<sub>2</sub>:MeOH = 20:1) yielded desired product as a yellow solid (81 %).



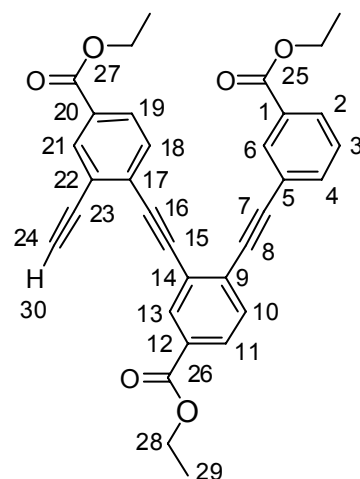
<sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>): δ(ppm) = 8.24 (d, <sup>4</sup>J(H,H) = 1.8 Hz, 1H, H-13), 8.23 (t, <sup>4</sup>J(H,H) = 1.7 Hz, 1H, H-6), 8.11 (d, <sup>4</sup>J(H,H) = 1.8 Hz, 1H, H-21), 8.02 (td, <sup>3</sup>J(H,H) = 7.8 Hz, <sup>4</sup>J(H,H) = 1.4 Hz, 1H, H-2), 8.00 (dd, <sup>3</sup>J(H,H) = 8.3 Hz, <sup>4</sup>J(H,H) = 1.8 Hz, 1H, H-19), 7.92 (dd, <sup>3</sup>J(H,H) = 8.1 Hz, <sup>4</sup>J(H,H) = 1.8 Hz, 1H, H-11), 7.71 (td, <sup>3</sup>J(H,H) = 7.7 Hz, <sup>4</sup>J(H,H) = 1.4 Hz, 1H, H-4), 7.63 (d, <sup>3</sup>J(H,H) = 8.1 Hz, 1H, H-18), 7.52 (d, <sup>3</sup>J(H,H) = 8.1 Hz, 1H, H-10), 7.41 (t, <sup>3</sup>J(H,H) = 7.8 Hz, 1H, H-3), 4.39 (q, <sup>3</sup>J(H,H) = 7.2 Hz, 2H, H-28), 4.37 (q, <sup>3</sup>J(H,H) = 7.2 Hz, 2H, H-28'), 4.36 (q, <sup>3</sup>J(H,H) = 7.0 Hz, 2H, H-28''), 1.39 (t, <sup>3</sup>J(H,H) = 7.1 Hz, 6H, H-29, H-29'), 1.35 (t, <sup>3</sup>J(H,H) = 7.1 Hz, 3H, H-29''), 0.21 (s, 9H, H-30).

<sup>13</sup>C-NMR (126 MHz, CDCl<sub>3</sub>): δ(ppm) = 165.7 (C-25), 165.4, 165.3 (C-26, C-27), 135.8 (C-4), 133.3 (C-6), 133.1, 132.9 (C-21, C-13), 131.9, 131.8 (C-18, C-10), 131.0, 130.2 (C-17, C-9), 130.2 (C-1), 130.0 (C-2), 129.8, 129.7 (C-12, C-20), 129.4, 129.0 (C-11, C-19), 128.6 (C-3), 126.0, 125.6 (C-22, C-14), 123.1 (C-5), 102.3, 100.2, 95.6, 93.8 (C-7, C-8, C-15, C-16), 92.3 (C-24), 88.5 (C-23), 61.4, 61.3, 61.2 (C-28), 14.3 (C-29), -0.2 (C-30).

EI-MS (120 °C): *m/z* = 590 (calcd 590 for C<sub>36</sub>H<sub>34</sub>O<sub>6</sub>Si<sup>+</sup>).

**Triethyl ethynyl-(*o*PE-trimer) 23**

TMS-ethynyl-(*o*PE-trimer) **22** (0.50 g, 0.8 mmol) and potassium carbonate (0.35 g, 2.5 mmol) were dissolved under nitrogen atmosphere in a solvent mixture of 5 mL ethanol, 4 mL THF, and 2 mL water. The solution was stirred at 50 °C for 3 h, and an excess of ethyl acetate and water was added to achieve phase separation; the organic phase was separated, washed with



aq. sat.  $\text{NH}_4\text{Cl}$ , and the aq. phases washed once with ethyl acetate. The combined org. phases were dried over  $\text{MgSO}_4$ , the solvent removed, and the obtained light yellow solid dried in vacuo (46 %).

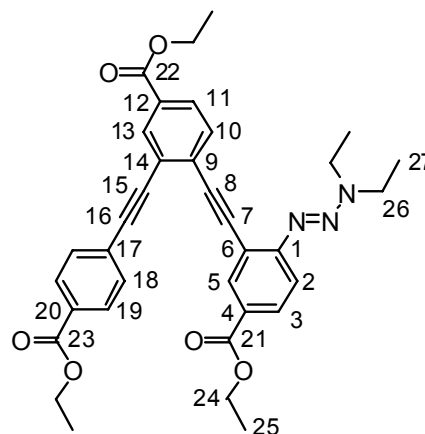
$^1\text{H-NMR}$  (500 MHz,  $\text{CDCl}_3$ ):  $\delta(\text{ppm}) = 8.27$  (dd,  $^4\text{J}(\text{H,H}) = 1.7$  Hz,  $^5\text{J}(\text{H,H}) = 0.6$  Hz, 1H, H-13),  $8.24$  (dt,  $^4\text{J}(\text{H,H}) = 1.7$  Hz,  $^5\text{J}(\text{H,H}) = 0.6$  Hz, 1H, H-6),  $8.20$  (d,  $^4\text{J}(\text{H,H}) = 1.8$  Hz, 1H, H-21),  $8.03$  (td,  $^3\text{J}(\text{H,H}) = 7.8$  Hz,  $^4\text{J}(\text{H,H}) = 1.2$  Hz, 1H, H-2),  $7.99$  (dd,  $^3\text{J}(\text{H,H}) = 8.1$  Hz,  $^4\text{J}(\text{H,H}) = 1.8$  Hz, 1H, H-19),  $7.97$  (dd,  $^3\text{J}(\text{H,H}) = 8.1$  Hz,  $^4\text{J}(\text{H,H}) = 1.8$  Hz, 1H, H-11),  $7.72$  (td,  $^3\text{J}(\text{H,H}) = 7.6$  Hz,  $^4\text{J}(\text{H,H}) = 1.2$  Hz, 1H, H-4),  $7.65$  (dd,  $^3\text{J}(\text{H,H}) = 7.4$  Hz,  $^5\text{J}(\text{H,H}) = 0.4$  Hz, 1H, H-18),  $7.63$  (dd,  $^3\text{J}(\text{H,H}) = 7.6$  Hz,  $^5\text{J}(\text{H,H}) = 0.6$  Hz, 1H, H-10),  $7.43$  (dt,  $^3\text{J}(\text{H,H}) = 7.8$  Hz,  $^5\text{J}(\text{H,H}) = 0.6$  Hz, 1H, H-3),  $4.39$  (q,  $^3\text{J}(\text{H,H}) = 7.2$  Hz, 2H, H-28),  $4.37$  (q,  $^3\text{J}(\text{H,H}) = 7.2$  Hz, 2H, H-28'),  $4.36$  (q,  $^3\text{J}(\text{H,H}) = 7.2$  Hz, 2H, H-29''),  $3.27$  (s, 1H, H-30),  $1.40$  (t,  $^3\text{J}(\text{H,H}) = 7.2$  Hz, 3H, H-29),  $1.39$  (t,  $^3\text{J}(\text{H,H}) = 7.2$  Hz, 3H, H-29'),  $1.36$  (t,  $^3\text{J}(\text{H,H}) = 7.2$  Hz, 3H, H-29'').

$^{13}\text{C-NMR}$  (126 MHz,  $\text{CDCl}_3$ ):  $\delta(\text{ppm}) = 165.7$  (C-25),  $165.3$ ,  $165.2$  (C-26, C-27),  $135.9$  (C-4),  $133.7$  (C-6),  $133.6$ ,  $133.0$  (C-21, C-13),  $132.2$ ,  $132.1$  (C-18, C-10),  $131.0$ ,  $130.3$  (C-17, C-9),  $130.2$  (C-1),  $130.0$  (C-2),  $129.9$ ,  $129.6$  (C-12, C-20),  $129.4$ ,  $129.3$  (C-11, C-19),  $128.6$  (C-3),  $125.4$ ,  $124.8$  (C-22, C-14),  $123.1$  (C-5),  $95.5$ ,  $93.9$ ,  $92.0$ ,  $88.4$  (C-7, C-8, C-15, C-16),  $82.4$  (C-24),  $81.1$  (C-23),  $61.5$ ,  $61.4$ ,  $61.3$  (C-28),  $14.3$  (C-29).

EI-MS (100 °C):  $m/z = 518, 490, 473, 462, 445, 434, 417, 389$  (calcd 518 for  $\text{C}_{33}\text{H}_{26}\text{O}_6^+$ ).

### Triethyl diethyltriazenyl-(*o*PE-trimer) 20

Ethynyl-(*o*PE-dimer)-diethyltriazenyl **7** (0.20 g, 0.5 mmol), ethyl 4-iodobenzoate (0.25 g, 0.9 mmol),  $\text{Pd}(\text{PPh}_3)_4$  (0.10 g, 0.1 mmol), and  $\text{CuI}$  (0.02 g, 0.1 mmol) were added to a solvent mixture of 5 mL dry  $\text{Et}(\text{iPr})_2\text{N}$ , 5 mL dry THF, and 1 mL dry MeCN under a nitrogen atmosphere. The yellow suspension was subjected to two Freeze-Pump-Thaw cycles, and heated to 80 °C where it turned into a yellow solution. After stirring for 23 h, the red-brown reaction mixture was concentrated, redissolved in toluene, filtrated, and the red filtrate concentrated. Purification by column chromatography ( $\text{CH}_2\text{Cl}_2:\text{MeOH} = 20:1$ ) yielded desired product as a yellow solid (75 %).



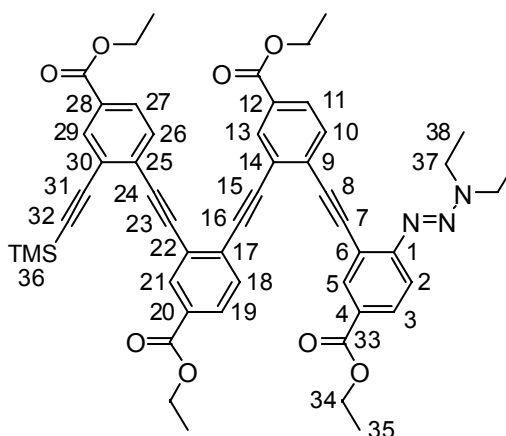
$^1\text{H-NMR}$  (500 MHz,  $\text{CDCl}_3$ ):  $\delta(\text{ppm}) = 8.27$  (d,  $^4\text{J}(\text{H,H}) = 1.9$  Hz, 1H, H-5),  $8.22$  (d,  $^4\text{J}(\text{H,H}) = 1.2$  Hz, 1H, H-13),  $7.98$  (td,  $^3\text{J}(\text{H,H}) = 8.5$  Hz,  $^4\text{J}(\text{H,H}) = 1.7$  Hz, 2H, H-19),  $7.98$  (td,  $^3\text{J}(\text{H,H}) = 8.6$  Hz,  $1.7$  Hz, 2H, H-19),  $7.96$  (m, 2H, H-3, H-11),  $7.60$  (td,  $^3\text{J}(\text{H,H}) = 8.6$  Hz,

$^4\text{J}(\text{H,H}) = 1.7 \text{ Hz}$ , 2H, H-18), 7.57 (d,  $^3\text{J}(\text{H,H}) = 8.1 \text{ Hz}$ , 1H, H-10), 7.51 (d,  $^3\text{J}(\text{H,H}) = 8.5 \text{ Hz}$ , 1H, H-2), 4.39 (q,  $^3\text{J}(\text{H,H}) = 7.2 \text{ Hz}$ , 2H, H-24), 4.37 (q,  $^3\text{J}(\text{H,H}) = 7.2 \text{ Hz}$ , 2H, H-24'), 4.34 (q,  $^3\text{J}(\text{H,H}) = 7.1 \text{ Hz}$ , 2H, H-24''), 3.77 (q,  $^3\text{J}(\text{H,H}) = 7.2 \text{ Hz}$ , 4H, H-26), 1.40 ( $^3\text{J}(\text{H,H}) = 7.2 \text{ Hz}$ , 3H, H-25), 1.37 (t,  $^3\text{J}(\text{H,H}) = 7.2 \text{ Hz}$ , 3H, H-25'), 1.32 (t,  $^3\text{J}(\text{H,H}) = 7.2 \text{ Hz}$ , 3H, H-25''), 1.29 (t,  $^3\text{J}(\text{H,H}) = 7.9 \text{ Hz}$ , 3H, H-27), 1.23 (t,  $^3\text{J}(\text{H,H}) = 6.9 \text{ Hz}$ , 3H, H-27').

EI-MS (150 °C):  $m/z = 593$  (calcd 593 for  $\text{C}_{35}\text{H}_{35}\text{N}_3\text{O}_6^+$ ).

### Tetraethyl TMS-ethynyl-(*o*PE-tetramer)-diethyltriazenyl 10

Ethynyl-(*o*PE-dimer)-diethyltriazenyl 7 (0.11 g, 0.25 mmol), TMS-ethynyl-(*o*PE-dimer)iodide 9 (0.13 g, 0.25 mmol),  $\text{Pd}(\text{PPh}_3)_4$  (40 mg, 34  $\mu\text{mol}$ ), and  $\text{CuI}$  (4 mg, 24  $\mu\text{mol}$ ) were added to a solvent mixture of 3 mL dry  $\text{Et}_3\text{N}$ , 3 mL dry THF, and 0.2 mL dry MeCN under a nitrogen atmosphere. The reaction solution was subjected to two Freeze-Pump-Thaw cycles, and stirred at 70 °C for 18 h. The red-brown reaction mixture was concentrated,



redissolved in toluene, filtrated, and the red filtrate concentrated. Purification by column chromatography (hexane:ethyl acetate = 3:1 and hexane: $\text{CH}_2\text{Cl}_2$  = 1:1) yielded desired product as a yellow solid (50 %).

$^1\text{H-NMR}$  (500 MHz,  $\text{CDCl}_3$ ):  $\delta(\text{ppm}) = 8.27$  (d,  $^4\text{J}(\text{H,H}) = 1.8 \text{ Hz}$ , 1H, H-5), 8.23 (d,  $^4\text{J}(\text{H,H}) = 1.7 \text{ Hz}$ , 1H, H-13), 8.19 (d,  $^4\text{J}(\text{H,H}) = 1.9 \text{ Hz}$ , 1H, H-21), 8.09 (d,  $^4\text{J}(\text{H,H}) = 1.7 \text{ Hz}$ , 1H, H-29), 7.98 (dd,  $^3\text{J}(\text{H,H}) = 8.1 \text{ Hz}$ ,  $^4\text{J}(\text{H,H}) = 1.8 \text{ Hz}$ , 1H, H-27), 7.96 (dd,  $^3\text{J}(\text{H,H}) = 8.1 \text{ Hz}$ ,  $^4\text{J}(\text{H,H}) = 1.7 \text{ Hz}$ , 1H, H-3), 7.90 (dd,  $^3\text{J}(\text{H,H}) = 8.5 \text{ Hz}$ ,  $^4\text{J}(\text{H,H}) = 1.9 \text{ Hz}$ , 1H, H-19), 7.83 (dd,  $^3\text{J}(\text{H,H}) = 8.1 \text{ Hz}$ ,  $^4\text{J}(\text{H,H}) = 1.8 \text{ Hz}$ , 1H, H-11), 7.67 (d,  $^3\text{J}(\text{H,H}) = 8.1 \text{ Hz}$ , 1H, H-26), 7.60 (d,  $^3\text{J}(\text{H,H}) = 8.3 \text{ Hz}$ , 1H, H-18), 7.59 (d,  $^3\text{J}(\text{H,H}) = 8.1$ , 1H, H-10), 7.44 (d,  $^3\text{J}(\text{H,H}) = 8.7 \text{ Hz}$ , 1H, H-2), 4.38 (q,  $^3\text{J}(\text{H,H}) = 7.2 \text{ Hz}$ , 2H, H-34), 4.36 (q,  $^3\text{J}(\text{H,H}) = 7.2 \text{ Hz}$ , 2H, H-34), 4.35 (q,  $^3\text{J}(\text{H,H}) = 7.0 \text{ Hz}$ , 2H, H-34), 4.31 (q,  $^3\text{J}(\text{H,H}) = 7.2 \text{ Hz}$ , 2H, H-34), 3.75 (q,  $^3\text{J}(\text{H,H}) = 7.2 \text{ Hz}$ , 4H, H-37), 1.38 (t,  $^3\text{J}(\text{H,H}) = 7.2 \text{ Hz}$ , 6H, H-35), 1.33 (t,  $^3\text{J}(\text{H,H}) = 7.2 \text{ Hz}$ , 3H, H-35), 1.31 (t,  $^3\text{J}(\text{H,H}) = 7.0 \text{ Hz}$ , 3H, H-35), 1.28 (t,  $^3\text{J}(\text{H,H}) = 7.6 \text{ Hz}$ , 3H, H-38), 1.21 (t,  $^3\text{J}(\text{H,H}) = 7.6 \text{ Hz}$ , 3H, H-38), 0.24 (H-36).

$^{13}\text{C-NMR}$  (126 MHz,  $\text{CDCl}_3$ ):  $\delta(\text{ppm}) = 165.8$  (C-33), 165.3 (C-33), 165.2 (C-33), 155.7 (C-1), 134.8 (C-5), 133.3 (C-13), 133.1 (C-21), 133.0 (C-29), 132.4 (C-26), 132.1 (C-18), 131.8 (C-10), 130.8 (C-3), 130.7 (C-9), 130.2 (C-17), 129.9 (C-25), 129.8 (C-28), 129.7 (C-20), 129.6 (C-12), 129.4 (C-19), 129.3 (C-11), 128.8 (C-27), 126.4 (C-4), 125.8 (C-30), 125.5 (C-

22), 125.2 (C-14), 117.3 (C-6), 116.6 (C-2), 102.3 (C-31), 99.8 (C-32), 95.4 (C-24), 94.8 (C-16), 93.7 (C-8), 92.4 (C-23), 92.2 (C-15), 91.7 (C-7), 61.3 (C-34), 61.2 (C-34), 60.8 (C-34), 49.4 (C-37), 42.2 (C-37), 14.3 (C-35), 10.9 (C-38), -0.2 (C-36).

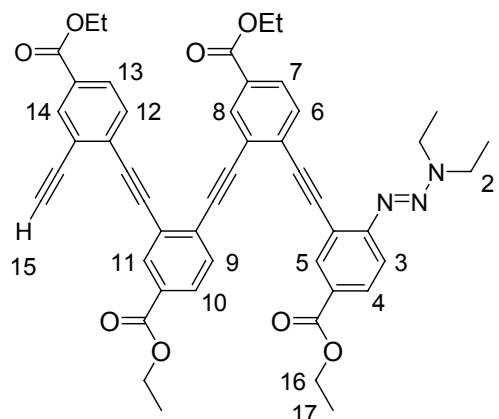
FAB-MS (MNBA/CH<sub>2</sub>Cl<sub>2</sub>):  $m/z$  = 862 (calcd 862 for C<sub>51</sub>H<sub>52</sub>N<sub>3</sub>O<sub>8</sub>Si<sup>+</sup>).

HPLC (MeOH:H<sub>2</sub>O = 95:5): 27.06 min (95 %)

### Tetraethyl ethynyl-(*o*PE-tetramer)-diethyltriazenyl 17

TMS-ethynyl-(*o*PE-tetramer)-diethyltriazenyl 10

(0.284 g, 0.33 mmol) was dissolved in 8.5 mL THF and 0.5 mL of a TBAF solution in THF (1M, 0.5 mmol) were added, turning the red reaction solution immediately black. The mixture was stirred for 1h and complete conversion was assumed (monitoring by TLC was not possible). The mixture was purified by a short silica gel column, and concentration of the first fraction yielded the desired product as brown solid (96%).



<sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$ (ppm) = 8.27 (d, <sup>4</sup>J(H,H) = 1.4 Hz, 1H, H-5), 8.25 (d, <sup>4</sup>J(H,H) = 1.4 Hz, 1H, H-8), 8.16 (d, <sup>4</sup>J(H,H) = 1.8 Hz, 1H, H-11), 8.09 (d, <sup>4</sup>J(H,H) = 1.6 Hz, 1H, H-14), 7.98 (dd, <sup>3</sup>J(H,H) = 8.1 Hz, <sup>4</sup>J(H,H) = 1.8 Hz, 1H, H-4), 7.94 (dd, <sup>3</sup>J(H,H) = 8.1 Hz, <sup>4</sup>J(H,H) = 1.8 Hz, 1H, H-13), 7.89 (dd, <sup>3</sup>J(H,H) = 8.6 Hz, <sup>4</sup>J(H,H) = 2.0 Hz, 1H, H-7), 7.84 (dd, <sup>3</sup>J(H,H) = 8.2 Hz, <sup>4</sup>J(H,H) = 1.7 Hz, 1H, H-10), 7.67 (d, <sup>3</sup>J(H,H) = 8.4 Hz, 1H, H-12), 7.58 (d, <sup>3</sup>J(H,H) = 8.1 Hz, 1H, H-9), 7.55 (d, <sup>3</sup>J(H,H) = 8.1 Hz, 1H, H-6), 7.41 (d, <sup>3</sup>J(H,H) = 8.6 Hz, 1H, H-3), 4.39 (q, <sup>3</sup>J(H,H) = 7.1 Hz, 2H, H-16), 4.36 (q, <sup>3</sup>J(H,H) = 7.1 Hz, 2H, H-16), 4.35 (q, <sup>3</sup>J(H,H) = 7.1 Hz, 2H, H-16), 4.31 (q, <sup>3</sup>J(H,H) = 7.1 Hz, 2H, H-16), 3.74 (q, <sup>3</sup>J(H,H) = 7.2 Hz, 4H, H-2), 3.26 (s, 1H, H-15), 1.39 (t, <sup>3</sup>J(H,H) = 7.1 Hz, 3H, H-17), 1.38 (t, <sup>3</sup>J(H,H) = 7.1 Hz, 3H, H-17), 1.35 (t, <sup>3</sup>J(H,H) = 7.1 Hz, 3H, H-17), 1.30 (t, <sup>3</sup>J(H,H) = 7.1 Hz, 3H, H-17), 1.27 (b, 3H, H-1), 1.21 (b, 3H, H-1).

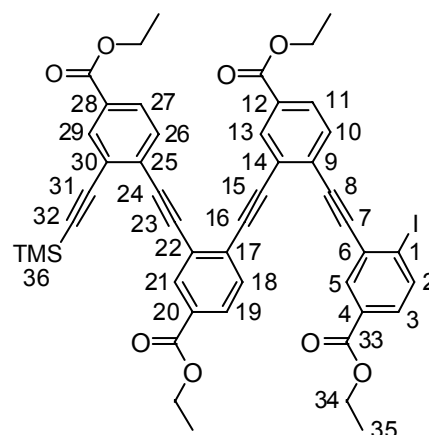
<sup>13</sup>C-NMR (126 MHz, CDCl<sub>3</sub>):  $\delta$ (ppm) = 165.8, 165.4, 165.3, 165.2, 155.6, 134.9, 133.5, 133.4, 132.5, 132.3, 131.8, 130.9, 130.8, 130.1, 130.0, 129.9, 129.7, 129.6, 129.4, 129.3, 129.1, 126.4, 125.4, 125.2, 124.7, 117.3, 116.6, 95.7, 95.4, 94.7, 93.9, 92.2, 92.1, 91.8, 82.2, 81.2, 61.4, 61.33, 61.29, 60.8, 49.4, 42.2, 14.31, 14.28, 14.26, 10.9.

ESI-MS:  $m/z$  = 790 (calcd 790 for C<sub>48</sub>H<sub>44</sub>N<sub>3</sub>O<sub>8</sub><sup>+</sup>).

HPLC (MeOH:H<sub>2</sub>O = 95:5, 0.8 mL/min): 13.36 min (97%).

**Tetraethyl TMS-ethynyl-(*o*PE-tetramer)-iodide 14**

TMS-ethynyl-(*o*PE-tetramer)-diethyltriazenyl **10** (103 mg, 0.12 mmol), was dissolved in 3 mL MeI within a preassembled vessel. Nitrogen was bubbled through the yellow clear solution, followed by a Freeze-Pump-Thaw cycle. The vessel was sealed tight and heated to 120°C for 22h. After cooling to rt, diethylether was added, the black precipitate was removed, and the filtrate concentrated yielding brown oil. Purification by column chromatography (CH<sub>2</sub>Cl<sub>2</sub>:MeOH = 100:1) gave the pure product as yellow-brown powder (89 %).



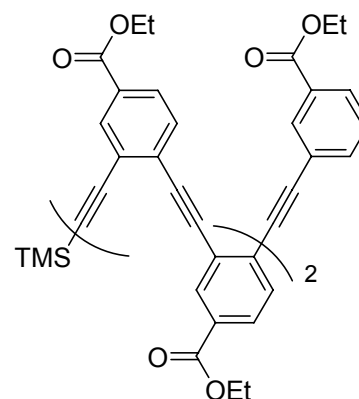
<sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$ (ppm) = 8.30 (d, <sup>4</sup>J(H,H) = 1.7 Hz, 1H, H-21), 8.25 (d, <sup>4</sup>J(H,H) = 1.8 Hz, 1H, H-13), 8.05 (d, <sup>4</sup>J(H,H) = 1.7 Hz, 1H, H-29), 8.04 (d, <sup>4</sup>J(H,H) = 2.1 Hz, 1H, H-5), 8.03 (dd, <sup>3</sup>J(H,H) = 6.5 Hz, <sup>4</sup>J(H,H) = 2.2 Hz, 1H, H-27), 7.01 (dd, <sup>3</sup>J(H,H) = 8.2 Hz, <sup>4</sup>J(H,H) = 1.8 Hz, 1H, H-19), 7.88 (d, <sup>3</sup>J(H,H) = 8.3 Hz, 1H, H-2), 7.83 (dd, <sup>3</sup>J(H,H) = 8.1 Hz, <sup>4</sup>J(H,H) = 1.7 Hz, 1H, H-11), 7.72 (d, <sup>3</sup>J(H,H) = 8.1 Hz, 1H, H-26), 7.71 (d, <sup>3</sup>J(H,H) = 8.1 Hz, 1H, H-10), 7.58 (dd, <sup>3</sup>J(H,H) = 8.2 Hz, <sup>4</sup>J(H,H) = 2.1 Hz, 1H, H-3), 7.52 (d, <sup>3</sup>J(H,H) = 8.1 Hz, 1H, H-18), 4.39 (q, <sup>3</sup>J(H,H) = 7.2 Hz, 2H, H-34), 4.37 (q, <sup>3</sup>J(H,H) = 7.2 Hz, 2H, H-34), 4.36 (q, <sup>3</sup>J(H,H) = 7.2 Hz, 2H, H-34), 4.32 (q, <sup>3</sup>J(H,H) = 7.1 Hz, 2H, H-34), 1.39 (t, <sup>3</sup>J(H,H) = 7.2 Hz, 6H, H-35), 1.35 (t, <sup>3</sup>J(H,H) = 7.2 Hz, 3H, H-35), 1.32 (t, <sup>3</sup>J(H,H) = 7.0 Hz, 3H, H-35), 0.24 (s, 9H, H-36).

<sup>13</sup>C-NMR (126 MHz, CDCl<sub>3</sub>):  $\delta$ (ppm) = 165.31 (C-33), 165.24 (C-33), 165.21 (C-33), 165.20 (C-33), 139.09 (C-2), 133.60 (C-5), 133.53 (C-29), 133.15 (C-13), 133.12 (C-21), 132.39, 132.08, 130.56, 130.44, 130.38, 130.30, 129.96, 129.68, 129.63, 129.54, 129.46, 129.39, 129.12, 128.84 (C-4), 125.85, 125.78, 125.41 (C-14, C-22, C-30), 106.57 (C-1), 102.28 (C-31), 99.93 (C-32), 97.32, 94.26, 93.88, 92.60, 92.42, 91.52 (C-7, C-8, C-15, C-16, C-23, C-24), 61.47 (C-34), 61.40 (C-34), 61.30 (C-34), 14.35 (C-35), 14.31 (C-35), 14.29 (C-35), 14.23 (C-35), -0.11 (C-36).

EI-MS (250 °C):  $m/z$  = 888 (calcd 888 for C<sub>47</sub>H<sub>41</sub>IO<sub>8</sub>Si<sup>+</sup>).

**Pentaethyl TMS-ethynyl-(*o*PE-pentamer) 15**

In a nitrogen atmosphere, Pd(PPh<sub>3</sub>)<sub>4</sub> (39  $\mu$ g, 0.03 mmol), CuI (3  $\mu$ g, 0.02 mmol), TMS-ethynyl-(*o*PE-tetramer)-iodide **14** (0.15 g, 0.17 mmol), and ethyl 3-ethynylbenzoate **13** (0.10 g,

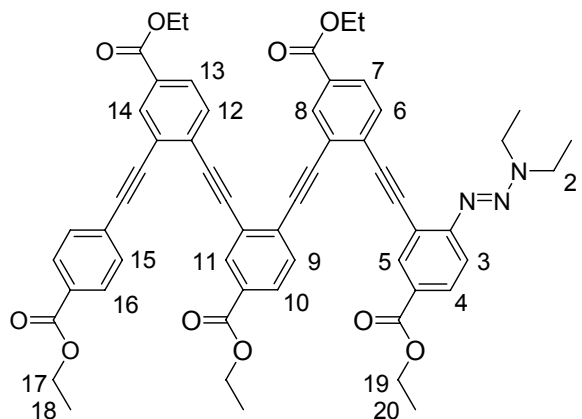


0.56 mmol) were dissolved in a mixture of dry Et<sub>3</sub>N (3 mL), THF (0.8 mL), and acetonitril (0.2 mL). Two freeze-pump-thaw cycles were run, and the reaction mixture was stirred at 50 °C for two days. Removal of solvent purification by column chromatography (first neat CH<sub>2</sub>Cl<sub>2</sub>, second column with hexane:ethyl acetate = 5:1) gave product as yellow-brown solid (47%).

<sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>): δ(ppm) = 8.31 (d, <sup>4</sup>J(H,H) = 1.7 Hz, 1H), 8.12 (d, <sup>4</sup>J(H,H) = 1.8 Hz, 1H), 8.04 (d, <sup>4</sup>J(H,H) = 1.8 Hz, 1H), 8.03 (d, <sup>4</sup>J(H,H) = 2.2 Hz, 1H), 8.01 (d, <sup>4</sup>J(H,H) = 1.7 Hz, 1H), 7.92 (dm, <sup>3</sup>J(H,H) = 8.1 Hz, <sup>4</sup>J(H,H) = 1.8 Hz, 2H), 7.82 (dd, <sup>3</sup>J(H,H) = 8.1 Hz, <sup>4</sup>J(H,H) = 1.8 Hz, 1H), 7.79 (dd, <sup>3</sup>J(H,H) = 8.2 Hz, <sup>4</sup>J(H,H) = 1.8 Hz, 1H), 7.71 (d, <sup>3</sup>J(H,H) = 8.1 Hz, 1H), 7.66 (dd, <sup>3</sup>J(H,H) = 8.4 Hz, <sup>4</sup>J(H,H) = 1.4 Hz, 1H), 7.64 (dd, <sup>3</sup>J(H,H) = 8.4 Hz, <sup>4</sup>J(H,H) = 1.4 Hz, 1H), 7.55 (d, <sup>3</sup>J(H,H) = 8.1 Hz, 1H), 7.51 (d, <sup>3</sup>J(H,H) = 8.1 Hz, 1H), 7.44 (d, <sup>3</sup>J(H,H) = 8.2 Hz, 1H), 7.29 (t, <sup>3</sup>J(H,H) = 7.8 Hz, 1H), 4.38 (q, <sup>3</sup>J(H,H) = 7.2 Hz, 2H, CH<sub>2</sub>), 4.37 (q, <sup>3</sup>J(H,H) = 7.2 Hz, 2H, CH<sub>2</sub>), 4.340 (q, <sup>3</sup>J(H,H) = 7.0 Hz, 2H, CH<sub>2</sub>), 4.338 (q, <sup>3</sup>J(H,H) = 7.2 Hz, 2H, CH<sub>2</sub>), 4.31 (q, <sup>3</sup>J(H,H) = 7.2 Hz, 2H, CH<sub>2</sub>), 1.38 (t, <sup>3</sup>J(H,H) = <sup>3</sup>J(H,H) = 6.6 Hz, 3H, CH<sub>3</sub>), 1.37 (t, <sup>3</sup>J(H,H) = 6.6 Hz, 3H, CH<sub>3</sub>), 1.36 (t, <sup>3</sup>J(H,H) = 6.6 Hz, 3H, CH<sub>3</sub>), 1.35 (t, <sup>3</sup>J(H,H) = 6.6 Hz, 3H, CH<sub>3</sub>), 1.33 (t, <sup>3</sup>J(H,H) = 6.6 Hz, 3H, CH<sub>3</sub>), 0.26 (s, 9H, TMS).  
EI-MS (250°C): *m/z* = 934 (calcd 934 for C<sub>58</sub>H<sub>50</sub>O<sub>10</sub>Si<sup>+</sup>).

### Pentaethyl (*o*PE-pentamer)-diethyltriazenyl **18**

A flame-dried Schlenk-tupe under argon atmosphere was loaded with catalysts Pd(PPh<sub>3</sub>)<sub>4</sub> (0.083 mg, 0.07 mmol) and CuI (0.006 mg, 0.03 mmol), followed by addition of a solution of ethynyl-(*o*PE-tetramer)-diethyltriazenyl **17** (0.259 g, 0.328 mmol) in 1.0 mL dry THF, ethyl *para*-iodobenzoate (0.11 mL, 0.66 mmol), 1.8 mL dry triethylamine, and 0.2 mL dry acetonitrile.



The mixture was submitted to three freeze-pump-thaw-cycles, and then heated to 70 °C, where suspension became brown homogeneous solution. Stirring was continued for 52 h. After cooling down to rt, CH<sub>2</sub>Cl<sub>2</sub> was added to the suspension, followed by filtration over celite. The filtrate was concentrated, and the obtained black solid purified by column chromatography (silica gel, gradient: neat CH<sub>2</sub>Cl<sub>2</sub> to CH<sub>2</sub>Cl<sub>2</sub>:ethyl acetate = 100:1) yielding a yellow solid (71%).



$^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta(\text{ppm}) = 8.27$  (d,  $^4\text{J}(\text{H,H}) = 1.4$  Hz, 1H, H-5),  $8.10$  (d,  $^4\text{J}(\text{H,H}) = 1.4$  Hz, 2H, H-8 & H-11),  $8.08$  (d,  $^4\text{J}(\text{H,H}) = 1.4$  Hz, 1H, H-14),  $7.99$  (dd,  $^3\text{J}(\text{H,H}) = 8.2$  Hz,  $^4\text{J}(\text{H,H}) = 1.7$  Hz, 1H, H-4),  $7.893$  (d,  $^3\text{J}(\text{H,H}) = 8.7$  Hz, 2H, H-16),  $7.888$  (d,  $^3\text{J}(\text{H,H}) = 8.5$  Hz, 1H, H-13),  $7.86$  (dd,  $^3\text{J}(\text{H,H}) = 8.6$  Hz,  $^4\text{J}(\text{H,H}) = 2.0$  Hz, 1H, H-7),  $7.78$  (dd,  $^3\text{J}(\text{H,H}) = 8.1$  Hz,  $^4\text{J}(\text{H,H}) = 1.7$  Hz, 1H, H-10),  $7.70$  (d,  $^3\text{J}(\text{H,H}) = 8.1$  Hz, 1H, H-12),  $7.49$  (d,  $^3\text{J}(\text{H,H}) = 8.1$  Hz, 1H, H-9),  $7.48$  (d,  $^3\text{J}(\text{H,H}) = 8.6$  Hz, 3H, H-6 & H-15),  $7.37$  (d,  $^3\text{J}(\text{H,H}) = 8.6$  Hz, 1H, H-3),  $4.38$  (q,  $^3\text{J}(\text{H,H}) = 7.1$  Hz, 2H, H-19),  $4.37$  (q,  $^3\text{J}(\text{H,H}) = 7.1$  Hz, 2H, H-19),  $4.34$  (q,  $^3\text{J}(\text{H,H}) = 7.1$  Hz, 2H, H-19),  $4.33$  (q,  $^3\text{J}(\text{H,H}) = 7.2$  Hz, 2H, H-19),  $4.26$  (q,  $^3\text{J}(\text{H,H}) = 7.2$  Hz, 2H, H-17),  $3.72$  (q,  $^3\text{J}(\text{H,H}) = 7.2$  Hz, 4H, H-2),  $1.40$  (t,  $^3\text{J}(\text{H,H}) = 7.2$  Hz, 3H, H-18),  $1.36$  (t,  $^3\text{J}(\text{H,H}) = 7.2$  Hz, 6H, H-20),  $1.35$  (t,  $^3\text{J}(\text{H,H}) = 7.1$  Hz, 3H, H-20),  $1.28$  (t,  $^3\text{J}(\text{H,H}) = 7.1$  Hz, 6H, H-20 & H-1),  $1.20$  (t,  $^3\text{J}(\text{H,H}) = 6.0$  Hz, 3H, H-1).

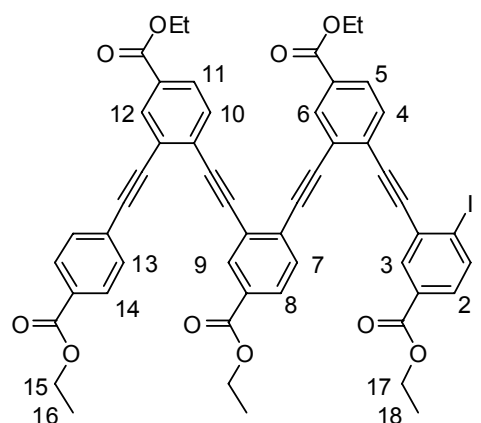
$^{13}\text{C-NMR}$  (100.6 MHz,  $\text{CDCl}_3$ ):  $\delta(\text{ppm}) = 165.92, 165.83, 165.26, 165.24, 165.23, 155.52, 134.94, 133.31, 133.16, 132.82, 132.44, 132.17, 131.68, 131.54, 130.76, 130.65, 130.21, 129.95, 129.74, 129.43, 129.40, 129.38, 129.26, 129.21, 128.87, 127.35, 126.30, 125.53, 125.44, 125.00, 117.41, 116.46, 95.68, 95.28, 94.96, 94.00, 93.45, 92.47, 91.92, 91.79, 90.26, 61.41, 61.29, 61.26, 61.04, 60.78, 49.43, 42.18, 14.32, 14.28, 10.90.$

ESI-MS (pos,  $\text{CH}_2\text{Cl}_2$ ):  $m/z = 937$  (calcd 937 for  $\text{C}_{57}\text{H}_{51}\text{N}_3\text{O}_{10}^+$ ).

HPLC ( $\text{MeOH}:\text{H}_2\text{O}$ , 0.8 mL/min): 22.17 min (95 %).

### Pentaethyl (*o*PE-pentamer)-iodide **19**

A flame-dried presurable Schlenk-vessel was filled under argon with a red solution of (*o*PE-pentamer)-diethyltriazenyl **18** (0.216 g, 0.23 mmol) in 5 mL MeI. The solution was submitted 3 to freeze-pump-thaw-cycles for degassing. The reaction flask was sealed tight and heated to 110-120 °C for 2 d under vigorous stirring. After cooling down to room temperature, the black suspension was concentrated



and impurities removed by washing the crude mixture with a mixture of hexanes:ethyl acetate = 2:1. The retained brown solid was purified by column chromatography ( $\text{CH}_2\text{Cl}_2:\text{MeOH} = 100:1$ ) yielding desired product as yellow solid (36 %).

$R_f$  ( $\text{CH}_2\text{Cl}_2:\text{MeOH} = 100:1$ ): 0.56

$^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta(\text{ppm}) = 8.28$  (dd,  $^4\text{J}(\text{H,H}) = 1.7$  Hz,  $^5\text{J}(\text{H,H}) = 0.4$  Hz, 1H, H-3),  $8.07$  (dd,  $^4\text{J}(\text{H,H}) = 1.7$  Hz,  $^5\text{J}(\text{H,H}) = 0.3$  Hz, 1H, H-6),  $8.03$  (dd,  $^4\text{J}(\text{H,H}) = 1.8$  Hz,  $^5\text{J}(\text{H,H}) = 0.3$  Hz, 1H, H-9),  $8.02$  (dd,  $^3\text{J}(\text{H,H}) = 8.2$  Hz,  $^4\text{J}(\text{H,H}) = 1.7$  Hz, 1H, H-11),  $7.94$  (d,

$^4J(\text{H,H}) = 2.0$  Hz, 1H, H-12), 7.90 (dd,  $^3J(\text{H,H}) = 8.2$  Hz,  $^4J(\text{H,H}) = 1.7$  Hz, 1H, H-8), 7.87 (d,  $^3J(\text{H,H}) = 8.6$  Hz, 2H, H-14), 7.78 (d,  $^3J(\text{H,H}) = 8.6$  Hz, 1H, H-1), 7.76 (dd,  $^3J(\text{H,H}) = 8.1$  Hz,  $^4J(\text{H,H}) = 1.7$  Hz, 1H, H-5), 7.72 (d,  $^3J(\text{H,H}) = 8.2$  Hz, 1H, H-4), 7.60 (dd,  $^3J(\text{H,H}) = 8.1$  Hz,  $^5J(\text{H,H}) = 0.4$  Hz, 1H, H-7), 7.51 (dd,  $^3J(\text{H,H}) = 8.3$  Hz,  $^4J(\text{H,H}) = 2.2$  Hz, 1H, H-2), 7.44 (d,  $^3J(\text{H,H}) = 8.5$  Hz, 2H, H-13), 7.39 (dd,  $^3J(\text{H,H}) = 8.1$  Hz,  $^5J(\text{H,H}) = 0.3$  Hz, 1H, H-10), 4.38 (q,  $^3J(\text{H,H}) = 7.1$  Hz, 4H, H-17), 4.33 (q,  $^3J(\text{H,H}) = 7.1$  Hz, 2H, H-17), 4.32 (q,  $^3J(\text{H,H}) = 7.1$  Hz, 2H, H-17), 4.24 (q,  $^3J(\text{H,H}) = 7.1$  Hz, 2H, H-15), 1.35 (m, 12H, H-18), 1.26 (t,  $^3J(\text{H,H}) = 7.2$  Hz, 3H, H-16).

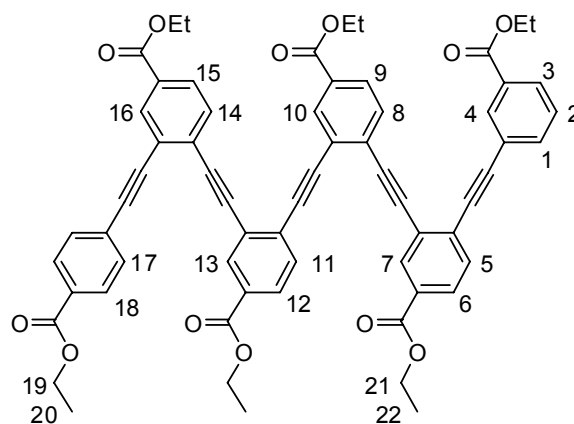
$^{13}\text{C-NMR}$  (100.6 MHz,  $\text{CDCl}_3$ ):  $\delta(\text{ppm}) = 165.85, 165.18, 165.17, 165.14, 138.82, 133.57, 133.39, 133.21, 132.79, 132.41, 132.09, 131.99, 131.51, 130.38, 130.29, 130.15, 130.01, 129.91, 129.61, 129.51, 129.36, 129.27, 129.20, 129.15, 128.78, 127.20, 125.72, 125.37, 125.15, 106.55, 97.17, 95.64, 94.40, 94.15, 93.53, 92.13, 91.61, 90.12, 61.42, 61.35, 61.32, 61.29, 61.03, 14.31, 14.25, 14.22, 14.13$ .

ESI-MS (pos.):  $m/z = 987$  (calcd 987 for  $\text{C}_{53}\text{H}_{41}\text{IO}_{10}\text{Na}^+$ ).

HPLC (acetonitrile:water = 95:5, 220nm): 30.42 min (89 %).

### Hexaethyl (*o*PE-hexamer) **16**

A flame-dried Schlenk-tube was loaded with (*o*PE-pentamer)-iodide **19** (0.077 g, 0.08 mmol), ethyl 3-ethynylbenzoate **13** (0.070 g, 0.40 mmol),  $\text{Pd}(\text{PPh}_3)_4$  (0.019 g, 0.02 mmol), and  $\text{CuI}$  (0.004 g, 0.02 mmol). Pre-degassed solvent mixture of 1.8 mL  $\text{Et}_3\text{N}$ , 1.0 mL THF, and 0.2 mL acetonitrile was added. The reaction mixture was submitted to one freeze-



pump-thaw cycle and afterwards heated to 75 °C and stirred for 2 d. The reaction suspension was cooled to room temperature, diluted with  $\text{CH}_2\text{Cl}_2$ , and washed subsequently with sat. aq.  $\text{NH}_4\text{Cl}$ , sat. aq.  $\text{NaHCO}_3$ , and sat. aq.  $\text{NaCl}$ . The organic phase was dried over  $\text{MgSO}_4$ , concentrated, and further purified by column chromatography (silica gel, 1<sup>st</sup> column: eluent gradient from  $\text{CH}_2\text{Cl}_2$ :hexane = 5:1 to  $\text{CH}_2\text{Cl}_2$ :MeOH = 100:1, 2<sup>nd</sup> column with  $\text{CH}_2\text{Cl}_2$ :MeOH = 200:1) to yield a yellow solid (90 %).

$^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta(\text{ppm}) = 8.17$  (dd,  $^4J(\text{H,H}) = 1.7$  Hz,  $^5J(\text{H,H}) = 0.4$  Hz, 1H, H-7), 8.06 (dd,  $^4J(\text{H,H}) = 1.7$  Hz,  $^5J(\text{H,H}) = 0.4$  Hz, 1H, H-10), 8.02 (d,  $^4J(\text{H,H}) = 1.3$  Hz, 1H, H-13), 8.01 (dd,  $^4J(\text{H,H}) = 1.7$  Hz,  $^5J(\text{H,H}) = 0.5$  Hz, 1H, H-4), 7.93 (d,  $^4J(\text{H,H}) = 1.2$  Hz, 1H, H-16), 7.91 (m, 2H, H-1, H-3), 7.88 (d,  $^3J(\text{H,H}) = 8.6$  Hz, 2H, H-18), 7.85 (dd,  $^3J(\text{H,H}) = 8.3$

Hz,  $^4J(\text{H,H}) = 1.7$  Hz, 1H, H-15), 7.79 (dd,  $^3J(\text{H,H}) = 8.1$  Hz,  $^4J(\text{H,H}) = 1.7$  Hz, 1H, H-12), 7.73 (dd,  $^3J(\text{H,H}) = 8.1$  Hz,  $^4J(\text{H,H}) = 1.7$  Hz, 1H, H-9), 7.60 (dd,  $^3J(\text{H,H}) = 8.2$  Hz,  $^5J(\text{H,H}) = 0.5$  Hz, 1H, H-5), 7.51 (dd,  $^3J(\text{H,H}) = 7.7$  Hz,  $^4J(\text{H,H}) = 1.4$  Hz, 1H, H-6), 7.47 (dd,  $^3J(\text{H,H}) = 8.2$  Hz,  $^5J(\text{H,H}) = 0.5$  Hz, 1H, H-8), 7.44 (d,  $^3J(\text{H,H}) = 8.6$  Hz, 2H, H-17), 7.41 (d,  $^3J(\text{H,H}) = 8.1$  Hz, 1H, H-11), 7.34 (dd,  $^3J(\text{H,H}) = 8.1$  Hz,  $^5J(\text{H,H}) = 0.4$  Hz, 1H, H-14), 7.28 (t,  $^3J(\text{H,H}) = 7.8$  Hz, 1H, H-2), 4.35 (m, 10H, H-21), 4.29 (q,  $^3J(\text{H,H}) = 7.1$  Hz, 2H, H-19), 1.35 (m, 18H, H-20, H-22).

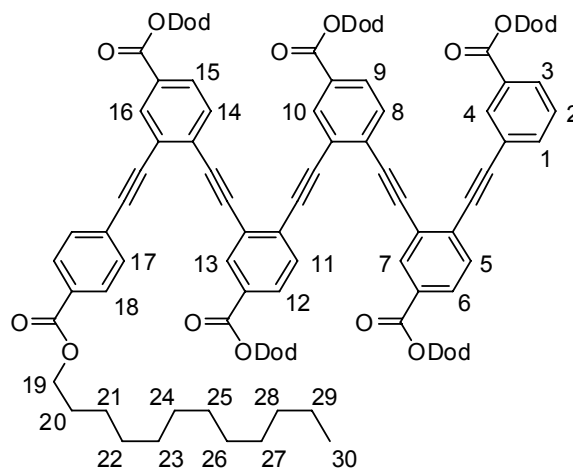
$^{13}\text{C}$ -NMR (126 MHz,  $\text{CDCl}_3$ ):  $\delta(\text{ppm}) = 165.52, 165.22, 164.83, 164.79, 164.70, 164.66, 135.31, 132.95, 132.80, 132.64, 132.39, 131.70, 131.62, 131.34, 131.14, 129.66, 129.65, 129.41, 129.23, 129.05, 128.97, 128.85, 128.80, 128.70, 128.65, 128.36, 127.90, 124.98, 122.60, 95.04, 93.92, 93.79, 93.11, 91.86, 91.77, 89.91, 88.14, 60.99, 60.92, 60.80, 60.68, 13.91, 13.85$ .

ESI-MS (pos.):  $m/z = 1033.3$  (calcd 1033.3 for  $\text{C}_{64}\text{H}_{50}\text{O}_{12}\text{Na}^+$ ).

HPLC (acetonitrile:water = 95:5), 220nm): 21.44 min, 88 %

### Hexadodecyl (*o*PE-hexamer) **24**

A flame-dried Schlenk-tube was loaded with hexaethyl *o*PE-hexamer **16** (0.025 g, 0.03 mmol),  $\text{K}_2\text{CO}_3$  (0.009 g, 0.06 mmol) and 0.67 mL dodecyl alcohol. 0.2 mL dry DMF were added and the stirred reaction mixture heated to 115 °C with an open inert gas connection. After 2 h, the pressure was slowly reduced down to 1 mbar within 3 h. The reaction mixture was cooled to 50 °C, and the vacuum



of an oil pump was applied overnight. The reaction mixture was cooled to room temperature, diluted with small amount of  $\text{CH}_2\text{Cl}_2$ , and precipitated in a 20-fold excess of cold methanol. The generated precipitate was isolated by centrifugation, washed with methanol, and two more times redissolved in  $\text{CH}_2\text{Cl}_2$  and precipitated in methanol. The obtained yellow solid was finally dried in vacuo (78 %).

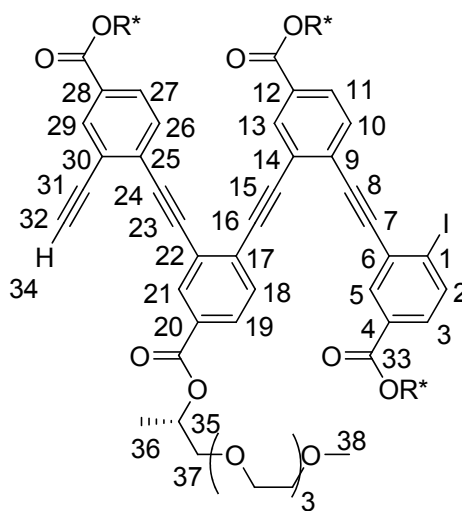
$^1\text{H}$ -NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta(\text{ppm}) = 8.18$  (d,  $^4J(\text{H,H}) = 1.5$  Hz, 1H, H-7), 8.05 (m, 3H, H-10, H-13, H-4), 7.97 (d,  $^4J(\text{H,H}) = 1.5$  Hz, 1H, H-16), 7.91 (m, 2H, H-1, H-3), 7.87 (d,  $^3J(\text{H,H}) = 8.5$  Hz, 2H, H-18), 7.85 (dd,  $^3J(\text{H,H}) = 8.2$  Hz,  $^4J(\text{H,H}) = 1.7$  Hz, 1H, H-15), 7.81 (dd,  $^3J(\text{H,H}) = 8.2$  Hz,  $^4J(\text{H,H}) = 1.7$  Hz, 1H, H-12), 7.74 (dd,  $^3J(\text{H,H}) = 8.2$  Hz,  $^4J(\text{H,H}) = 1.7$  Hz, 1H, H-9), 7.59 (d,  $^3J(\text{H,H}) = 8.1$  Hz, 1H, H-5), 7.52 (d,  $^3J(\text{H,H}) = 7.7$  Hz, 1H, H-6), 7.46

(d,  $^3J(\text{H,H}) = 7.9$  Hz, 1H, H-8), 7.45 (d,  $^3J(\text{H,H}) = 8.2$  Hz, 2H, H-17, H-14), 7.37 (d,  $^3J(\text{H,H}) = 8.1$  Hz, 1H, H-11), 7.28 (t,  $^3J(\text{H,H}) = 7.8$  Hz, 1H, H-2), 4.28 (m, 10H, H-19), 4.20 (t,  $^3J(\text{H,H}) = 6.8$  Hz, 2H, H-19), 1.73 (m, 12H, H-20), 1.24 (b, 108H, H-21 – H-29), 0.86 (m, 18H, H-30). MS (ESI):  $m/z = 1850$  (calcd 1851 for  $\text{C}_{124}\text{H}_{170}\text{O}_{12}^+$ ). GPC (40 °C, THF): 96 %.

*Soluble support approach.*

### Ethynyl-(*o*PE-tetramer)-iodide with chiral tetraethylene glycol side chain **25**

A flame-dried flask was loaded under argon with tetraethyl TMS-ethynyl-(*o*PE-tetramer)-iodide **14** (0.149 g, 0.17 mmol), chiral tetraglyme alcohol **97** (0.747 g, 3.36 mmol),  $\text{K}_2\text{CO}_3$  (0.046 g, 0.34 mmol), and dry DMF (1.2 mL). The reaction mixture was stirred overnight at 70 °C, then pressure was slowly reduced down to 1 mbar within 3 h while the temperature was increased to 110 °C. Finally the mixture was concentrated in vacuo and the obtained crude product purified by column chromatography



(silica gel,  $\text{CH}_2\text{Cl}_2:\text{MeOH} = 30:1$ ) yielding 0.18 g product as brown oil (70 %).

$^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta(\text{ppm}) = 8.28$  (d,  $^4J(\text{H,H}) = 1.5$  Hz, 1H, H-21), 8.25 (d,  $^4J(\text{H,H}) = 1.6$  Hz, 1H, H-13), 8.02 (d,  $^4J(\text{H,H}) = 1.7$  Hz, 2H, H-5, H-29), 8.01 (dd,  $^3J(\text{H,H}) = 7.9$  Hz,  $^4J(\text{H,H}) = 1.7$  Hz, 1H, H-27), 7.98 (dd,  $^3J(\text{H,H}) = 8.2$  Hz,  $^4J(\text{H,H}) = 1.7$  Hz, 1H, H-19), 7.83 (dd,  $^3J(\text{H,H}) = 8.2$  Hz,  $^4J(\text{H,H}) = 1.7$  Hz, 1H, H-11), 7.81 (d,  $^3J(\text{H,H}) = 8.2$  Hz, 1H, H-2), 7.71 (d,  $^3J(\text{H,H}) = 8.3$  Hz, 1H, H-10), 7.69 (d,  $^3J(\text{H,H}) = 8.3$  Hz, 1H, H-18), 7.55 (dd,  $^3J(\text{H,H}) = 8.3$  Hz,  $^4J(\text{H,H}) = 2.1$  Hz, 1H, H-3), 7.46 (d,  $^3J(\text{H,H}) = 8.1$  Hz, 1H, H-26), 5.29 (m, 4H, H-35), 3.70 - 3.4 (m, 52H,  $\text{CH}_2\text{O}$ , H-37), 3.34 (s, 3H, H-38), 3.33 (s, 3H, H-38), 3.32 (s, 3H, H-38), 3.31 (s, 12H, H-38), 3.28 (s, 1H, H-34), 3.25 (t,  $^3J(\text{H,H}) = 8.4$  Hz, 4H, H-37'), 1.35 (d,  $^3J(\text{H,H}) = 6.5$  Hz, 3H, H-36), 1.33 (d,  $^3J(\text{H,H}) = 6.5$  Hz, 6H, H-38), 1.28 (d,  $^3J(\text{H,H}) = 6.5$  Hz, H-38).

$^{13}\text{C-NMR}$  (100.6 MHz,  $\text{CDCl}_3$ ):  $\delta(\text{ppm}) = 164.4, 138.6, 133.3, 133.1, 132.2, 131.8, 130.2, 130.0, 129.7, 129.1, 128.9, 124.3, 106.3, 95.3, 93.5, 91.2, 82.2, 73.3, 73.2, 71.5, 70.5, 70.4, 70.3, 70.2, 70.1, 70.1, 65.9, 58.6, 18.0, 16.5, 16.4, 16.3$ .

ESI-MS (pos., MeOH):  $m/z = 1520$  (calcd 1520 for  $\text{C}_{76}\text{H}_{97}\text{IO}_{24}^+$ ).

GPC (30 °C, THF):  $M_n$  (PDI) = 2900 (1.03), 95 % purity.

**Polymerization of Ethynyl-(*o*PE-tetramer)-iodide with chiral tetraethylene glycol side chain **26****

A flame-dried flask was loaded with *o*PE-tetramer **26** (0.099 g, 0.07 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (0.011 g, 0.01 mmol), and CuI (0.002 g, 0.01 mmol). A solvent mixture of degassed Et<sub>3</sub>N (5.0 mL), and MeCN (5.0 mL) was added, the reaction mixture submitted to a freeze-pump-thaw cycle and stirred at rt for 5 h. The mixture was concentrated, redissolved in CH<sub>2</sub>Cl<sub>2</sub>, and filtrated. The oligomers were isolated by preparative TLC (acetone:CH<sub>2</sub>Cl<sub>2</sub> = 2:1), and the obtained fractions further purified by a second preparative TLC (acetone:CH<sub>2</sub>Cl<sub>2</sub> = 2:1 or CH<sub>2</sub>Cl<sub>2</sub>:MeOH = 15:1).

GPC (30 °C, THF): oligomeric mixture: Mn (PDI) = 7200 (1.24)

**26a** (octamer): Mn (PDI) = 6500 (1.05). Purity (UV230, UV280, RI): 68, 63, 85; content tetramer: 15, 20, 4; content dodecamer: 17, 17, 11.

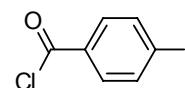
**26b** (dodecamer): Mn (PDI) = 7000 (1.05). Purity (UV230, UV280, RI): 70, 60, 65; content octamer: 19, 21, 19; content hexadecamer: 11, 19, 17.

**26c** (hexadecamer): Mn (PDI) = 9900 (1.17). Purity (UV230, UV280, RI): 84, 83, - ; content dodecamer: 8, 9, - ; content polymer: 8, 7, - .

*Soluble support approach.*

**4-iodobenzoic acid chloride **28****

4-Iodobenzoic acid **27** (3.720 g, 15.00 mmol) and oxalyl chloride (1.9 mL, 22.50 mmol) were dissolved in 18 mL CH<sub>2</sub>Cl<sub>2</sub>. After addition of three drops of DMF, the reaction solution is refluxed at 50 °C for 3 h. The orange solution is cooled down to rt, concentrated, and the obtained acid chloride in form of an orange solid dried in vacuo and used as it without further purification. Yield: 3.99 g (quantitative).



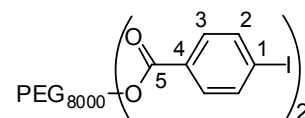
<sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): δ(ppm) = 7.88 (d, <sup>3</sup>J(H,H) = 8.8 Hz, 2H), 7.79 (d, <sup>3</sup>J(H,H) = 8.7 Hz, 2H).

<sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>): δ(ppm) = 168.0, 138.4, 132.7, 132.4, 104.3.

EI-MS (20 °C): *m/z* = 266 (calcd 266 for C<sub>7</sub>H<sub>4</sub>ClIO<sup>+</sup>).

**PEG<sub>8000</sub>-bis(4'-iodobenzoate) 29**

4-Iodobenzoic acid chloride **28** was added in small portions to a solution of PEG-8000 (24.000 g, 3.00 mmol), Et<sub>3</sub>N (4.2 mL, 30.00 mmol), and DMAP (0.090 g, 0.80 mmol) in 24 mL CH<sub>2</sub>Cl<sub>2</sub> cooled



to 0°C. After 1 h of stirring, the reaction suspension was warmed to rt and stirred for 2 d. The reaction mixture was diluted with CH<sub>2</sub>Cl<sub>2</sub>, the precipitate filtered off, and the volume concentrated to ~40 mL. The solution was poured into 400 mL Et<sub>2</sub>O, and the generated precipitate collected, dried, and subsequently dissolved in CH<sub>2</sub>Cl<sub>2</sub> and reprecipitated in ethanol and Et<sub>2</sub>O, respectively. Drying in vacuo yielded yellow solid powder (25.80 g, quantitative).

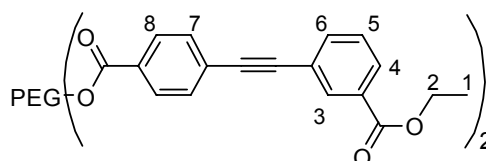
<sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>): δ(ppm) = 7.59 (d, <sup>3</sup>J(H,H) = 8.5 Hz, 4H, H-2), 7.55 (d, <sup>3</sup>J(H,H) = 8.7 Hz, 4H, H-3), 4.24 (t, <sup>3</sup>J(H,H) = 4.7 Hz, 4H, Ar-COOCH<sub>2</sub>-), 3.43 (b, PEG).

<sup>13</sup>C-NMR (126 MHz, CDCl<sub>3</sub>): δ(ppm) = 165.9 (C-5), 137.6 (C-2), 131.0 (C-3), 129.6 (C-4), 100.5 (C-1), 70.5 (PEG), 69.0 (Ar-COOCH<sub>2</sub>-CH<sub>2</sub>-), 64.2 (Ar-COOCH<sub>2</sub>-).

GPC (THF, 40 °C, RI): M<sub>n</sub> = 10200 (PDI = 1.10).

**PEG<sub>8000</sub>-bis(4-((ethyl-3'-benzoyl)ethynyl)benzoate) 30**

A flame-dried 2-neck-flask w/ gas inlet and septum was loaded with PEG-bis(4'-iodobenzoate) **29** (5.00 g, 0.625 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (0.029 g, 0.025 mmol), CuI (0.005 g, 0.025 mmol), ethyl 3-ethynylbenzoate

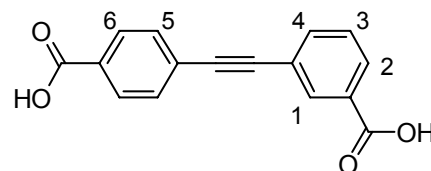


**13** (0.218 g, 1.25 mmol), and 8 mL dry and degassed Et<sub>3</sub>N. The beige suspension was stirred for 24 h at rt, and then heated to 70°C for 2 h during which the suspension turned black. The suspension was filtered to remove gray solid, then concentrated, the product extracted three times with toluene. The organic phases were combined, concentrated, and subsequently recrystallized from diethyl ether, cold ethanol, and again diethyl ether (4.94 g, 99%).

<sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>): δ(ppm) = 8.00 (s, 2H, H-3), 7.85 (d, <sup>3</sup>J(H, H) = 7.7 Hz, 4H, H-8), 7.53 (d, <sup>3</sup>J(H, H) = 7.6 Hz, 2H, H-6), 7.41 (d, <sup>3</sup>J(H, H) = 8.0 Hz, 4H, H-7), 7.37 (d, <sup>3</sup>J(H, H) = 6.7 Hz, 2H, H-4), 7.27 (t, <sup>3</sup>J(H, H) = 8.1 Hz, 2H, H-5), 4.28 (b, 4H, Ar-COO-CH<sub>2</sub>-PEG), 4.20 (q, <sup>3</sup>J(H, H) = 6.7 Hz, 4H, H-2), 3.44 (b, PEG), 1.22 (t, <sup>3</sup>J(H, H) = 7.1 Hz, 6H, H-1).

**1,2-diphenylacetylene-3,4'-dicarboxylic acid 31**

PEG-bis(4-((ethyl-3'-benzoyl)ethynyl)benzoate) **30** (0.496 g, 0.062 mmol) was dissolved in a mixture of 15 mL 1M aq. NaOH and 25 mL distilled water. The reaction



solution was refluxed overnight, cooled to rt, and acidified with aq. 1M HCl until pH<7 (~15 mL) leading to a turbation of the aqueous solution. The desired product is extracted several times with diethyl ether, the organic phases were dried over MgSO<sub>4</sub>, filtered and concentrated, and the obtained white powder finally dried in vacuo (0.015 g, 45 %).

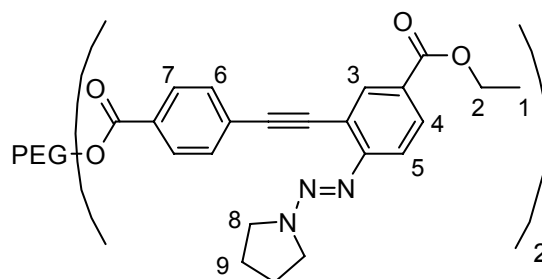
<sup>1</sup>H-NMR (250 MHz, d<sup>6</sup>-DMSO): δ(ppm) = 8.07 (s, 1H, H-1), 7.95 (d, <sup>3</sup>J(H, H) = 8.2 Hz, 2H, H-6), 7.75 (d, <sup>3</sup>J(H, H) = 7.3 Hz, 1H, H-2), 7.63 (d, <sup>3</sup>J(H, H) = 8.2 Hz, 2H, H-5), 7.54 (d, <sup>3</sup>J(H, H) = 8.2 Hz, 1H, H-4), 7.44 (t, <sup>3</sup>J(H, H) = 7.3 Hz, 1H, H-3).

EI-MS (60 °C): *m/z* = 266 (266 calcd for C<sub>16</sub>H<sub>10</sub>O<sub>4</sub><sup>+</sup>).

HPLC (MeOH:H<sub>2</sub>O=70:30 + 0.1% TFA, 254 nm): 6.14 min (82 %).

### PEG<sub>8000</sub>-bis(4-((ethyl 5'-pyrrolidyltriazenyl-3'-benzoyl)ethynyl)benzoate) **32**

A flame-dried flask was loaded with PEG-bis(4'-iodobenzoate) **29** (8.00 g, 1.00 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (0.046 g, 0.04 mmol), CuI (0.008 g, 0.04 mmol), ethyl 4-pyrrolidyltriazenyl-3-ethynylbenzoate **6b** (0.597 g, 2.2 mmol). Dry and degassed 16 mL Et<sub>3</sub>N and 3 mL THF were added and the reaction

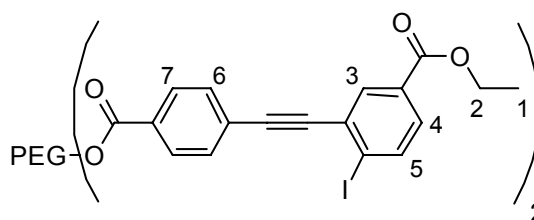


mixture was heated to 70°C for 30h. The brown mixture was concentrated, redissolved in 40 mL CH<sub>2</sub>Cl<sub>2</sub>, and poured into 600 mL diethyl ether. The solid was isolated by filtration, washed subsequently with Et<sub>2</sub>O, ice-cold ethanol, and again diethyl ether until corresponding filtrates stayed colorless, and finally dried in vacuo (8.00 g, quantitative).

<sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>): δ(ppm) = 8.08 (s, 2H, H-3), 7.89 (d, <sup>3</sup>J(H, H) = 8.1 Hz, 4H, H-7), 7.81 (d, <sup>3</sup>J(H, H) = 8.6 Hz, 2H, H-4), 7.45 (d, <sup>3</sup>J(H, H) = 8.1 Hz, 4H, H-6), 7.38 (d, <sup>3</sup>J(H, H) = 8.6 Hz, 2H, H-5), 4.34 (b, 4H, Ar-COO-CH<sub>2</sub>-PEG), 4.24 (q, <sup>3</sup>J(H, H) = 7.2 Hz, 4H, H-2), 3.87 (b, 4H, H-8), 3.70 (b, 4H, H-8'), 3.51 (b, PEG), 1.96 (m, 8H, H-9), 1.33 (t, <sup>3</sup>J(H, H) = 7.6 Hz, 6H, H-1).

### PEG<sub>8000</sub>-bis(4-((ethyl 5'-iodo-3'-benzoyl)ethynyl)benzoate) **33**

The PEG-bound and triazene-terminated phenylene ethynylene dimer **32** (0.500 g, 0.063 mmol) was dissolved in 8 mL MeI in a presurable test tube with stirring bar. The reaction apparatus was sealed and the dark-red solution degassed by



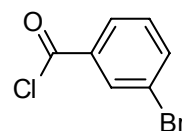
a freeze-pump-thaw cycle and finally heated to 120 °C for two days. The mixture was cooled down, concentrated, and the obtained dark-red solid redissolved in 5 mL DCM, precipitated in

50 mL diethyl ether. The generated solid was isolated, thoroughly washed with ice-cold ethanol and diethyl ether, and dried in vacuo (0.50 g, quantitative).

$^1\text{H-NMR}$  (500 MHz,  $\text{CDCl}_3$ ):  $\delta(\text{ppm}) = 8.08$  (d,  $^4\text{J}(\text{H}, \text{H}) = 1.9$  Hz, 2H, H-3), 7.98 (d,  $^3\text{J}(\text{H}, \text{H}) = 8.4$  Hz, 4H, H-7), 7.90 (d,  $^3\text{J}(\text{H}, \text{H}) = 8.3$  Hz, 2H, H-5), 7.58 (d, 8.3 Hz, 6H, H-6, H-4), 4.40 (b, 4H, Ar-COO- $\text{CH}_2$ -PEG), 4.30 (q,  $^3\text{J}(\text{H}, \text{H}) = 7.2$  Hz, 4H, H-2), 3.55 (b, PEG), 1.32 (t,  $^3\text{J}(\text{H}, \text{H}) = 7.2$  Hz, 6H, H-1).

### 3-Bromobenzoic acid chloride

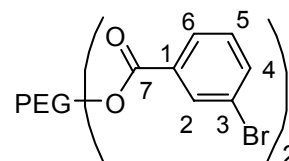
3-Bromobenzoic acid **ME06** (4.020 g, 20.00 mmol) was suspended in 25 mL  $\text{CH}_2\text{Cl}_2$  under a nitrogen atmosphere. Oxalyl chloride (2.6 ml, 30.00 mmol) was added. The addition of 3 drops of DMF led to the generation of gas.



The reaction mixture was refluxed for 3 h refluxing at 50-55 °C, upon which it became a yellow solution. The solution was concentrated and the orange oil dried in vacuo (quantitative). The acid chloride was immediately used as obtained.

### PEG-bis(3'-bromobenzoate) **36**

A flame-dried reaction flask was loaded with bishydroxy-terminated PEG (32.00 g, 4.00 mmol) a solvent mixture of dried  $\text{Et}_3\text{N}$  (6 mL) and  $\text{CH}_2\text{Cl}_2$  (55.0 mL). The solution was cooled to 0°C and a solution of 3-bromobenzoic acid chloride (4.389 g, 20.00 mmol) in 5 mL dry



$\text{CH}_2\text{Cl}_2$  was slowly added via syringe. Finally, DMAP (0.122 g, 1.00 mmol) was added, and the viscous colorless solution turned into a yellow milky suspension. After 1 h, the suspension was warmed to rt and stirred overnight. The reaction mixture was diluted with  $\text{CH}_2\text{Cl}_2$ , filtrated, the volume was reduced to 150 mL, and poured into 1000 mL of stirring  $\text{Et}_2\text{O}$ . The generated white dense precipitate was isolated by filtration, and subsequently washed with ice-cold ethanol and diethyl ether, and dried in vacuo (34.40 g, quantitative).

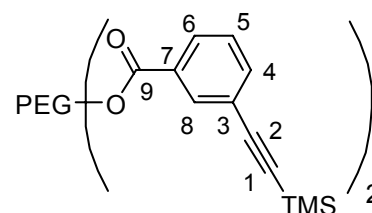
$^1\text{H-NMR}$  (500 MHz,  $\text{CDCl}_3$ ):  $\delta(\text{ppm}) = 8.07$  (t,  $^4\text{J}(\text{H}, \text{H}) = 1.8$  Hz, 2H, H-2), 7.87 (dt,  $^3\text{J}(\text{H}, \text{H}) = 7.8$  Hz,  $^4\text{J}(\text{H}, \text{H}) = 1.3$  Hz, 2H, H-6), 7.58 (dq,  $^3\text{J}(\text{H}, \text{H}) = 8.0$  Hz,  $^4\text{J}(\text{H}, \text{H}) = 1.1$  Hz, 2H, H-4), 7.22 (t,  $^3\text{J}(\text{H}, \text{H}) = 7.8$  Hz, 2H, H-5), 4.36 (t,  $^3\text{J}(\text{H}, \text{H}) = 4.8$  Hz, 4H, Ar-COO- $\text{CH}_2$ -PEG), 3.53 (b, PEG).

$^{13}\text{C-NMR}$  (126 MHz,  $\text{CDCl}_3$ ):  $\delta(\text{ppm}) = 165.1$  (C-7), 135.9 (C-4), 132.6 (C-2), 132.1 (C-1), 130.0 (C-5), 128.3 (C-6), 122.4 (C-3), 70.7 – 70.5 (PEG), 69.1 (Ar-COO- $\text{CH}_2$ - $\text{CH}_2$ -PEG), 64.5 (Ar-COO- $\text{CH}_2$ -PEG).



**PEG-bis(3'-TMS-ethynylbenzoate) 37**

A flame-dried flask was loaded with PEG-bis(3'-bromobenzoate) **36** (33.456 g, 4.00 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (0.139 g, 0.12 mmol), CuI (0.023 g, 0.12 mmol). A solvent mixture of dry and degassed CH<sub>2</sub>Cl<sub>2</sub> (50 mL) and 20 mL Et<sub>3</sub>N was added,



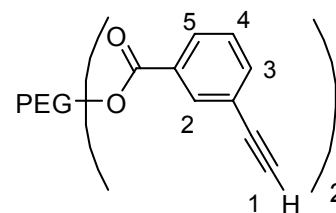
the the solution submitted to a freeze-pump-thaw cycle. Finally, TMS-acetylene (3.0 mL, 21.00 mmol) were injected. The reaction mixture was stirred at 75 °C for 24 h, and the yellow suspension diluted with CH<sub>2</sub>Cl<sub>2</sub>. A gray solid was removed by filtration and the filtrate concentrated, redissolved in 200 mL CH<sub>2</sub>Cl<sub>2</sub>, poured into 1100 mL Et<sub>2</sub>O, and the generated solid subsequently washed with diethyl ether and ice-cold ethanol. Again, the solid was dissolved in CH<sub>2</sub>Cl<sub>2</sub> and precipitated in diethyl ether, isolated, and the obtained beige solid dried in vacuo (30.70 g, 91 %).

<sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>): δ(ppm) = 8.07 (t, <sup>4</sup>J(H, H) = 1.2 Hz, 2H, H-8), 7.93 (dt, <sup>3</sup>J(H, H) = 8.0 Hz, <sup>4</sup>J(H, H) = 1.4 Hz, 2H, H-6), 7.57 (dt, <sup>3</sup>J(H, H) = 7.7 Hz, <sup>4</sup>J(H, H) = 1.4 Hz, 2H, H-4), 7.32 (t, <sup>3</sup>J(H, H) = 7.8 Hz, 2H, H-5), 4.41 (t, <sup>3</sup>J(H, H) = 4.9 Hz, 4H, Ar-COO-CH<sub>2</sub>-), 3.57 (b, PEG), 0.19 (s, 9H, TMS).

<sup>13</sup>C-NMR (126 MHz, CDCl<sub>3</sub>): δ(ppm) = 165.6 (C-9), 136.0 (C-4), 133.0 (C-8), 130.2 (C-7), 129.4 (C-6), 128.2 (C-5), 123.4 (C-3), 103.7 (C-2), 95.3 (C-1), 70.5 – 70.4 (PEG), 69.0 (Ar-COO-CH<sub>2</sub>-CH<sub>2</sub>-PEG), 64.2 (Ar-COO-CH<sub>2</sub>-PEG), -0.2 (TMS).

**PEG-bis(3'- ethynylbenzoate) 37a**

PEG-bis(3'-TMS-ethynylbenzoate) **37** (1.680 g, 0.20 mmol) was dissolved in dry THF (8 mL) and CH<sub>2</sub>Cl<sub>2</sub> (2 mL). A solution of 1M TBAF in THF (1.6 mL) was added, and the reaction solution was stirred at 50-60 °C for 3 h, concentrated, redissolved in

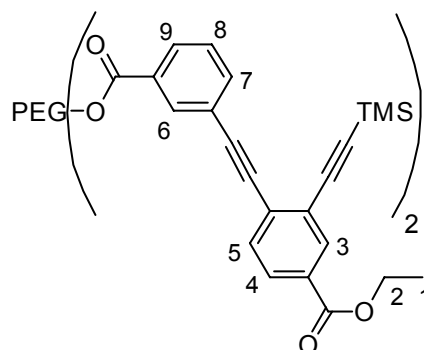


CH<sub>2</sub>Cl<sub>2</sub>, filtered, and precipitated in diethyl ether. The generated solid was thoroughly washed with ice-cold ethanol, redissolved in CH<sub>2</sub>Cl<sub>2</sub>, precipitated again in Et<sub>2</sub>O, isolated, and the obtained beige solid dried in vacuo (1.67 g, quantitative).

<sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>): δ(ppm) = 8.11 (t, <sup>4</sup>J(H, H) = 1.7 Hz, 2H, H-2), 7.97 (dt, <sup>3</sup>J(H, H) = 8.0 Hz, <sup>4</sup>J(H, H) = 1.4 Hz, 2H, H-5), 7.61 (dt, <sup>3</sup>J(H, H) = 7.7 Hz, <sup>4</sup>J(H, H) = 1.4 Hz, 2H, H-3), 7.36 (t, <sup>3</sup>J(H, H) = 7.8 Hz, 2H, H-4), 4.42 (t, <sup>3</sup>J(H, H) = 4.9 Hz, 4H, Ar-COO-CH<sub>2</sub>-PEG), 3.59 (b, PEG), 3.11 (2H, H-1).

**PEG-bis(3-((ethyl 2'-(TMS-ethynyl)-4'-benzoyl)ethynyl)benzoate) 38**

A flame-dried flask was loaded with PEG-bis(3'-ethynylbenzoate) **37a** (1.670 g, 0.20 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (0.007 g, 0.006 mmol), CuI (0.001 g, 0.006 mmol), and *ortho*-Monomer ethyl 3-(TMS-ethynyl)-4-iodobenzoate **5** (0.223 g, 0.60 mmol). Dry degassed Et<sub>3</sub>N (1 mL) and CH<sub>2</sub>Cl<sub>2</sub> (2.5 mL) was added, the red solution submitted to a freeze-pump-thaw cycle, warmed up to rt, and stirred at

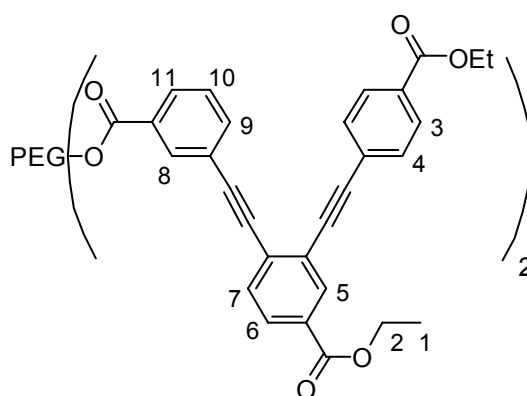


rt overnight. The red-brown suspension was diluted with CH<sub>2</sub>Cl<sub>2</sub>, a gray solid was filtered off, and the red filtrate concentrated. The brown solid was dissolved in CH<sub>2</sub>Cl<sub>2</sub>, precipitated in 10-fold excess diethyl ether, the generated solid isolated, subsequently washed with Et<sub>2</sub>O, ice-cold ethanol, redissolved in CH<sub>2</sub>Cl<sub>2</sub>, and again precipitated in Et<sub>2</sub>O, the beige solid isolated, and dried in vacuo (1.056 g, 60 %).

<sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>): δ(ppm) = 8.18 (s, 2H, H-6), 8.10 (s, 2H, H-3), 7.99 (d, <sup>3</sup>J(H, H) = 7.8 Hz, 2H, H-4), 7.89 (d, <sup>3</sup>J(H, H) = 8.2 Hz, 2H, H-9), 7.68 (d, <sup>3</sup>J(H, H) = 7.7 Hz, 2H, H-7), 7.53 (d, <sup>3</sup>J(H, H) = 7.7 Hz, 2H, H-5), 7.40 (t, <sup>3</sup>J(H, H) = 7.7 Hz, 2H, H-8), 4.43 (t, <sup>3</sup>J(H, H) = 4.7 Hz, 4H, Ar-COO-CH<sub>2</sub>-PEG), 4.32 (q, <sup>3</sup>J(H, H) = 7.3 Hz, 4H, H-2), 3.57 (b, PEG), 1.35 (t, <sup>3</sup>J(H, H) = 7.1 Hz, 6H, H-1), 0.22 (s, 9H, TMS).

**PEG-bis(diethyl *ortho*-phenylene ethynylene trimer) 39**

PEG-derivate **38** (1.056 g, 0.121 mmol) was dissolved in dry THF (5 mL) and dry CH<sub>2</sub>Cl<sub>2</sub> (2 mL). A solution of 1M TBAF in THF (1.2 mL) was added, and the reaction solution stirred at 50-60 °C for 3 h. The solution was concentrated, the obtained solid redissolved in CH<sub>2</sub>Cl<sub>2</sub>, filtered, and the filtrate precipitated in excess Et<sub>2</sub>O. The generated solid was thoroughly washed with ice-



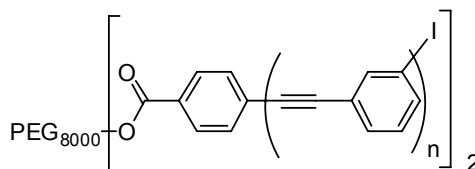
cold ethanol, redissolved in CH<sub>2</sub>Cl<sub>2</sub>, and precipitated in Et<sub>2</sub>O. The beige solid was isolated, dried in vacuo and used as obtained. The deprotected starting material was added to a flame-dried flask together with Pd(PPh<sub>3</sub>)<sub>4</sub> (0.004 g, 0.004 mmol), CuI (0.001 g, 0.004 mmol), and ethyl 4-bromobenzoate (0.12 mL, 0.73 mmol). A solvent mixture of dry and degassed Et<sub>3</sub>N (1.7 mL) and CH<sub>2</sub>Cl<sub>2</sub> (2.5 mL) was added and the reaction mixture submitted to a freeze-pump-thaw cycle and subsequently stirred at rt overnight. The brown suspension was diluted with CH<sub>2</sub>Cl<sub>2</sub>, a gray solid filtered off, and the filtrate concentrated. The brown solid was

dissolved in  $\text{CH}_2\text{Cl}_2$ , precipitated in a 10-fold excess diethyl ether, and the generated solid isolated, washed with ice-cold ethanol, redissolved in  $\text{CH}_2\text{Cl}_2$  and precipitated in  $\text{Et}_2\text{O}$ . The generated solvent was isolated and dried in vacuo (1.021 g, 95 %).

$^1\text{H-NMR}$  (500 MHz,  $\text{CDCl}_3$ ):  $\delta(\text{ppm}) = 8.22$  (s, 2H, H-8), 8.19 (s, 2H, H-5), 8.00 (d,  $^3\text{J}(\text{H}, \text{H}) = 7.6$  Hz, 2H, H-11), 7.97 (d,  $^3\text{J}(\text{H}, \text{H}) = 8.1$  Hz, 4H, H-3), 7.89 (d, 7.4 Hz, 2H, H-6), 7.67 (d,  $^3\text{J}(\text{H}, \text{H}) = 7.6$  Hz, 2H, H-9), 7.59 (d,  $^3\text{J}(\text{H}, \text{H}) = 6.8$  Hz, 2H, H-7), 7.58 (d,  $^3\text{J}(\text{H}, \text{H}) = 7.6$  Hz, 4H, H-4), 7.41 (t,  $^3\text{J}(\text{H}, \text{H}) = 7.0$  Hz, 2H, H-10), 4.43 (b, Ar-COO- $\text{CH}_2$ -PEG), 4.33 (m, 8H, H-2), 3.58 (b, PEG), 1.34 (m, 12H, H-1).

### **Poly(*meta*-phenylene-ethynylene)-*block*-poly(ethylene glycol)-*block*-poly(*meta*-phenylene ethynylene) 79**

a) PEG<sub>8000</sub>-bis(4'-iodobenzoate) **29** (76 mg, 9  $\mu\text{mol}$ ), 3-(2-trimethylsilylethynyl)-iodobenzene **77** (0.27 g, 0.9 mmol),  $\text{Pd}(\text{PPh}_3)_4$  (62 mg, 54  $\mu\text{mol}$ ),  $\text{CuI}$  (17 mg, 90  $\mu\text{mol}$ ), DBU (0.8 mL, 5.4 mmol), and water (0.2



mL, 9.0 mmol) were dissolved in a solvent mixture of 3 mL toluene and 0.5 mL  $\text{CH}_2\text{Cl}_2$ . The rc mixture was subjected to two Freeze-Pump-Thaw cycles, and finally left stirring at rt under argon for 3 d. The rc-mixture was filtered, and solids washed with hot toluene. The combined filtrates were concentrated to ~20ml volume, and poured into ice-cold 250 mL diethyl ether. The generated precipitate was filtered off, washed with ether, and dried in vacuo (84 %).

GPC (THF, 40 °C):  $M_n$  (PDI) = 14200 (1.03).

b) The procedure was analogous to the above synthesis using acetonitrile as solvent (81 %).

GPC (THF, 40 °C):  $M_n$  (PDI) = 12200 (1.06).

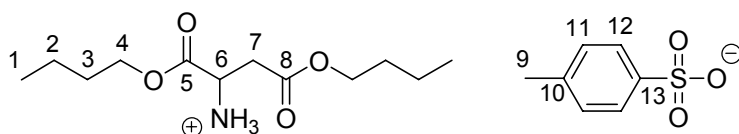
c) PEG<sub>8000</sub>-bis(4'-iodobenzoate) **29** (76 mg, 9  $\mu\text{mol}$ ), 3-ethynyl-iodobenzene **78** (0.21 g, 0.9 mmol),  $\text{Pd}(\text{PPh}_3)_4$  (62 mg, 54  $\mu\text{mol}$ ), and  $\text{CuI}$  (17 mg, 90  $\mu\text{mol}$ ) were dissolved in a solvent mixture of 3 mL dry  $\text{Et}_3\text{N}$  and 1 mL dry  $\text{CH}_2\text{Cl}_2$ . The rc mixture was subjected to two Freeze-Pump-Thaw cycles and allowed to stir at rt for 3 d under argon atmosphere. The rc-mixture was filtered, the solids washed with  $\text{CH}_2\text{Cl}_2$ , the combined filtrates concentrated to ~20ml volume, and poured into 250 mL ice-cold diethyl ether. The generated precipitate was filtered off, washed with ether, and dried in vacuo (86 %).

GPC (THF, 40 °C):  $M_n$  (PDI) = 9800 (1.32).

*Chiral branched polar side chain.*

### Dibutyl-2-amoniumsuccinate tosylate **56**

Aspartic acid **55** (4.53 g, 34.0 mmol) and *p*-toluolsulfonic acid monohydrate (7.76 g, 40.8 mmol) were dissolved in a



solvent mixture of 145 mL toluene and 85 mL *n*-butanol. The rc mixture was heated to 130 °C over night and generated water continuously removed with a Dean-Stark-apparatus. After cooling down to rt, solvent was removed, and the obtained solid grained and dispersed in ice-cold diethyl ether. Filtration and drying in vacuo yielded desired tosyl salt as white solid (quantitative).

$^1\text{H-NMR}$  (250 MHz,  $\text{CDCl}_3$ ):  $\delta(\text{ppm}) = 8.30$  (s, 1H,  $\text{NH}_3$ ), 7.73 (d,  $^3\text{J}(\text{H,H}) = 8.2$  Hz, 2H, H-12), 7.10 (d,  $^3\text{J}(\text{H,H}) = 7.3$ , 2H, H-11), 4.40 (b, 1H, H-6), 4.01 (m, 4H, H-4), 3.07 (dq,  $^2\text{J}(\text{H,H}) = 16.4$ ,  $^3\text{J}(\text{H,H}) = 5.5$ , 2H, H-7), 2.32 (s, 3H, H-9), 1.49 (m, 4H, H-3), 1.25 (m, 4H, H-2), 0.84 (m, 6H, H-1).

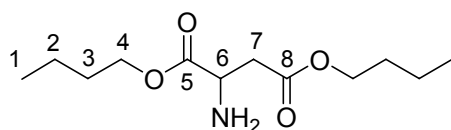
$^{13}\text{C-NMR}$  (62.9 MHz,  $\text{CDCl}_3$ ):  $\delta(\text{ppm}) = 170.2$ , 168.0, 141.7, 140.1, 128.7, 126.1, 66.6, 65.4, 49.6, 33.8, 30.4, 30.2, 21.2, 18.9, 18.8, 13.6, 13.5.

ESI-MS (pos.,  $\text{CH}_2\text{Cl}_2$ ):  $m/z = 246$  (calcd 246 for  $\text{C}_{12}\text{H}_{24}\text{NO}_4^+$ ), 491 ( $\text{M}_2\text{H}^+$ ).

ESI-MS (neg.,  $\text{CH}_2\text{Cl}_2$ ):  $m/z = 171$  (calcd 171 for  $\text{C}_7\text{H}_7\text{O}_3\text{S}^-$ ).

### Dibutyl-2-aminosuccinate **56a**

Dibutyl-2-amoniumsuccinate tosylate **56** was dissolved in 100  $\text{CH}_2\text{Cl}_2$  and the solution washed with 50 mL aq. 5%  $\text{K}_2\text{CO}_3$ , dried over  $\text{MgSO}_4$ , concentrated, and dried in vacuo yielding desired product as colorless oil (88 %).

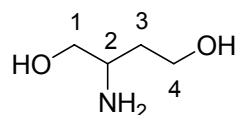


$^1\text{H-NMR}$  (500 MHz,  $\text{CDCl}_3$ ):  $\delta(\text{ppm}) = 4.06$  (m, 4H, H-4), 3.74 (dd,  $^3\text{J}(\text{H,H}) = 7.3$  Hz,  $^3\text{J}(\text{H,H}) = 4.7$ , 1H, H-6), 2.73 (dd,  $^2\text{J}(\text{H,H}) = 16.5$  Hz,  $^3\text{J}(\text{H,H}) = 4.8$  Hz, 1H, H-7), 2.64 (dd,  $^2\text{J}(\text{H,H}) = 16.4$  Hz,  $^3\text{J}(\text{H,H}) = 7.2$  Hz, 1H, H-7), 1.56 (m, 4H, H-3), 1.32 (m, 4H, H-2), 0.87 (t,  $^3\text{J}(\text{H,H}) = 7.4$  Hz, 6H, H-1).

FAB-MS (pos.,  $\text{CH}_2\text{Cl}_2$ ):  $m/z = 246$  (calcd 246 for  $\text{C}_{12}\text{H}_{24}\text{NO}_4^+$ ).

### 2-Aminobutane-1,4-diol **57**

$\text{LiAlH}_4$  powder (9.25 g, 243.7 mmol) was suspended in ice-cold 200 mL dry THF under  $\text{N}_2$  atmosphere. Dibutyl-2-aminosuccinate **56** (17.81 g,



72.6 mmol) was dissolved in small amounts of dry THF and added dropwise to the suspension. The mixture was refluxed at 80 °C over night, cooled down to 0 °C, diluted with THF, and quenched with excess of Bäckstrom reagent. The suspension was filtrated, the solid suspended in *i*PrOH, and the crude product obtained via Soxhlet extraction over night. Removal of solvent gave a yellow oil. Purification by Kugelrohr distillation (~180 °C, in vacuo) gave pure product as light yellow oil (76 %).

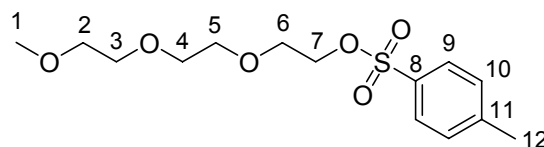
<sup>1</sup>H-NMR (d<sup>6</sup>-DMSO): δ(ppm) = 3.48 (t, <sup>3</sup>J(H,H) = 6.4 Hz, 2H, H-4), 3.24 (dd, <sup>2</sup>J(H,H) = 10.9 Hz, <sup>3</sup>J(H,H) = 4.6 Hz, 1H, H-1), 3.11 (dd, <sup>2</sup>J(H,H) = 10.0 Hz, <sup>3</sup>J(H,H) = 6.4 Hz, 1H, H-1'), 2.69 (m, 1H, H-2), 1.47 (m, 1H, H-3), 1.25 (m, 1H, H-3').

<sup>13</sup>C-NMR (d<sup>6</sup>-DMSO): δ(ppm) = 67.2, 59.2, 51.2, 36.7.

FAB-MS (pos., glycerol): *m/z* = 106 (calcd 106 for C<sub>4</sub>H<sub>12</sub>NO<sub>2</sub><sup>+</sup>).

### Triethylene glycol monomethyl tosylate **63**

Triglyme glycol monomethyl ether **61** (15.7 mL, 100.0 mmol) was dissolved in 200ml THF and a solution of NaOH (6.4 g, 160.0 mmol) in 50 mL



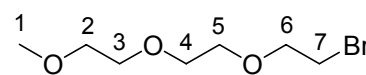
water was added. After cooling to 0 °C, a solution of *p*-toluolsulfonyl chloride (24.8 g, 130.0 mmol) in 50 mL THF was added dropwise during 1 h. The mixture was allowed to stir over night at 0 °C and quenched with an ice-cold solution of 10 g NaCl in 500 mL water. The product was extracted 4x with ethyl acetate, the combined organic phases washed subsequently with sat. aq. NH<sub>4</sub>Cl and brine, dried over MgSO<sub>4</sub>, and concentrated. Purification by a short column chromatography (silica gel, gradient hexane:ethyl acetate = 10:1 – 1:10) gave product as a light yellow oil (93 %).

<sup>1</sup>H-NMR (250 MHz, CDCl<sub>3</sub>): δ(ppm) = 7.77 (d, <sup>3</sup>J(H,H) = 8.2 Hz, 2H, H-9), 7.31 (d, <sup>3</sup>J(H,H) = 8.2 Hz, 2H, H-10), 4.15 (t, <sup>3</sup>J(H,H) = 5.0 Hz, 2H, H-7), 3.66 (t, <sup>3</sup>J(H,H) = 5.0 Hz, 2H, H-6), 3.56 (m, 6H, H-3 – H-5), 3.49 (m, 2H, H-2), 3.34 (s, 3H, H-1), 2.42 (s, 3H, H-12).

HPLC (MeOH:H<sub>2</sub>O = 50:50): 6.51 min (93 %).

### Triethylene glycol monomethyl bromide **62**

Triethylene glycol monomethyl ether **61** (70.0 mL, 446.8 mmol ) was dissolved in 1L of dry diethyl ether under N<sub>2</sub>



atmosphere. The stirring mixture was cooled to 0 °C, PBr<sub>3</sub> (23.5 mL, 250.5 mmol) was added slowly, and stirring was continued for 2h. Methanol (64 mL) was added and the mixture was warmed up to rt and stirred for another 30 min. Rc was cooled down to 0 °C, brine (100 mL) was added. The product was extracted 3x with ethyl acetate, the org. phases

were combined and washed with sat. aq.  $\text{NaHCO}_3$ , dried over  $\text{MgSO}_4$ , and concentrated. Product was obtained as light brown oil after drying in vacuo (36 %).

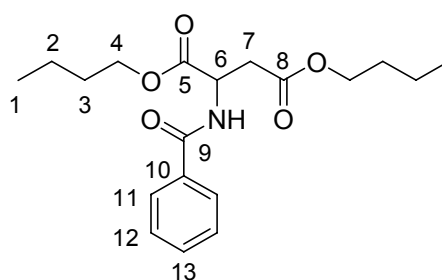
$^1\text{H-NMR}$  (250 MHz,  $\text{CDCl}_3$ ):  $\delta(\text{ppm}) = 3.78$  (t,  $^3\text{J}(\text{H,H}) = 5.9$  Hz, 2H, H-6), 3.65 (m, 6H, H-3 – H-5), 3.53 (m, 2H, H-2), 3.45 (t,  $^3\text{J}(\text{H,H}) = 6.4$  Hz, 2H, H-7), 3.36 (s, 3H, H-1).

$^{13}\text{C-NMR}$  (62.9 MHz,  $\text{CDCl}_3$ ):  $\delta(\text{ppm}) = 71.83, 71.10, 70.51, 70.49, 70.43, 58.93, 30.19$ .

EI-MS ( $-1$  °C):  $m/z = 226$  (calcd 226 for  $\text{C}_7\text{H}_{15}\text{BrO}_3^+$ ).

#### Dibutyl N-(benzoyl)aspartate 64

In an Argon atmosphere, the tosyl salt of dibutyl aspartate **56** (1.27 g, 3.04 mmol) was dissolved in 2.6 mL freshly distilled  $\text{CHCl}_3$  and cooled down to 0 to  $-5$  °C. Dry  $\text{Et}_3\text{N}$  (0.90 mL, 6.38 mmol) was added, followed by dropwise addition of a solution of benzoyl chloride (0.37 mL, 3.19 mmol) in 0.5 mL  $\text{CHCl}_3$ . The



mixture was stirred over night while allowed to slowly warm up to rt. The reaction mixture was diluted with  $\text{CHCl}_3$ , subsequently washed with sat. aq.  $\text{NH}_4\text{Cl}$ , sat. aq.  $\text{NaHCO}_3$ , and sat. aq.  $\text{NaCl}$ . The organic phase was dried over  $\text{MgSO}_4$ , concentrated, and dried in vacuo yielding a colorless oil, that crystallized with time to a white solid (100%).

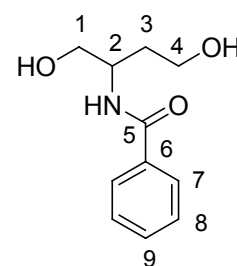
$^1\text{H-NMR}$  (300 MHz,  $\text{CDCl}_3$ ):  $\delta(\text{ppm}) = 7.78$  (dd,  $^3\text{J}(\text{H,H}) = 6.9$  Hz,  $^4\text{J}(\text{H,H}) = 1.7$  Hz, 2H, H-13), 7.44 (m, 3H, H-12, H-13), 7.22 (s, NH), 5.01 (q,  $^3\text{J}(\text{H,H}) = 4.3$  Hz, H-6), 4.16 (dt,  $^3\text{J}(\text{H,H}) = 6.9$  Hz,  $^4\text{J}(\text{H,H}) = 2.6$  Hz, 2H, H-4), 4.06 (dt,  $^3\text{J}(\text{H,H}) = 6.5$  Hz,  $^4\text{J}(\text{H,H}) = 1.7$  Hz, 2H, H-4'), 3.11 (dd,  $^2\text{J}(\text{H,H}) = 17.2$  Hz,  $^3\text{J}(\text{H,H}) = 4.3$  Hz, 1H, H-7), 2.94 (dd,  $^2\text{J}(\text{H,H}) = 17.2$  Hz,  $^3\text{J}(\text{H,H}) = 4.3$  Hz, 1H, H-7), 1.57 (m, 4H, H-3), 1.33 (m, 4H, H-2), 0.89 (t,  $^3\text{J}(\text{H,H}) = 7.3$  Hz, 3H, H-1), 0.88 (t,  $^3\text{J}(\text{H,H}) = 7.3$  Hz, 3H, H-1').

$^{13}\text{C-NMR}$  (75 MHz,  $\text{CDCl}_3$ ):  $\delta(\text{ppm}) = 171.2, 170.8, 166.9, 133.8, 131.7, 128.5, 127.1, 65.7, 64.9, 49.1, 36.3, 30.5, 19.0, 13.5$ .

EI-MS (95°C):  $m/z = 349$  (calcd 349 for  $\text{C}_{19}\text{H}_{27}\text{NO}_5^+$ ).

#### N-(benzoyl)-2-aminobutane-1,4-diol 65

a) Dry THF (10 mL) was cooled to  $-10$  to  $-13$  °C under nitrogen and  $\text{LiBH}_4$  (0.09g, 3.93 mmol) was added under stirring. After some time, the suspension became more homogeneous, and a solution of dibutyl N-(benzoyl)aspartate **64** (0.54 g, 1.54 mmol) in THF (5ml) was added dropwise causing minor bubbling in the reaction mixture. Stirring was continued over night while temperature slowly rose to rt. The now milky suspension was



cooled with ice and quench with aq. 1M HCl until pH=7 was reached and a clear solution was obtained. The solution was partly concentrated, and the product extracted with ethyl acetate. The organic phase was washed with sat. aq. NaCl, dried over MgSO<sub>4</sub>, concentrated, and dried in vacuo. Purification by column chromatography (CH<sub>2</sub>Cl<sub>2</sub>:MeOH = 20:1) yielded a colorless oil (71%).

b) Instead of LiBH<sub>4</sub>, equimolar amounts of lithium chloride (1.67 g, 39.27 mmol) and sodium borohydride (1.49 g, 39.27 mmol) were suspended in 100ml cooled dry THF and the solution of bisester (5.38 g, 15.4 mmol) in 50 mL dry THF was added dropwise. The reaction mixture had to be refluxed for 24 h for complete conversion. Work-up similar as before (87 %).

<sup>1</sup>H-NMR (d<sup>6</sup>-DMSO): δ(ppm) = 8.05 (d, <sup>3</sup>J(H,H) = 8.3 Hz, 1H, NH), 7.84 (dd, <sup>3</sup>J(H,H) = 8.2 Hz, <sup>4</sup>J(H,H) = 1.5 Hz, 2H, H-7), 7.46 (m, 3H, H-8, H-9), 4.03 (m, 1H, H-2), 3.45 (m, 4H, H-1, H-4), 1.78 (m, 1H, H-3), 1.63 (m, 1H, H-3').

<sup>13</sup>C-NMR (d<sup>6</sup>-DMSO): δ(ppm) = 166.4, 134.9, 131.1, 128.3, 127.4, 63.2, 58.3, 49.1, 34.2.

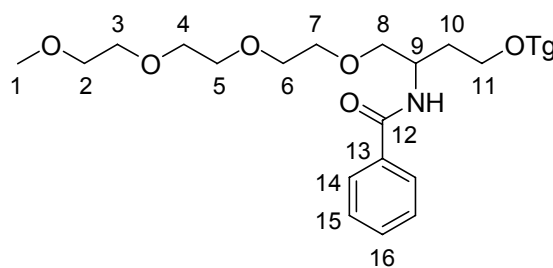
EI-MS (125°C): *m/z* = 209 (calcd 209 for C<sub>11</sub>H<sub>15</sub>NO<sub>3</sub><sup>+</sup>).

HPLC (MeOH:H<sub>2</sub>O = 85:15, 0.2 mL/min): 1.61 min (93 %).

GC (0.8 bar H<sub>2</sub>): 17.68 min, 85%.

### 1,4-Bis(3,6,9-trioxadecanyl)-N-(benzoyl)-2-aminobutane-1,4-diol ether 66

a) In an Argon atmosphere, N-(benzoyl)-2-aminobutane-1,4-diol **65** (0.21 g, 1.00 mmol), monomethyl triethylene glycol bromide (0.64 g, 2.8 mmol), and tetrabutylammonium iodide (0.09 g, 0.25 mmol) were dissolved in 2.5 mL dry THF. Under ice-cooling, sodium hydride (60%



suspension in mineral oil, 0.10 g, 2.4 mmol) was added slowly generating strong gas evolution. The reaction mixture was stirred over night while allowed to warm up to rt. Next morning, additional monomethyl triethylene glycol bromide (0.13 g, 0.56 mmol) and sodium hydride (0.02 g, 0.48 mmol) were added under cooling. The reaction was allowed to stir at rt for another half a day before filtrating the suspension. The filtrate was concentrated, the residue redissolved in DCM and washed with sat. aq. NaCl. The organic phase was dried over MgSO<sub>4</sub>, concentrated and the obtained oil dried in vacuo. Purification by column chromatography (CH<sub>2</sub>Cl<sub>2</sub>:MeOH = 20:1) yielded desired product as colorless clear oil (38%).

b) Instead of triglyme bromide, triglyme tosylate was used facilitating reaction monitoring, and purification, and increasing yield to 81 %.

$^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta(\text{ppm}) = 7.73$  (dd,  $^3\text{J}(\text{H,H}) = 7.5$  Hz,  $^4\text{J}(\text{H,H}) = 1.6$  Hz, 2H, H-14), 7.36 (m, 3H, H-15, H-16), 7.08 (d,  $^3\text{J}(\text{H,H}) = 8.0$  Hz, 1H, NH), 4.33 (m, 1H, H-9), 3.55 (m, 24H, H-2 – H-7), 3.44 (m, 4H, H-8, H-11), 3.27 (s, 6H, H-1), 1.91 (m, 2H, H-10).

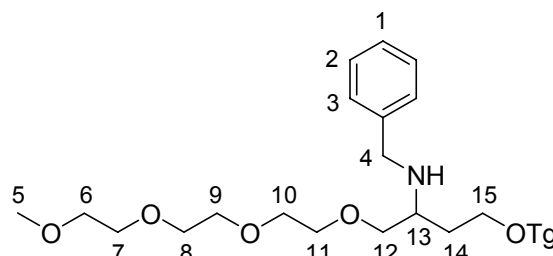
$^{13}\text{C-NMR}$  (100.6 MHz,  $\text{CDCl}_3$ ):  $\delta(\text{ppm}) = 166.9, 134.6, 131.2, 128.3, 127.0, 71.9, 70.52, 70.5, 70.4, 70.3, 68.6, 58.9, 47.9, 30.9$ .

ESI-MS (pos., MeOH):  $m/z = 502.23, 524.31$  (calcd 502.30 for  $\text{C}_{25}\text{H}_{44}\text{NO}_9^+$  and 524.28 for  $\text{C}_{25}\text{H}_{43}\text{NO}_9\text{Na}^+$ ).

HPLC (MeOH:H<sub>2</sub>O = 50:50, 0.8 mL/min): 7.42 min (97 %).

### 1,4-Bis(3,6,9-trioxadecanyl)-N-benzyl-2-aminobutane-1,4-diol ether **67**

In an argon atmosphere,  $\text{LiAlH}_4$  was suspended in 20 mL dry, ice-cooled THF. A solution of 1,4-Bistriglyme-N-benzoyl-aspartinolate **66** (2.152 g, 4.29 mmol) in 10 mL dry THF was drop wise added to the stirring suspension, causing major gas evolution. The mixture was allowed to warm



up to rt, and then heated to reflux overnight. The reaction suspension was cooled down to 0 °C and the excess hydride quenched carefully with Bäckstrom reagent. The solids were filtered off and thoroughly washed with THF. The combined filtrates were concentrated and dried in vacuo yielding a colorless oil. Separation from leftover starting material by column chromatography (gradient ethyl acetate:methanol = 20:1 to 5:1) gave desired product as pale yellow oil (30%). Reducing again isolated starting material for 24 h gave again a mixture of starting material and product. Total yield: 50-60%.

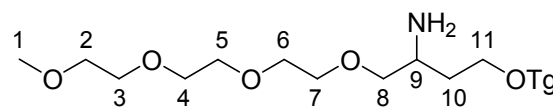
$^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta(\text{ppm}) = 7.30$  (m, 5H, H-1 – H-3), 3.78 (d,  $^4\text{J}(\text{H,H}) = 1.5$  Hz, 2H, H-4), 3.61 (m, 20H, H-6 – H-10), 3.52 (m, H-11, H-12, H-15), 3.34 (s, 6H, H-5), 2.89 (m, 1H, H-13), 2.48 (b, 1H, NH), 1.73 (m, 2H, H-14).

$^{13}\text{C-NMR}$  (100.6 MHz,  $\text{CDCl}_3$ ):  $\delta(\text{ppm}) = 128.5, 128.3, 128.2, 126.8, 73.5, 71.9, 70.6, 70.6, 70.54, 70.49, 70.2, 68.9, 59.0, 54.7, 51.3, 31.6$ .

ESI-MS (pos.):  $m/z = 487, 501$  (calcd 487 for  $\text{C}_{25}\text{H}_{46}\text{NO}_8^+$  and 501 for  $\text{C}_{25}\text{H}_{45}\text{NO}_8\text{Na}^+$ ).

### 1,4-Bis(3,6,9-trioxadecanyl)-2-aminobutane-1,4-diol ether **42**

a) 1,4-Bis(3,6,9-trioxadecanyl)-N-benzyl-2-aminobutane-1,4-diol ether **67** (0.676 g, 1.15 mmol) were dissolved in 15 mL methanol inside



of a presurable reactor,  $\text{Pd}(\text{OH})_2/\text{C}$  (20%, 115 mg, 0.58 mmol) and acetic acid (66  $\mu\text{L}$ , 1.15



mmol) were added, and the reactor sealed. Several cycles of mild evacuating and flooding with hydrogen were performed before applying a hydrogen pressure of 6 bar. The reaction mixture was stirred at rt for 2 d. After releasing the pressure, the mixture was filtered over celite, washed with sat. aq. NaHCO<sub>3</sub>/NaCl, dried over MgSO<sub>4</sub>, concentrated, and dried in vacuo, yielding the desired product as pale yellow oil (96%).

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): δ(ppm) = 3.62 (m, 24H, H-2 – H-7), 3.54 (m, 4H, H-8 & H-11), 3.38 (s, 3H, H-1), 3.36 (s, 3H, H-1), 3.20 (b, 1H, H-9), 2.15 (m, 1H, H-10), 1.94 (m, 1H, H-10).

<sup>13</sup>C-NMR (100.6 MHz, CDCl<sub>3</sub>): δ(ppm) = 71.8, 71.7, 70.62, 71.61, 70.31, 70.26, 70.22, 70.16, 70.12, 70.09, 69.9, 69.7, 69.4, 68.2, 58.9, 51.7, 28.4.

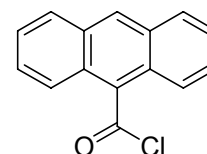
ESI-MS (pos.): *m/z* = 398 (calcd 398 for C<sub>18</sub>H<sub>40</sub>NO<sub>8</sub><sup>+</sup>).

b) 1,4-Bistriglyme-N-benzoyl-aspartinolate **66** (0.196 g, 0.39 mmol) was suspended in 10 mL aq. 10N NaOH (4.0 g NaOH in 10 mL dist. water). The mixture was heated to reflux in an argon atmosphere and stirred overnight. After cooling down to rt, organic adducts were extracted several times with CH<sub>2</sub>Cl<sub>2</sub>. The combined organic phases were dried over MgSO<sub>4</sub>, concentrated, and dried in vacuo. TLC and NMR show only starting material.

c) 1,4-Bistriglyme-N-benzoyl-aspartinolate **66** (0.196 g, 0.39 mmol) was suspended in 10 mL aq. 6N HCl in an argon atmosphere and heated to reflux for 3 h. After cooling the yellow solution down to rt, NaCl salt is added (aq. phase became colorless), and organic adducts were extracted several times with CH<sub>2</sub>Cl<sub>2</sub>. The combined organic phases were dried over MgSO<sub>4</sub>, concentrated, and dried in vacuo yielding a red semi-solid oil (70 mg). TLC and NMR indicate a mixture of benzoic acid and glycol fragments. Subsequently, the aq. phase was made basic with solid NaOH, and organic adducts were extracted several times with CH<sub>2</sub>Cl<sub>2</sub>. The combined organic phases were dried over MgSO<sub>4</sub>, concentrated, and the obtained colorless oil dried in vacuo. Analysis by TLC, NMR, and MS lead to the conclusion, that the benzoyl-group was successfully cleaved, but at the same time the triglyme chains were fragmented.

### Anthracene-9-carbonyl chloride **68**

In an argon atmosphere, anthracene-9-carboxylic acid (7.512 g, 33.80 mmol) was dissolved in 45 mL CH<sub>2</sub>Cl<sub>2</sub>. Oxalyl chloride (4.93 mL, 57.46 mmol) was added dropwise to the yellow suspension causing slight

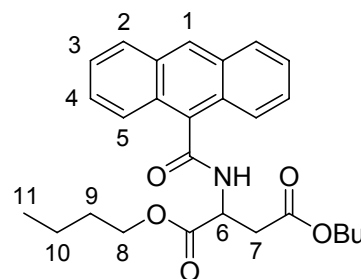


bubbling. After addition of few drops of DMF, stronger gas evolution took place and the reaction mixture was heated to reflux at 60 °C for 3 h. The now clear orange solution was cooled down to rt, concentrated, and the obtained yellow solid dried in vacuo (quantitative).

$R_f$  (hexanes:ethyl acetate = 20:1): 0.2

### Dibutyl N-anthracenoyl-aspartate **69**

In an argon atmosphere, the ammonium tosylate salt of dibutyl aspartate **56** (13.361 g, 32.00 mmol) was dissolved in a mixture of 17 mL freshly distilled  $\text{CHCl}_3$  and 9.9 mL of dry triethylamine and cooled in to 0 to  $-5^\circ\text{C}$ . A solution of anthracenoyl chloride **68** (8.164 g, 33.92 mmol) in 17 mL dry  $\text{CHCl}_3$  was added slowly, and the reaction mixture was stirred



over night while allowed to slowly warm up to rt. The mixture was diluted with  $\text{CHCl}_3$  and thoroughly washed with sat. aq.  $\text{NH}_4\text{Cl}$ , sat. aq.  $\text{NaHCO}_3$ , sat. aq.  $\text{NH}_4\text{Cl}/1\text{M-HCl}$ , and finally sat. aq.  $\text{NaCl}$ . The organic phase was dried over  $\text{MgSO}_4$ , concentrated, and the obtained dark red, viscous oil dried in vacuo (100%).

$R_f$  ( $\text{CH}_2\text{Cl}_2$ : MeOH = 40:1): 0.7

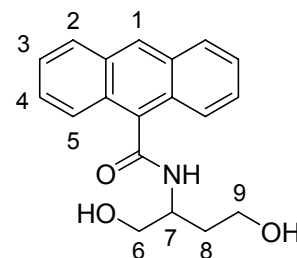
$^1\text{H-NMR}$  (300 MHz,  $\text{CDCl}_3$ ):  $\delta$ (ppm) = 8.46 (s, 1H, H-1), 7.98 (dd,  $^3J(\text{H}, \text{H}) = 7.8$  Hz,  $^4J(\text{H}, \text{H}) = 1.9$  Hz, 4H, H-2 & H-5), 7.48 (m, 4H, H-3 & H-4), 7.06 (d,  $^3J(\text{H}, \text{H}) = 8.4$  Hz, 1H, NH), 5.38 (m, 1H, H-6), 4.24 (m, 2H, H-8), 4.04 (m, 2H, H-8), 3.23 (dd,  $^2J(\text{H}, \text{H}) = 17.2$  Hz,  $^3J(\text{H}, \text{H}) = 4.9$  Hz, 1H, H-7), 3.09 (dd,  $^2J(\text{H}, \text{H}) = 17.0$  Hz,  $^3J(\text{H}, \text{H}) = 4.5$  Hz, 1H, H-7), 1.67 (m, 2H, H-9), 1.51 (m, 2H, H-9), 1.42 (m, 2H, H-10), 1.31 (m, 2H, H-10), 0.94 (t,  $^3J(\text{H}, \text{H}) = 7.4$  Hz, 3H, H-11), 0.84 (t,  $^3J(\text{H}, \text{H}) = 7.3$  Hz, 3H, H-11).

$^{13}\text{C-NMR}$  (75 MHz,  $\text{CDCl}_3$ ):  $\delta$ (ppm) = 171.0, 170.5, 169.2, 131.0, 128.6, 128.4, 128.1, 126.9, 126.7, 125.4, 124.9, 66.0, 65.1, 49.0, 36.5, 30.5, 30.4, 19.0, 13.6.

EI-MS ( $160^\circ\text{C}$ ):  $m/z = 449$  (calcd 449 for  $\text{C}_{27}\text{H}_{31}\text{NO}_5^+$ ).

### N-anthracenoyl-2-aminobutane-1,4-diol **70**

In an argon atmosphere,  $\text{LiBH}_4$  powder (1.812 g, 83.20 mmol) was added to 200 mL dry THF at  $-10$  to  $-13^\circ\text{C}$ . Under stirring, a dark red solution of dibutyl N-anthracenoyl aspartate **69** (14.385 g, 32.00 mmol) in 100 mL) was slowly added via a dropping funnel causing minor gas evolution in the reaction suspension. After complete



addition, stirring was continued overnight while the temperature raised slowly to rt. The mixture was cooled in an ice bath and excess hydride quenched carefully with aq. 1M HCl until pH=7 was reached and the red-brown suspension turned into a clear yellow-green solution. The solution was made basic with aq. 1M NaOH, and organic products were extracted twice with lots of ethyl acetate. The combined organic phases were washed with sat.

aq. NaCl, dried over MgSO<sub>4</sub>, and concentrated to yield crude product. Purification by column chromatography (silica gel, gradient hexanes:ethyl acetate = 10:1 to 1:1, then ethyl acetate:MeOH gradient = 20:1 to 5:1) yielded desired orange solid product as third fraction (65%).

R<sub>f</sub> (ethyl acetate:MeOH = 20:1): 0.3

<sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): δ(ppm) = 8.32 (s, 1H, H-1), 7.92 (d, <sup>3</sup>J(H,H) = 8.1 Hz, 2H, H-2), 7.88 (dd, <sup>3</sup>J(H,H) = 8.2 Hz, <sup>4</sup>J(H,H) = 1.8 Hz, 2H, H-5), 7.39 (m, 4H, H-3 & H-4), 6.69 (d, <sup>3</sup>J(H,H) = 8.2 Hz, 1H, NH), 4.40 (m, 1H, H-7), 3.70 (m, 2H, H-6), 3.62 (m, 2H, H-9), 3.4 (b, OH), 1.78 (m, 1H, H-8), 1.60 (m, 1H, H-8).

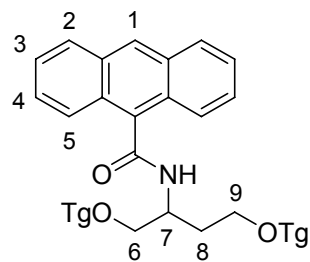
<sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>): δ(ppm) = 170.6, 131.1, 130.9, 128.5, 128.4, 127.9, 126.9, 125.5, 124.7, 64.9, 58.9, 49.8, 34.1.

EI-MS (200 °C): *m/z* = 309 (calcd 309 for C<sub>19</sub>H<sub>19</sub>NO<sub>3</sub><sup>+</sup>).

HPLC (MeOH:H<sub>2</sub>O=1:1, 220nm): 92.2%

#### 1,4-Bis(3,6,9-trioxadecanyl)-N-(anthracenoyl)-2-aminobutane-1,4-diol ether **71**

In an argon atmosphere, sodium hydride (60% suspension in mineral oil, 2.070 g, 51.75 mmol) was added slowly to 30 mL dry, cooled below 0 °C, THF. A solution of N-(anthracenoyl)-2-aminobutane-1,4-diol **70** (6.404 g, 20.70 mmol) in 30 mL dry THF was slowly added to the milky suspension. After stirring for 30 min,



monomethyl triethylene glycol tosylate (13.840 g, 43.47 mmol), crown ether 15-C-5 (0.08 mL, 0.41 mmol), and tetrabutylammonium iodide (1.911 g, 5.175 mmol) were added creating a red, intense reaction suspension. After stirring for 4 h, additional NaH (0.497 g, 12.42 mmol) and triglyme tosylate (3.295 g, 10.35 mmol) were added and the reaction mixture was stirred overnight while allowed to warm up to rt. The suspension was cooled in an ice bath, and the excess hydride quenched carefully with aq. 1M HCl until the reaction mixture became a clear red solution (pH < 7). Solid NaCl and sat. aq. NaCl were added and the organic products extracted thoroughly several times with lots of CH<sub>2</sub>Cl<sub>2</sub>. The combined organic phases were dried over MgSO<sub>4</sub>, concentrated, and the obtained orange oil purified by column chromatography (CH<sub>2</sub>Cl<sub>2</sub>:MeOH gradient = 20:1 to 10:1) yielding the desired product as pale orange oil (40%).

R<sub>f</sub> (CH<sub>2</sub>Cl<sub>2</sub>:MeOH = 10:1) = 0.5

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): δ(ppm) = 8.41 (s, 1H, H-1), 8.10 (d, <sup>3</sup>J(H,H) = 8.5 Hz, 2H, H-2), 7.96 (d, <sup>3</sup>J(H,H) = 8.1 Hz, 2H, H-5), 7.46 (m, 4H, H-3 & H-4), 6.88 (d, <sup>3</sup>J(H,H) = 8.4 Hz,

<sup>1</sup>H, NH), 4.71 (m, 1H, H-7), 3.8-3.3 (m, 28H, CH<sub>2</sub>O), 3.29 (s, 3H, CH<sub>3</sub>), 3.25 (s, 3H, CH<sub>3</sub>), 2.03 (m, 2H, H-8).

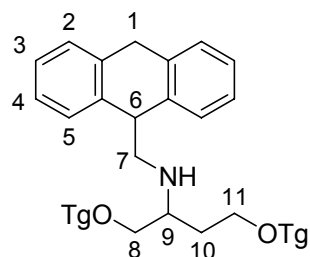
<sup>13</sup>C-NMR (100.6 MHz, CDCl<sub>3</sub>): δ(ppm) = 169.0, 132.4, 131.1, 128.3, 128.0, 127.9, 126.4, 125.4, 125.3, 72.4, 71.9, 71.8, 70.6, 70.50, 70.47, 70.40, 70.33, 70.30, 70.28, 70.24, 68.4, 58.9, 48.1, 31.2.

EI-MS (210 °C): *m/z* = 601 (calcd 601 for C<sub>33</sub>H<sub>47</sub>NO<sub>9</sub><sup>+</sup>).

IR (Kap.): 3296 (m, νN-H), 3053 (m, νC-H<sub>Ar</sub>), 2870 (s, νCH<sub>2</sub>), 1658 (s, νC=O), 1523 (m, δN-H), 1108 (s, δC-O).

### 1,4-Bis(3,6,9-trioxadecanyl)-N-(9,10-dihydroanthracenylmethyl)-2-aminobutane-1,4-diol ether **72**

In an argon atmosphere, LiAlH<sub>4</sub> powder (0.051 g, 1.33 mmol) was suspended in 1.5 mL dry, ice-cold THF. A solution of 1,4-Bistriglyme-N-anthracenoyl-aspartinolate **71** (0.187 g, 0.31 mmol) in 1.5 mL dry THF was added drop wise causing major gas evolution. The mixture was allowed to warm up to rt, and then



heated to reflux for 24 h. The mixture was cooled down in an ice-bath and excess hydride carefully quenched with Bäckström reagent. Solids were filtered off and thoroughly washed with THF. The combined filtrates were concentrated and dried in vacuo yielding an orange oil. Purification by column chromatography (silica gel, gradient: neat CH<sub>2</sub>Cl<sub>2</sub> to CH<sub>2</sub>Cl<sub>2</sub>:MeOH = 10:1) gave above depicted product (91%).

R<sub>F</sub> (CH<sub>2</sub>Cl<sub>2</sub>:MeOH = 10:1): 0.4

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): δ(ppm) = 7.34 (m, 2H, H<sub>Ar</sub>), 7.26 (m, 3H, H<sub>Ar</sub>), 7.19 (m, 3H, H<sub>Ar</sub>), 4.11 (d, <sup>2</sup>J(H, H) = 18.0 Hz, 1H, H-1), 3.84 (d, <sup>2</sup>J(H, H) = 18.0 Hz, 1H, H-1), 3.71 (m, 1H, H-6), 3.60 (m, 17H, CH<sub>2</sub>O), 3.52 (m, 11H, CH<sub>2</sub>O), 3.35 (s, 3H, CH<sub>3</sub>O), 3.34 (s, 3H, CH<sub>3</sub>O), 2.91 (m, 2H, H-7), 2.77 (m, 1H, H-9), 1.64 (m, 2H, H-10).

<sup>13</sup>C-NMR (100.6 MHz, CDCl<sub>3</sub>): δ(ppm) = 136.2, 128.4, 128.3, 127.9, 127.8, 126.4, 126.3, 72.5, 71.9, 70.6, 70.53, 70.49, 70.1, 68.5, 61.7, 59.0, 35.3.

ESI-MS (pos.): *m/z* = 590, 612 (calcd 590 for C<sub>33</sub>H<sub>52</sub>NO<sub>8</sub><sup>+</sup> and 612 for C<sub>33</sub>H<sub>51</sub>NO<sub>8</sub>Na<sup>+</sup>).

IR (Kap.): 3331 (w, νN-H), 2872 (s, νCH<sub>2</sub>), 1110 (s, δC-O).

#### *Alternative reduction of N-anthracenoyl-amide.*

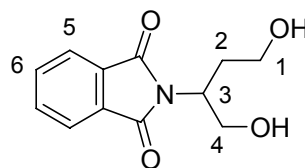
In an argon atmosphere, 1.24 mL of a solution of BH<sub>3</sub> (1M, 1.24 mmol) in THF was cooled in an ice-bath. A solution of 1,4-Bistriglyme-N-anthracenoyl-aspartinolate (0.187 g, 0.31 mmol) in 1.8 mL dry THF was added dropwise causing strong bubbling. The mixture was warmed up to rt, then heated to reflux for 24 h. After cooling down to rt, excess hydride was quenched

carefully with distilled water. The solvent was removed under reduced pressure, and 10 mL aq. 6N HCl were added. The mixture was stirred for 1 h at rt, in the end heated to boiling for a few seconds. The mixture was made basic with solid NaOH, saturated with solid NaCl salt, and organic adducts extracted several times with CH<sub>2</sub>Cl<sub>2</sub>. The combined organic phases were dried over MgSO<sub>4</sub>, concentrated, and the obtained oil dried in vacuo.

NMR shows traces of starting material, otherwise very broad signals in <sup>1</sup>H-NMR and many signals in <sup>13</sup>C-NMR, probably due to unsaponified borates.

### N-(1,4-dihydroxybutan-2-yl)phthalimide **60**

Under nitrogen and at rt, a solution of aspartinol **57** (0.28 g, 2.7 mmol) in 3.5 mL dry toluene was added dropwise to a solution of phthalic anhydride (0.39 g, 2.7 mmol) in 20 mL dry toluene. Heat



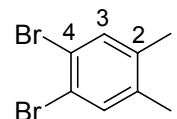
was generated and a precipitate formed. After complete addition, reaction was further stirred for 4 h. Anhydrous ZnBr<sub>2</sub> (0.12 g, 0.5 mmol) was added at once, the reaction was heated to 90°C, and a solution of HMDS (0.85 mL, 4.0 mmol) in 3.5 mL dry toluene was slowly added over 30 min. After addition, the reaction was continued to reflux for another 6 h. After being cooled down to rt, the reaction mixture was poured into 50 mL 0.5N aq. HCl. Extraction with ethyl acetate (three times), followed by washing of the combined organic phases with sat. aq. NaHCO<sub>3</sub> and sat. aq. NaCl, and subsequent drying over MgSO<sub>4</sub>, and removal of solvent gave an orange solid, that was further dried in vacuo.

<sup>1</sup>H-NMR (d<sup>6</sup>-DMSO): δ(ppm) = 7.81 (s, 5H, ?), 7.67 (m, 1H, H-5), 7.57 (m, 1H, H-6), 4.31 (m, 1H, H-3), 3.83 (t, <sup>2</sup>J(H,H) = 10.0 Hz, 1H, H-4), 3.57 (dd, <sup>2</sup>J(H,H) = 10.9 Hz, <sup>3</sup>J(H,H) = 5.5 Hz, 1H, H-4), 3.37 (m, 2H, H-1), 2.01 (m, 1H, H-2), 1.81 (m, 1H, H-2).

*Aromatic core.*

### 1,2-Dibromo-4,5-dimethylbenzene **48**<sup>[2]</sup>

o-Xylene **47** (6.0 mL, 50.0 mmol) and iodine (0.08 g) were dissolved in 4 mL diethyl ether, cooled to 0 °C and isolated from light. Within 25 min bromine (5.4 mL, 105.0 mmol) was added drop-wise, and the reaction solution was stirred over night at rt. The reaction solution was diluted with diethyl ether and washed 2x with 2N aq. NaOH and 2x with brine. The organic solution was dried over MgSO<sub>4</sub> and the solvent removed. Recrystallization in MeOH yielded product as snow-white crystals (50 %).



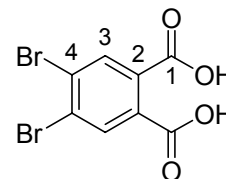
<sup>1</sup>H-NMR (250 MHz, CDCl<sub>3</sub>): δ(ppm) = 7.35 (s, 2H, H-3), 2.17 (s, 6H, H-1).

<sup>13</sup>C-NMR (63 MHz, CDCl<sub>3</sub>): δ(ppm) = 137.6 (C-2), 134.2 (C-3), 121.1 (C-4), 19.0 (C-1).

EI-MS (30 °C): *m/z* = 262 (calcd 262 for C<sub>8</sub>H<sub>8</sub>Br<sub>2</sub><sup>+</sup>).

**3,4-Dibromophthalic acid 49**

1,2-Dibromo-4,5-dimethylbenzene **48** (1.06 g, 4.0 mmol), Na<sub>2</sub>CO<sub>3</sub> (0.55 g, 5.2 mmol), and trimethyl-octylammonium chloride (0.14 g) were dissolved in 20 mL distilled water. Potassium permanganate (4.17 g, 26.4 mmol) were added and the mixture refluxed for 45 min. Generated MnO<sub>2</sub> was filtered off while still hot and washed 2x with little amounts of hot water. The light yellow aq. filtrate was made colorless by adding sodium hydrogen sulfite. Upon acidifying with half-concentrated sulfuric acid a voluminous white precipitate if formed and isolated after prolonged cooling at 4 °C. Recrystallization in water yielded snow-white, slightly metallic reflecting white solid (74 %).



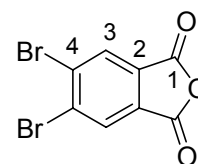
<sup>1</sup>H-NMR (250 MHz, d<sub>6</sub>-DMSO): δ(ppm) = 8.20 (s, 2H, H-3).

<sup>13</sup>C-NMR (63 MHz, d<sub>6</sub>-DMSO): δ(ppm) = 166.3 (C-1), 135.6 (C-3), 134.5 (C-2), 126.7 (C-4).

EI-MS (200 °C): *m/z* = 322, 304, 232 (calcd 322 for C<sub>8</sub>H<sub>4</sub>Br<sub>2</sub>O<sub>4</sub><sup>+</sup>).

**3,4-Dibromophthalic anhydride 43**

a) 3,4-Dibromophthalic acid **49** (0.32 g, 1.0 mmol) and oxalyl chloride (0.86 mL, 10.0 mmol) are dissolved in 2 mL CH<sub>2</sub>Cl<sub>2</sub> under nitrogen atmosphere. After addition of one drop of DMF, the reaction mixture is refluxed for 3 h. The yellow/light green solution is cooled down to rt, the solvent is removed, and the yellow solid dried in vacuo (quantitative).



b) Alternatively, the dibromophthalic acid was dissolved in hot acetic anhydride and refluxed over night. Upon cooling, the product started to precipitate. The solid was isolated and recrystallized from toluene (quantitative).

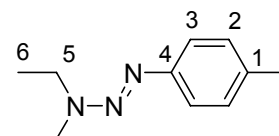
<sup>1</sup>H-NMR (250 MHz, d<sup>6</sup>-DMSO): δ(ppm) = 8.50 (s, 2H, H-3), 7.99 (s, 2H, H-?).

<sup>13</sup>C-NMR (63 MHz, d<sup>6</sup>-DMSO): δ(ppm) = 166.6 (C-1), 133.5 (C-3), 126.9 (C-2, C-4).

EI-MS (90 °C): *m/z* = 304, 260, 232, 181, 153, 101, 74 (calcd 304 for C<sub>8</sub>H<sub>2</sub>Br<sub>2</sub>O<sub>3</sub><sup>+</sup>).

**1-Iodo-4-(diethyltriazenyl)benzene 45**

The procedure was analogous to the synthesis of 1-Iodo-3-(diethyltriazenyl)benzene **88** using 4-iodoaniline **44** as starting material (98 %).



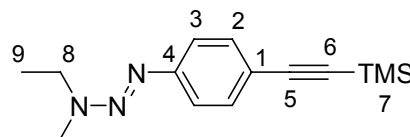
<sup>1</sup>H-NMR (250 MHz, CDCl<sub>3</sub>): δ(ppm) = 7.62 (d, <sup>3</sup>J(H,H) = 9.1 Hz, 2H, H-2), 7.19 (d, <sup>3</sup>J(H,H) = 9.1 Hz, 2H, H-3), 3.73 (q, <sup>3</sup>J(H,H) = 7.3 Hz, 4H, H-5), 1.25 (t, <sup>3</sup>J(H,H) = 6.8 Hz, 6H, H-6).

$^{13}\text{C}$ -NMR (63 MHz,  $\text{CDCl}_3$ ):  $\delta(\text{ppm}) = 150.8$  (C-4), 137.5 (C-2), 122.4 (C-3), 88.9 (C-1), 46.8 (C-5), 44.1 (C-5'), 12.8 (C-6).

EI-MS (30 °C):  $m/z = 303, 231, 203$  (303 calcd for  $\text{C}_{10}\text{H}_{14}\text{IN}_3^+$ ).

### 1-(2-(Trimethylsilyl)ethynyl)-4-(diethyltriazenyl)benzene **41**<sup>[3]</sup>

The procedure was analogous to the synthesis of 1-(TMS-ethynyl)-3-(diethyltriazenyl)benzene **89** using 1-iodo-4-



(diethyltriazenyl)benzene **45** as starting material (52 %).

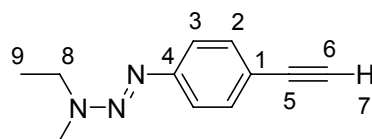
$^1\text{H}$ -NMR (250 MHz,  $\text{CDCl}_3$ ):  $\delta(\text{ppm}) = 7.46$  (d,  $^3\text{J}(\text{H,H}) = 8.2$  Hz, 2H, H-2), 7.38 (d,  $^3\text{J}(\text{H,H}) = 9.1$  Hz, 2H, H-3), 3.73 (q,  $^3\text{J}(\text{H,H}) = 7.3$  Hz, 4H, H-8), 1.25 (t,  $^3\text{J}(\text{H,H}) = 7.3$  Hz, 6H, H-9), 0.29 (s, 9H, H-7).

$^{13}\text{C}$ -NMR (63 MHz,  $\text{CDCl}_3$ ):  $\delta(\text{ppm}) = 151.1$  (C-4), 132.5 (C-2), 120.2 (C-3), 119.2 (C-1), 105.8 (C-5), 93.3 (C-6), 45.6 (C-8), 12.6 (C-9), 0.0 (C-7).

EI-MS (30 °C):  $m/z = 273$  (273 calcd for  $\text{C}_{15}\text{H}_{23}\text{N}_3\text{Si}^+$ ).

### 1-Ethynyl-4-(diethyltriazenyl)benzene **46**

a) 1-(TMS-ethynyl)-4-(diethyltriazenyl)benzene **41** (0.36 g, 1.30 mmol) and  $\text{K}_2\text{CO}_3$  (0.54 g, 3.90 mmol) were dissolved in



a mixture of 5 mL ethanol, 4 mL THF, and 2 mL water.  $\text{N}_2$  was bubbled several minutes through the orange solution; subsequently the rc was stirred for 3 h at 50 °C. Ethyl acetate and brine were added; the organic phase was separated, washed with sat. aq.  $\text{NH}_4\text{Cl}$ , dried over  $\text{MgSO}_4$ , and concentrated. Final purification by short column chromatography (hexane:ethyl acetate = 10:1) yielded desired product as light yellow solid (98 %).

b)<sup>[4]</sup> 1-(TMS-ethynyl)-4-(diethyltriazenyl)benzene **41** (1.07 g, 3.9 mmol) was dissolved in 40 mL THF. 0.2 mL distilled water and 5.5 mL of a 1M solution of TBAF in THF were added. The reaction solution was stirred for 25 min at rt and then filtered thru a silica gel plug with hexanes:ethyl acetate = 10:1 as eluent. The first fractions were concentrated and the obtained solid dried in vacuo (quantitative).

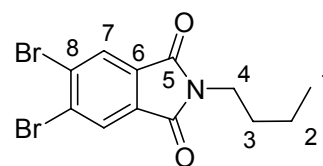
$^1\text{H}$ -NMR (250 MHz,  $\text{CDCl}_3$ ):  $\delta(\text{ppm}) = 7.44$  (d,  $^3\text{J}(\text{H,H}) = 9.1$  Hz, 2H, H-2), 7.35 (d,  $^3\text{J}(\text{H,H}) = 8.2$  Hz, 2H, H-3), 3.75 (q,  $^3\text{J}(\text{H,H}) = 7.3$  Hz, 4H, H-8), 3.05 (s, 1H, H-7), 1.25 (t,  $^3\text{J}(\text{H,H}) = 6.8$  Hz, 6H, H-9).

$^{13}\text{C}$ -NMR (62.9 MHz,  $\text{CDCl}_3$ ):  $\delta(\text{ppm}) = 151.5, 132.8, 120.3, 118.2, 84.3, 76.6, 44.3, 12.7$ .

EI-MS (40 °C):  $m/z = 201$  (calcd 201 for  $\text{C}_{12}\text{H}_{15}\text{N}_3^+$ ).

**N-butyl-4,5-dibromophthalimide 50**

4,5-Dibromophthalic anhydride **43** (0.23 g, 0.75 mmol) was dissolved in 6 mL toluene in an N<sub>2</sub> atmosphere. *n*-butylamine (0.08 mL, 0.75 mmol) was dissolved in 2.5 mL toluene and added dropwise to the stirred solution of anhydride, during which a



precipitate was formed. After complete addition, stirring was continued for 1h. ZnBr<sub>2</sub> (0.03 g, 0.15 mmol) was added at once, the rc mixture was heated to 80 °C, and a solution of HMDS (0.24 mL, 1.13 mmol) in 2.5 mL toluene was slowly added over 30 min. After complete addition, rc mixture was refluxed for another hour, cooled down to rt, and poured into 0.5 N HCl. Product was extracted 3x with ethyl acetate, the combined org. phases washed with sat. NaHCO<sub>3</sub> and brine, and dried over MgSO<sub>4</sub>. Removal of solvent and drying in vacuo yielded desired product as solid (99 %).

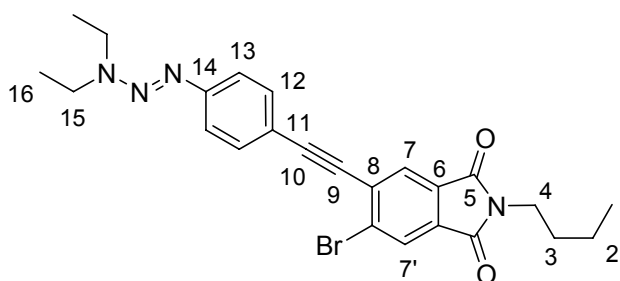
<sup>1</sup>H-NMR (250 MHz, CDCl<sub>3</sub>): δ(ppm) = 8.05 (s, 2H, H-7), 3.65 (t, <sup>3</sup>J(H,H) = 7.3 Hz, 2H, H-4), 1.62 (m, 2H, H-3), 1.34 (m, 2H, H-2), 0.92 (t, <sup>3</sup>J(H,H) = 7.3 Hz, 3H, H-1).

<sup>13</sup>C-NMR (62.9 MHz, CDCl<sub>3</sub>): δ(ppm) = 160.6, 134.3, 130.5, 128.3, 38.3, 30.4, 20.0, 13.5.

EI-MS (80°C): *m/z* = 359 (calcd 359 for C<sub>12</sub>H<sub>11</sub>Br<sub>2</sub>NO<sub>2</sub><sup>+</sup>).

**N-butyl-4-(4-diethyltriazenylphenylethynyl)-5-bromophthalimide 51**

In an nitrogen atmosphere, N-butyl-4,5-dibromophthalimide **50** (0.18 g, 0.5 mmol), 1-ethynyl-4-(diethyltriazenyl)benzene **46** (0.11 g, 0.53 mmol), and catalysts Pd(PPh<sub>3</sub>)<sub>4</sub> (0.06 g, 0.05 mmol) and CuI (0.01 g, 0.05 mmol) were



dissolved in a solvent mixture of 2 mL dry triethylamine and dry THF. After two freeze-pump-thaw cycles, rc was stirred at 80 °C for 24h. The rc mixture was cooled down to rt, diluted with THF, and filtrated. The filtrate was concentrated and purified by column chromatography (silica gel, gradient hexane:ethyl acetate = 20:1 – 1:1) yielding desired product as yellow solid (50 %).

<sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>): δ(ppm) = 8.04 (s, 1H H-7'), 7.92 (s, 1H, H-7), 7.54 (d, <sup>3</sup>J(H,H) = 8.2 Hz, 2H, H-13), 7.41 (d, <sup>3</sup>J(H,H) = 9.1 Hz, 2H, H-12), 3.77 (q, <sup>3</sup>J(H,H) = 7.0 Hz, 4H, H-15), 3.65 (t, <sup>3</sup>J(H,H) = 7.3 Hz, 2H, H-4), 1.63 (m, 2H, H-3), 1.35 (m, 2H, H-2), 1.27 (t, <sup>3</sup>J(H,H) = 8.2 Hz, 6H, H-16), 0.92 (t, <sup>3</sup>J(H,H) = 7.3 Hz, 3H, H-1).

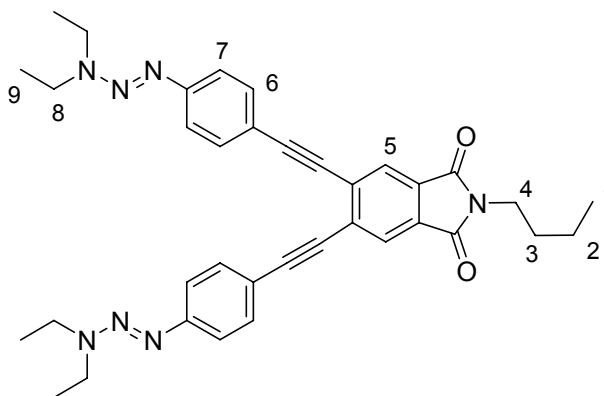
<sup>13</sup>C-NMR (126 MHz, CDCl<sub>3</sub>): δ(ppm) = 167.2, 166.74, 152.2, 133.9, 133.6, 132.8, 131.5, 131.2, 130.9, 128.4, 127.3, 127.0, 120.6, 117.9, 100.0, 87.3, 45.9, 38.1, 30.5, 20.1, 13.6, 12.7



EI-MS (170°C):  $m/z = 480$  (calcd 480 for  $C_{24}H_{25}BrN_4O_2^+$ ).

As a side product, **N-butyl-4,5-bis(4-diethyltriazenylphenylethynyl)phthalimide** was isolated (26 %).

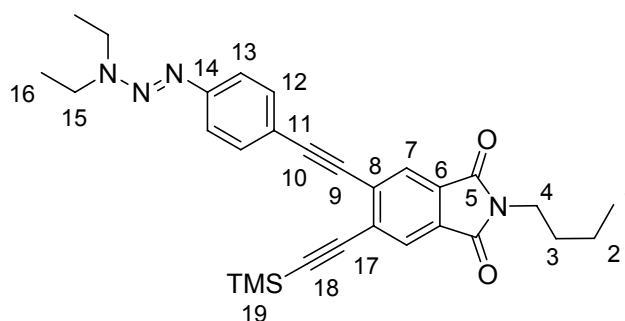
$^1H$ -NMR (500 MHz,  $CDCl_3$ ):  $\delta$ (ppm) = 7.94 (s, 2H, H-5), 7.55 (d,  $^3J(H,H) = 8.2$  Hz, 4H, H-7), 7.43 (d,  $^3J(H,H) = 8.2$  Hz, 4H, H-6), 3.79 (q,  $^3J(H,H) = 7.0$  Hz, 8H, H-8), 3.66 (t,  $^3J(H,H) = 7.3$  Hz, 2H, H-4), 1.65 (m, 2H, H-3), 1.37 (m, 2H, H-2), 1.27 (t,  $^3J(H,H) = 7.3$  Hz, 12H, H-9), 0.93 (t,  $^3J(H,H) = 7.3$  Hz, 3H, H-1).



EI-MS (150-170°C):  $m/z = 601$  (calcd 601 for  $C_{36}H_{39}N_7O_2^+$ ).

### **N-butyl-4-(4-diethyltriazenylphenylethynyl)-5-bromophthalimide 52**

In an nitrogen atmosphere, N-butyl-4-(4-diethyltriazenylphenylethynyl)-5-bromophthalimide **51** (0.11 g, 0.22 mmol) and catalysts  $Pd(PPh_3)_4$  (51 mg, 0.4 mmol) and  $CuI$  (8 mg, 0.04 mmol) were dissolved in a solvent mixture of 1.5 mL dry triethylamine and 0.5 mL dry THF.



After two freeze-pump-thaw cycles, degassed TMS acetylene (0.1 mL, 0.7 mmol) was injected and reaction was stirred at 80 °C for 24h. The reaction mixture was cooled down to rt, diluted with THF, and filtrated. The filtrate was concentrated and purified by column chromatography (silica gel, gradient hexane:ethyl acetate = 20:1 – 10:1) yielding desired product as yellow solid (61 %).

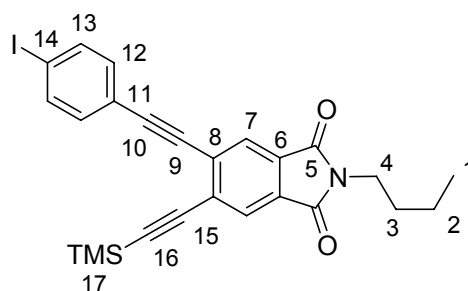
$^1H$ -NMR (500 MHz,  $CDCl_3$ ):  $\delta$ (ppm) = 7.89 (s, 2H, H-7), 7.52 (d,  $^3J(H,H) = 8.2$  Hz, 2H, H-13), 7.41 (d,  $^3J(H,H) = 9.1$  Hz, 2H, H-12), 3.77 (q,  $^3J(H,H) = 7.0$  Hz, 4H, H-15), 3.65 (t,  $^3J(H,H) = 7.3$  Hz, 2H, H-4), 1.64 (m, 2H, H-3), 1.35 (m, 2H, H-2), 1.26 (t,  $^3J(H,H) = 7.7$  Hz, 6H, H-16), 0.92 (t,  $^3J(H,H) = 7.3$  Hz, 3H, H-1), 0.28 (s, 9H, H-19).

$^{13}C$ -NMR (126 MHz,  $CDCl_3$ ):  $\delta$ (ppm) = 167.4, 152.0, 132.8, 132.1, 130.8, 130.1, 128.5, 126.8, 125.9, 120.6, 118.3, 103.8, 102.2, 99.1, 87.3, 44.7, 38.1, 30.6, 20.1, 13.6, 13.0, -0.2.

EI-MS (160°C):  $m/z = 498$  (calcd 498 for  $C_{29}H_{34}N_4O_2Si^+$ ).

**N-butyl-4-(4-iodophenylethynyl)-5-(trimethylsilyl-ethynyl)phthalimide 53**

N-butyl-4-(4-diethyltriazenylphenylethynyl)-5-(trimethylsilyl-ethynyl)phthalimide **52** (0.07 g, 0.2 mmol) were dissolved in 5 mL MeI in a presurable vessel. The yellow solution was subjected to 3x freeze-pump-thaw cycles and heated to 110 °C for 19 h. The solution was concentrated and the obtained black oil purified by column chromatography (silica gel, neat CH<sub>2</sub>Cl<sub>2</sub>) yielding yellow solid (82 %).



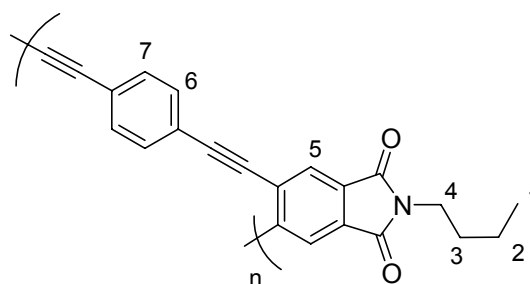
<sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>): δ(ppm) = 7.89 (s, 2H, H-7), 7.71 (d, <sup>3</sup>J(H,H) = 8.2 Hz, 2H, H-13), 7.26 (d, <sup>3</sup>J(H,H) = 8.2 Hz, 2H, H-12), 3.65 (t, 7.3 Hz, 2H, H-4), 1.63 (m, 2H, H-3), 1.35 (m, 2H, H-2), 0.92 (t, <sup>3</sup>J(H,H) = 7.3 Hz, 3H, H-1), 0.27 (s, 9H, H-17).

<sup>13</sup>C-NMR (126 MHz, CDCl<sub>3</sub>): δ(ppm) = 167.1, 137.7, 133.2, 131.1, 131.0, 130.9, 130.7, 126.8, 126.1, 121.7, 104.1, 101.9, 96.6, 95.5, 88.5, 38.1, 30.5, 20.1, 13.6, -0.2.

EI-MS (100-120°C): *m/z* = 525 (calcd 525 for C<sub>25</sub>H<sub>24</sub>INO<sub>2</sub>Si<sup>+</sup>).

**Poly(ortho-N-butyl-phthalimide-alternating-para-phenylene diethynylene) 54**

In an argon atmosphere, N-butyl *ortho*-alt-*para*-monomer **53** (60 mg, 0.12 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (8 mg, 7 μmol), and CuI (2 mg, 12 μmol) were dissolved in 2 mL degassed toluene. DBU (0.1 mL, 0.7 mmol) and water (0.02 mL, 1.2 mmol) were added, and the reaction mixture subjected to

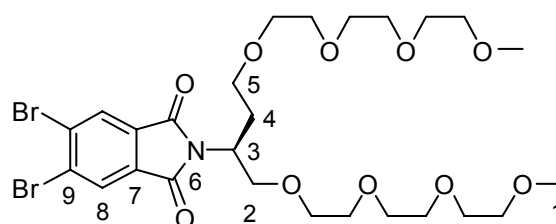


two freeze-pump-thaw cycles. The rc was stirred for 3d at rt, filtered, and the solids washed with hot toluene. The solids were split into a CH<sub>2</sub>Cl<sub>2</sub> soluble fraction (“DCM”) and a non-soluble fraction (“RS”).

GPC (THF, 40 °C, 254 nm): “DCM”: Mn = 2600, PDI = 1.06, DP = 7 – 8; „RS“: Mn = 4500, PDI = 1.24, DP = 14. Both GPC-samples were not completely soluble in THF.

**Dibromophthalimide with branched chiral side chain 73**

To a solution of anhydride **43** (0.664 g, 2.17 mmol) in toluene (16 mL) was added under argon dropwise at rt a solution of side chain amine **42** (0.906 g, 2.28 mmol) in toluene (8 mL). After complete addition, the reaction was



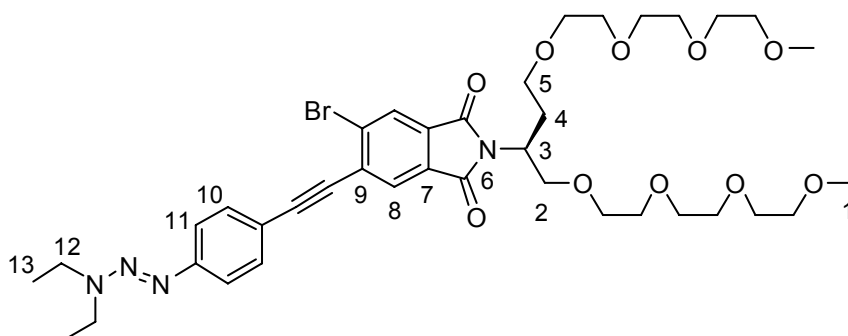
stirred for 1 h. Dry ZnBr<sub>2</sub> (0.098 g, 0.43 mmol) was added at once and the reaction was heated to 80°C becoming a clear solution, while a solution of HMDS (0.69 mL, 3.26 mmol) in toluene (6 mL) was slowly added over 30min. The reaction was refluxed for 1 h. Finally, the now turbid mixture was cooled down to rt, poured into 0.5N HCl, and the crude product extracted with ethyl acetate. The organic phase was washed with aq. sat. NaHCO<sub>3</sub> and aq. sat. NaCl, dried over MgSO<sub>4</sub>, concentrated, and the obtained orange oil purified by column chromatography (silica gel, eluent gradient CH<sub>2</sub>Cl<sub>2</sub>:MeOH = 100:1 to 40:1) giving the desired product in 75 % yield.

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): δ(ppm) = 8.00 (s, 2H, H-8), 4.58 (m, 1H, H-3), 3.96 (t, <sup>3</sup>J(H,H) = 9.9 Hz, 1H, H-2), 3.64-3.33 (m, 27H, CH<sub>2</sub>O), 3.33 (s, 6H, H-1), 2.24 (m, 1H, H-4), 1.91 (m, 1H, H-4').

<sup>13</sup>C-NMR (100.6 MHz, CDCl<sub>3</sub>): δ(ppm) = 166.5 (C-6), 131.8 (C-9), 131.1 (C-7), 128.2 (C-8), 71.9 (C-2), 70.5-70.2 (CH<sub>2</sub>O), 68.3 (C-5), 59.0 (C-1), 49.3 (C-3), 28.5 (C-4).

EI-MS (180 °C): 685 (calcd 685 for C<sub>26</sub>H<sub>39</sub>Br<sub>2</sub>NO<sub>10</sub><sup>+</sup>).

#### 4-(4-diethyltriazenylphenylethynyl)-5-bromophthalimide with chiral branched side chain 74



A flame-dried flask under argon was loaded with dibromoimide **73** (0.225 g, 0.33 mmol), 1-ethynyl-4-diethyltriazenylbenzene **46** (0.066 g, 0.33 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (0.054 g, 0.05 mmol), and CuI (0.006 g, 0.03 mmol). A mixture of degassed Et<sub>3</sub>N (2 mL), THF (1 mL), and MeCN (0.2 mL) was added, the reaction mixture submitted to a freeze-pump-thaw cycle, and heated to 75 °C for 1 d. The reaction was diluted with CH<sub>2</sub>Cl<sub>2</sub>, washed subsequently with aq. sat. NH<sub>4</sub>Cl, aq. sat. NaHCO<sub>3</sub>, and aq. sat. NaCl, dried over MgSO<sub>4</sub>, and concentrated. Crude product was purified by column chromatography (silica gel, eluent gradient CH<sub>2</sub>Cl<sub>2</sub>:MeOH = 50:1 to 20:1) yielding 240 mg of product (91 %).

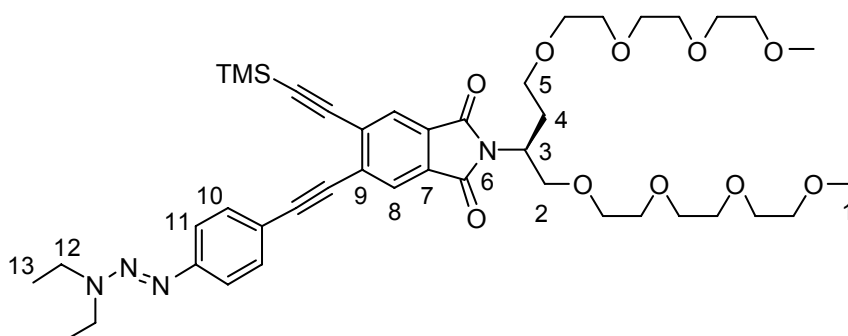
<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): δ(ppm) = 8.02 (d, <sup>5</sup>J(H,H) = 2.6 Hz, 1H, H-8), 7.90 (d, <sup>5</sup>J(H,H) = 2.1 Hz, 1H, H-8'), 7.53 (d, <sup>3</sup>J(H,H) = 8.6 Hz, 2H, H-10), 7.41 (d, <sup>3</sup>J(H,H) = 8.7 Hz, 2H, H-11), 4.60 (m, 1H, H-3), 3.99 (t, <sup>3</sup>J(H,H) = 10.7 Hz, 1H, H-2), 3.77 (q, <sup>3</sup>J(H,H) = 7.2 Hz, 4H,

H-12), 3.8-3.4 (m,  $\text{CH}_2\text{O}$ ), 3.33 (s, 6H, H-1), 2.27 (m, 1H, H-4), 1.94 (m, 1H, H-4'), 1.26 (b, 6H, H-13).

$^{13}\text{C}$ -NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta(\text{ppm}) = 167.4, 166.9, 132.8, 132.2, 131.4, 131.2, 130.2, 128.6, 128.4, 126.9, 120.6, 117.8, 99.8, 87.3, 71.9, 70.5-70.2, 68.4, 59.0, 49.2, 28.7$ .

ESI-MS (pos., MeOH):  $m/z = 804$  (calcd 804 for  $\text{C}_{38}\text{H}_{53}\text{BrN}_4\text{O}_{10}^+$ ).

#### 4-(4-diethyltriazenylphenylethynyl)-5-(TMS-ethynyl)phthalimide with chiral branched side chain 75

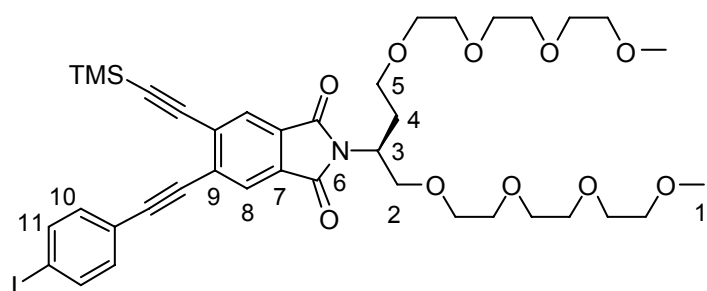


A flame-dried flask was loaded under argon with bromophthalimide **74** (0.230 g, 0.29 mmol), TMSA (0.16 mL, 1.14 mmol),  $\text{Pd}(\text{PPh}_3)_4$  (0.049 g, 0.04 mmol), and  $\text{CuI}$  (0.005 g, 0.03 mmol). A degassed solvent mixture of  $\text{Et}_3\text{N}$  (1.5 mL), THF (1.0 mL), and MeCN (0.15 mL) was added and the reaction mixture submitted to a freeze-pump-thaw cycle and stirred at 75 °C for 22 h. The dark red solution was diluted  $\text{CH}_2\text{Cl}_2$ , washed with  $\text{NH}_4\text{Cl}$ , aq. sat.  $\text{NaHCO}_3$ , and aq. sat.  $\text{NaCl}$ , dried over  $\text{MgSO}_4$ , and concentrated. Purification by column chromatography (silica gel,  $\text{CH}_2\text{Cl}_2:\text{MeOH} = 40:1$ ) yielding 240 mg of the desired product (quantitative).

$^1\text{H}$ -NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta(\text{ppm}) = 7.86$  (s, 1H, H-8), 7.85 (s, 1H, H-8'), 7.51 (d,  $^3\text{J}(\text{H,H}) = 8.4$  Hz, 2H, H-10), 7.40 (d,  $^3\text{J}(\text{H,H}) = 8.5$  Hz, 2H, H-11), 4.59 (m, 1H, H-3), 3.99 (t,  $^3\text{J}(\text{H,H}) = 10.7$  Hz, 1H, H-2), 3.76 (q,  $^3\text{J}(\text{H,H}) = 7.2$  Hz, 4H, H-12), 3.51 (m, 27H,  $\text{CH}_2\text{O}$ ), 3.32 (s, 6H, H-1), 2.28 (m, 1H, H-4), 1.94 (m, 1H, H-4'), 1.25 (b, 6H, H-13), 0.26 (s, 9H, TMS).

$^{13}\text{C}$ -NMR (100.6 MHz,  $\text{CDCl}_3$ ):  $\delta(\text{ppm}) = 167.7, 167.6, 152.1, 133.0, 132.4, 128.7, 128.6, 126.9, 126.1, 120.7, 118.6, 103.9, 102.4, 99.2, 95.8, 87.5, 72.1, 70.7, 70.5, 68.6, 59.2, 49.3, 28.9, 0.1$ .

ESI-MS (pos., MeOH):  $m/z = 822$  (calcd 822 for  $\text{C}_{43}\text{H}_{62}\text{N}_4\text{O}_{10}\text{Si}^+$ ).

**4-(4-iodophenylethynyl)-5-(TMS-ethynyl)phthalimide with chiral branched side chain****40**

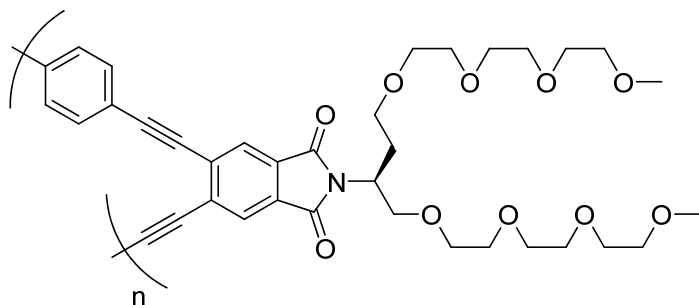
A presurable vessel was loaded with the triazene compound **75** (0.115 g, 0.14 mmol) and MeI (10 mL). The reaction solution was degassed by two freeze-pump-thaw cycles, sealed tight, and heated to 110 °C for 24 h. The dark solution was diluted with CH<sub>2</sub>Cl<sub>2</sub>, filtered, the filtrate concentrated, and purified by column chromatography (silica gel, CH<sub>2</sub>Cl<sub>2</sub>:MeOH = 40:1) (95 mg, 80 %).

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): δ(ppm) = 7.87 (s, 1H, H-8), 7.86 (s, 1H, H-8'), 7.71 (d, <sup>3</sup>J(H,H) = 8.5 Hz, 2H, H-10), 7.26 (d, <sup>3</sup>J(H,H) = 8.4 Hz, 2H, H-11), 4.60 (m, 1H, H-3), 3.99 (t, <sup>3</sup>J(H,H) = 10.0 Hz, 1H, H-2), 3.51 (m, 27H, CH<sub>2</sub>O), 3.33 (s, 6H, H-1), 2.26 (m, 1H, H-4), 1.93 (m, 1H, H-4'), 0.25 (s, 9H, TMS).

<sup>13</sup>C-NMR (100.6 MHz, CDCl<sub>3</sub>): δ(ppm) = 167.28, 167.25, 137.81, 137.68, 133.21, 133.11, 130.95, 130.83, 126.79, 126.03, 121.77, 104.07, 101.89, 96.66, 95.50, 88.53, 71.87, 70.5-70.2, 68.36, 58.98, 49.12, 28.63, -0.19.

ESI-MS (pos., MeOH): *m/z* = 872 (calcd 872 for C<sub>39</sub>H<sub>52</sub>INO<sub>10</sub>SiNa<sup>+</sup>).

ESI-HRMS (pos., CH<sub>2</sub>Cl<sub>2</sub>): *m/z* = 872.229 (calcd 872.230 for C<sub>39</sub>H<sub>52</sub>INO<sub>10</sub>SiNa<sup>+</sup>).

**Poly(*ortho*-phthalimide-alternating-*para*-phenylene diethynylene with chiral branched side chain) **76****

A small Schlenk-tube was loaded with monomer **40** (0.025 g, 0.03 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (0.003 g, 0.003 mmol), CuI (0.001 g, 0.003 mmol), and pre-degassed MeCN (0.2 mL), toluene (0.2 mL), DBU (0.03 mL, 0.18 mmol), and distilled water (0.005 mL, 0.3 mmol). The reaction mixture was submitted to 2 freeze-pump-thaw cycles and stirred at rt for 3d. The mixture was

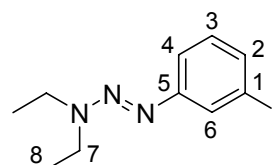
diluted with  $\text{CH}_2\text{Cl}_2$ , filtered, washed subsequently with sat. aq.  $\text{NH}_4\text{Cl}$ , sat. aq.  $\text{NaHCO}_3$ , and sat. aq.  $\text{NaCl}$ . The organic phase was dried over  $\text{MgSO}_4$ , concentrated, and the obtained brown oil dried in vacuo (quantitative).

GPC (40 °C, THF): Mn (PDI) = 2700 (2.3).

### 5.3 Block Copolymers and Graft Copolymers

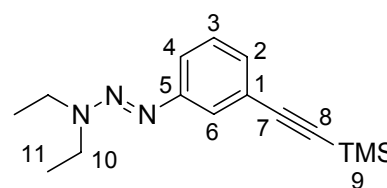
#### 1-Iodo-3-(diethyltriazenyl)benzene **88**<sup>[6]</sup>

3-Iodoaniline **87** (4.2 mL, 34.8 mmol) was added to a solution of 10 mL 37%-HCl, 66 mL water, and 20 mL acetonitrile at 0 °C. To this yellow suspension, an ice-cooled solution of  $\text{NaNO}_2$  (2.46 g, 38.3 mmol) in 35 mL water was added, turning the reaction mixture to a



dark red solution. After stirring for 30 min, an ice-cooled solution of  $\text{K}_2\text{CO}_3$  (7.40 g, 53.5 mmol) and diethylamine (5.5 mL, 52.2 mmol) in 55 mL water was added slowly and the solution stirred for another hour. The product is extracted with diethyl ether, the organic phase separated and dried over  $\text{MgSO}_4$ , the solvent removed, and the obtained dark red oil dried in vacuo (99 %).

$^1\text{H-NMR}$  (250 MHz,  $\text{CDCl}_3$ ):  $\delta(\text{ppm}) = 7.77$  (t,  $4J(\text{H,H}) = 1.8$  Hz, 1H, H-6),  $7.41$  (dd,  $3J(\text{H,H}) = 9.1$  Hz,  $4J(\text{H,H}) = 1.8$  Hz, 1H, H-2),  $7.35$  (dd,  $3J(\text{H,H}) = 8.2$  Hz,  $4J(\text{H,H}) = 1.8$  Hz, 1H, H-4),  $7.03$  (t,  $3J(\text{H,H}) = 7.7$  Hz, 1H, H-3),  $3.74$  (q,  $3J(\text{H,H}) = 7.0$  Hz, 4H, H-7),  $1.25$  (t,  $3J(\text{H,H}) = 6.8$  Hz, 6H, H-8).



$^{13}\text{C-NMR}$  (63 MHz,  $\text{CDCl}_3$ ):  $\delta(\text{ppm}) = 152.5$  (C-5),  $133.6$  (C-2),  $130.2$  (C-6),  $129.0$  (C-3),  $120.3$  (C-4),  $94.5$  (C-1),  $47.8$  (C-7),  $44.7$  (C-7'),  $12.8$  (C-8).

EI-MS (30 °C): 303, 274, 231, 203 (calcd 303 for  $\text{C}_{10}\text{H}_{14}\text{IN}_3^+$ ).

#### 1-(2-(Trimethylsilyl)ethynyl)-3-(diethyltriazenyl)benzene **89**<sup>[6]</sup>

1-Iodo-3-(diethyltriazenyl)benzene **88** (3.94 g, 12.0 mmol), TMS-acetylene (2.6 mL, 18.0 mmol),  $\text{Pd}(\text{PPh}_3)_4$  (1.39 g, 1.2 mmol), and  $\text{CuI}$  (0.23 g, 1.2 mmol) were added to a solution of 40 mL dried  $\text{Et}_3\text{N}$  and 2 mL DMF. The reaction mixture was subjected to two Freeze-Pump-Thaw cycles and then stirred for 17 h at 50-60 °C becoming a brown suspension. The solvent

was removed, the solid redissolved in toluene, filtrated, and the filtrate concentrated. Purification by column chromatography (hexane:ethyl acetate = 20:1) yielded desired product as yellow oil (74 %).

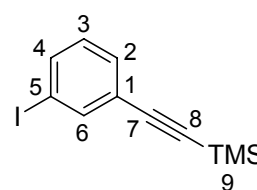
$^1\text{H-NMR}$  (500 MHz,  $\text{CDCl}_3$ ): 7.50 (dt,  $^4\text{J(H,H)} = 1.5$  Hz,  $^5\text{J(H,H)} = 0.6$  Hz, 1H, H-6), 7.33 (td,  $^3\text{J(H,H)} = 7.0$  Hz,  $^4\text{J(H,H)} = 2.1$  Hz, 1H, H-4), 7.19 (dt,  $^3\text{J(H,H)} = 7.6$  Hz,  $^5\text{J(H,H)} = 0.6$  Hz, 1H, H-3), 7.18 (m, 1H, H-2), 3.68 (q,  $^3\text{J(H,H)} = 7.2$  Hz, 4H, H-10), 1.19 (t,  $^3\text{J(H,H)} = 6.9$  Hz, 6H, H-11), 0.21 (s, 9H, H-9).

$^{13}\text{C-NMR}$  (63 MHz,  $\text{CDCl}_3$ ):  $\delta(\text{ppm}) = 151.1$  (C-5), 128.5 (C-2), 128.4 (C-3), 123.8 (C-6), 123.4 (C-1), 121.0 (C-4), 105.6 (C-7), 93.3 (C-8), 44.8 (C-10), 12.8 (C-11), 0.0 (C-9).

EI-MS (80 °C):  $m/z = 273, 258, 201, 173, 73$  (calcd 273 for  $\text{C}_{15}\text{H}_{23}\text{N}_3\text{Si}^+$ ).

### 1-(TMS-ethynyl)-3-iodobenzene 77<sup>[6]</sup>

a) 1-(2-(Trimethylsilyl)ethynyl)-3-(diethyltriazenyl)benzene **89** (1.64 g, 6.0 mmol) was dissolved in 25 mL methyl iodide within a pleasurable-tube. The clear rc-solution was subjected to three Freeze-Pump-Thaw cycles, the flask sealed tight, and the solution heated to



110 °C for 19 h. The now black suspension was diluted with diethyl ether, the solid filtered off, and the red filtrate concentrated affording black oil. Purification by column chromatography yielded yellow solid (89 %).

b) A flame-dried Schlenk-tube was loaded with  $\text{Pd(PPh}_3)_4$  (2.383 g, 2.06 mmol),  $\text{CuI}$  (0.381 g, 2.00 mmol), and 1,3-diiodobenzene **90** (8.248 g, 25.00 mmol). A solvent mixture of pre-degassed and dry 20 mL  $\text{Et}_3\text{N}$ , 20 mL THF, and 3 mL MeCN were added, followed by degassed TMS-acetylene (3.59 mL, 25.25 mmol). The reaction suspension was kept under strong stirring for 1h at rt, then over night at 40 °C. The final suspension was concentrated, dissolved in ethyl acetate, filtrated through a short silica plug, again concentrated, finally purified by column chromatography (silica gel, neat hexanes) to remove starting material and bis(TMS-ethynyl)benzene. The desired monocoupled product was isolated as pale yellow solid. Yield: 4.416 g (59 %)

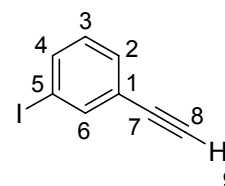
$^1\text{H-NMR}$  (250 MHz,  $\text{CDCl}_3$ ):  $\delta(\text{ppm}) = 7.80$  (d,  $^4\text{J(H,H)} = 1.8$  Hz, 1H, H-6), 7.62 (dd,  $^3\text{J(H,H)} = 9.1$  Hz,  $^4\text{J(H,H)} = 1.8$  Hz, 1H, H-4), 7.40 (dd,  $^3\text{J(H,H)} = 7.3$  Hz,  $^4\text{J(H,H)} = 1.8$  Hz, 1H, H-2), 7.00 (dt,  $^3\text{J(H,H)} = 8.2$  Hz,  $^4\text{J(H,H)} = 2.7$  Hz, 1H, H-3), 0.23 (s, 9H, H-9).

$^{13}\text{C-NMR}$  (63 MHz,  $\text{CDCl}_3$ ):  $\delta(\text{ppm}) = 140.6$  (C-6), 137.5 (C-4), 131.0 (C-2), 129.7 (C-3), 125.3 (C-1), 103.2 (C-7), 95.9 (C-8), 93.5 (C-5), -0.1 (C-9).

EI-MS (30 °C):  $m/z = 300, 285$  (calcd 300 for  $\text{C}_{11}\text{H}_{13}\text{ISi}^+$ ).

**1-Ethynyl-3-iodobenzene 78**

1-(2-(Trimethylsilyl)ethynyl)-3-iodobenzene **77** (0.36 g, 1.2 mmol) and potassium carbonate (0.50 g, 3.6 mmol) are dissolved in a solvent mixture of 5 mL ethanol, 4 mL THF, and 2 mL water. Nitrogen was bubbled through the mixture for several minutes before being stirred



for 3 h at 50 °C. Enough ethyl acetate and brine were added for phase separation to occur, and the org. phase was isolated, washed with aq. sat. NH<sub>4</sub>Cl, and dried over MgSO<sub>4</sub>. After removal of solvent a light beige-white solid was obtained (82 %).

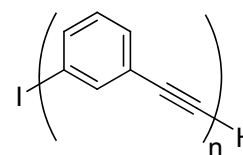
<sup>1</sup>H-NMR (250 MHz, CDCl<sub>3</sub>): δ(ppm) = 7.82 (d, <sup>4</sup>J(H,H) = 1.8 Hz, 1H, H-6), 7.66 (d, <sup>3</sup>J(H,H) = 8.2 Hz, 1H, H-4), 7.43 (d, <sup>3</sup>J(H,H) = 7.3 Hz, 1H, H-2), 7.03 (t, <sup>3</sup>J(H,H) = 7.7 Hz, 1H, H-3), 3.10 (s, 1H, H-9).

<sup>13</sup>C-NMR (63 MHz, CDCl<sub>3</sub>): δ(ppm) = 140.7 (C-6), 137.9 (C-4), 131.2 (C-2), 129.7 (C-3), 124.3 (C-1), 93.5 (C-5), 81.9 (C-7), 78.5 (C-8).

EI-MS (30 °C): *m/z* = 228, 203 (calcd 228 for C<sub>8</sub>H<sub>5</sub>I<sup>+</sup>).

**Poly(*meta*-phenylene ethynylene) 92**

a) A Schlenk-tube was loaded with Pd(PPh<sub>3</sub>)<sub>4</sub> (0.139 g, 0.12 mmol), CuI (0.027 g, 0.14 mmol), 1-(TMS-ethynyl)-3-iodobenzene **77** (0.300 g, 1.00 mmol), and pre-degassed DBU (0.90 mL, 6 mmol), distilled water (0.18 mL, 10.00 mmol), and toluene (2.0 mL). The reaction mixture was



submitted to two freeze-pump-thaw cycles and stirred at rt for 3 d. The mixture was diluted with CH<sub>2</sub>Cl<sub>2</sub>, filtered, and the filtrate poured into MeOH at 0 °C. The generated light yellow precipitate was isolated and dried in vacuo (quantitative).

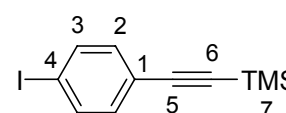
GPC (40 °C, THF): Mn (PDI) = 2300 (1.09).

b) In an analogous way, 1-ethynyl-3-iodobenzene **78** was polymerized at temperatures of 25 - 40 °C using dry toluene or acetonitrile as solvent and triethylamine as base. Yields: 81 - 89 %.

GPC (40 °C, THF): Mn (PDI) = 1700 - 2200 (1.30 - 1.90).

**1-(TMS-ethynyl)-4-iodobenzene 85<sup>[5]</sup>**

The procedure was analogous to the synthesis of 1-(TMS-ethynyl)-3-iodobenzene **77** using 1-(TMS-ethynyl)-4-(diethyltriazenyl)benzene **41** as starting material (90%).



<sup>1</sup>H-NMR (250 MHz, CDCl<sub>3</sub>): δ(ppm) = 7.61 (d, <sup>3</sup>J(H,H) = 8.2 Hz, 2H, H-3), 7.16 (d, <sup>3</sup>J(H,H) = 8.2 Hz, 2H, H-2), 0.24 (s, 9H, H-7).

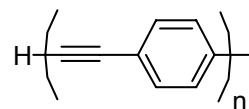


$^{13}\text{C}$ -NMR (63 MHz,  $\text{CDCl}_3$ ):  $\delta(\text{ppm}) = 137.4$  (C-3), 133.4 (C-2), 122.7 (C-1), 104.0 (C-5), 95.9 (C-6), 94.4 (C-4), -0.1 (C-7).

EI-MS (40 °C):  $m/z = 300, 285$  (calcd 300 for  $\text{C}_{11}\text{H}_{13}\text{Si}^+$ ).

### Poly(para-phenylene ethynylene) **86**

A flame-dry Schlenk tube was loaded with  $\text{Pd}(\text{PPh}_3)_4$  (0.139 g, 0.12 mmol),  $\text{CuI}$  (0.027 g, 0.14 mmol), and *p*-(TMS-ethynyl)iodobenzene **85** (0.300 g, 1.00 mmol). 3 mL of toluene was added, followed by 0.90 mL (6.00 mmol) DBU and 0.18 mL (10.00 mmol) distilled water. The reaction mixture was submitted to two freeze-pump-thaw-cycles, and stirred at rt for 3 d. Solid material was filtered off and washed with hot toluene, and the obtained filtrates reduced in volume, and poured into excess ice-cold methanol. The yellow precipitate was isolated and dried in vacuo (175 mg, quantitative yield).



GPC (THF, 40 °C):  $M_n$  (PDI) = 1400 (1.06) (soluble fraction).

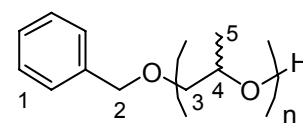
### Benzyl alkoxide

Fresh sodium chunks were added to dry toluene, the suspension cooled to 0 °C followed by careful addition of the benzyl alcohol. The mixture was stirred at 0 °C for 30 min, then 24 h at 50 °C. The obtained yellow suspension was used as obtained (0.45 mol/l).

### Poly(propylene oxide)s

*General procedure for polymerization of propylene oxide:*

A flame dried Schlenk tube under argon was loaded with PO monomer and dry solvent, the tube was cooled to 0 °C, then the suspension containing the alkoxide (0.45 mol/l) and the TIBAL



(0.99 mol/l) solution were added. The reaction tube was closed, kept at 0 °C and heavily stirred for 3 hours. The reaction was quenched with a mixture of  $\text{HCl}/\text{EtOH}$ . The reaction mixture was concentrated and dried in vacuo. Yield: Quantitative.

*Racemic PO/atactic PPO:* Crude polymer was milky viscous liquid. Purification by acidic and basic washing and by precipitation in water:methanol mixture gave colorless clear oil.

*Enantiopure PO/isotactic PPO:* Crude polymer is white solid. Purification by recrystallization from acetone at -20 °C.

*Atactic PPOs:***80a (5k)**

Used reagents: PO 3 mL (42.87 mmol), BnONa suspension 1.381 mL (0.62 mmol), TIBAL 4.395 mL (4.35 mmol), heptane (2.0 mL).

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): δ (ppm) = 7.26 (d, <sup>3</sup>J(H,H) = 4.6 Hz, 4H, H-1<sub>o,m</sub>), 4.49 (d, <sup>4</sup>J(H,H) = 3.4 Hz, 2H, H-2), 3.48 (m, 167H, H-3), 3.34 (m, 85H, H-4), 1.08 (d, <sup>3</sup>J(H,H) = 6.0 Hz, 126 H, H-5), 1.07 (<sup>3</sup>J(H,H) = 6.0 Hz, 126 H, H-5').

<sup>13</sup>C-NMR (100.6 MHz, CDCl<sub>3</sub>): δ (ppm) = 75.40, 75.24, 75.21, 75.01 (4x C-4), 73.28, 73.25, 73.23, 72.87, 72.82, 72.78, 72.73 (7x C-3), 17.35, 17.23 (2x C-5).

GPC (THF, 30 °C, RI): Mn = 12800 (PDI = 1.48).

Mn (<sup>1</sup>H-NMR endgroup analysis) = 4990, Mn (theory): 4000

**80b (10k)**

Used reagents: PO 3 mL (42.87 mmol), BnONa suspension 0.476 mL (0.21 mmol), TIBAL 1.516 mL (1.50 mmol), heptane (5.7 mL).

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): δ (ppm) = 7.29 (d, <sup>3</sup>J(H,H) = 4.7 Hz, 4 H, H-1<sub>o,m</sub>), 4.51 (d, <sup>4</sup>J(H,H) = 4.1 Hz, 2H, H-2), 3.50 (m, 359 H, H-3), 3.36 (m, 181 H, H-4), 1.10 (d, <sup>3</sup>J(H,H) = 6.1 Hz, 271 H, H-5), 1.09 (d, <sup>3</sup>J(H,H) = 6.1 Hz, 271 H, H-5').

<sup>13</sup>C-NMR (100.6 MHz, CDCl<sub>3</sub>): δ (ppm) = 75.15, 74.99, 74.95, 74.75 (4x C-4), 72.99, 72.60, 72.55, 72.51, 72.46 (5x C-3), 17.08, 16.95 (2x C-5).

GPC (THF, 30 °C, RI): Mn = 32400 (PDI = 1.23)

Mn (<sup>1</sup>H-NMR endgroup analysis) = 10560, Mn (theory): 11600

**80c (20k)**

Used reagents: PO 3 mL (42.87 mmol), BnONa suspension 0.238 mL (0.11 mmol), TIBAL 0.758 mL (0.75 mmol), heptane (6.7 mL).

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): δ (ppm) = 7.31 (d, <sup>3</sup>J(H,H) = 4.5 Hz, 4 H, H-1<sub>o,m</sub>), 4.53 (d, <sup>4</sup>J(H,H) = 4.5 Hz, 2 H, H-2), 3.52 (m, 713 H, H-3), 3.38 (m, 367 H, H-4), 1.12 (d, <sup>3</sup>J(H,H) = 6.1 Hz, 530 H, H-5), 1.11 (d, <sup>3</sup>J(H,H) = 6.1 Hz, 530 H, H-5').

<sup>13</sup>C-NMR (100.6 MHz, CDCl<sub>3</sub>): δ (ppm) = 75.17, 75.01, 74.97, 74.76 (4x C-4), 73.02, 72.62, 72.57, 72.53, 72.48 (5x C-3), 17.11, 16.99 (2x C-5).

GPC (THF, 30 °C, RI): Mn = 43800 (PDI = 1.23).

Mn (<sup>1</sup>H-NMR endgroup analysis) = 20840, Mn (theory): 23230.

*Isotactic PPOs:***81a (5k)**

Used reagents: PO 3 mL (42.87mmol), BnONa suspension 1.381 mL (0.62 mmol), TIBAL 4.395 mL (4.35 mmol), 1.95 mL heptane.

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): δ (ppm) = 7.29 (d, <sup>3</sup>J(H,H) = 4.4 Hz, 4H, H-1<sub>o,m</sub>), 4.51 (d, <sup>4</sup>J(H,H) = 0.9 Hz, 2H, H-2), 3.50 (m, 180H, H-3), 3.36 (m, 91H, H-4), 1.09 (d, <sup>3</sup>J(H,H) = 6.2 Hz, 292H, H-5).

<sup>13</sup>C-NMR (100.6 MHz, CDCl<sub>3</sub>): δ (ppm) = 128.3 (C<sub>m-Ar</sub>), 127.5 (C<sub>o-Ar</sub>), 75.5 (C-4), 73.4 (C-3), 17.4 (C-5).

GPC (40 °C, THF): Mn (PDI) = 6500 (1.90).

Mn (<sup>1</sup>H-NMR endgroup analysis) = 5300, Mn (theory): 4100.

**81b (10k)**

Used reagents: PO 3 mL (42.87mmol), BnONa suspension 0.476 mL (0.21 mmol), TIBAL 1.516 mL (1.50 mmol), 5.7 mL heptane.

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): δ(ppm) = 7.27 (d, <sup>3</sup>J(H,H) = 4.7 Hz, 4H, H-1<sub>o,m</sub>), 4.91 (s, 2H, H-2), 3.49 (m, 347H, H-3), 3.35 (m, 173H, H-4), 1.07 (d, <sup>3</sup>J(H,H) = 6.1 Hz, 522H, H-5).

<sup>13</sup>C-NMR (100.6 MHz, CDCl<sub>3</sub>): δ(ppm) = 128.2 (C<sub>m-Ar</sub>), 127.5 (C<sub>o-Ar</sub>), 75.4 (C-4), 73.3 (C-3), 65.5 (C-2), 17.4 (C-5).

GPC (40 °C, THF): Mn (PDI) = 14300 (2.30).

Mn (<sup>1</sup>H-NMR endgroup analysis) = 12000, Mn (theory): 11600.

**81c (20k)**

Used reagents: PO 3 mL (42.87mmol), BnONa suspension 0.286 mL (0.13 mmol), TIBAL 0.909 mL (0.90 mmol), 6.6 mL heptane.

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): δ(ppm) = 7.29 (d, <sup>3</sup>J(H,H) = 4.5 Hz, 4H, H-1<sub>o,m</sub>), 4.50 (s, 2H, H-2), 1202H, H-3), 3.37 (m, 627H, H-4), 1.09 (d, <sup>3</sup>J(H,H) = 6.1 Hz, 1781H, H-5).

<sup>13</sup>C-NMR (100.6 MHz, CDCl<sub>3</sub>): δ(ppm) = 75.5 (C-4), 73.4 (C-3), 17.4 (C-5).

GPC (40 °C, THF): Mn (PDI) = 50000 (1.25).

Mn (<sup>1</sup>H-NMR endgroup analysis) = 24700, Mn (theory): 19400.

**81d (2k)**

Used reagents: PO 3 mL (42.87 mmol), BnONa suspension 2.858 mL (1.286 mmol), TIBAL 6.495 mL (6.43 mmol).

$^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta(\text{ppm}) = 7.28$  (d,  $^3\text{J}(\text{H,H}) = 4.2$  Hz, 4H, H-1<sub>o,m</sub>), 4.50 (d,  $^4\text{J}(\text{H,H}) = 0.8$  Hz, 2H, H-2), 3.49 (m, 109H, H-3), 3.36 (m, 54H, H-4), 1.09 (d,  $^3\text{J}(\text{H,H}) = 6.2$  Hz, 180H, H-5).

$^{13}\text{C-NMR}$  (100.6 MHz,  $\text{CDCl}_3$ ):  $\delta(\text{ppm}) = 138.4$  (C-1), 128.2 (C-1'), 127.4 (C-1''), 75.4 (C-4), 73.4 (C-3), 65.5 (C-2), 17.4 (C-5).

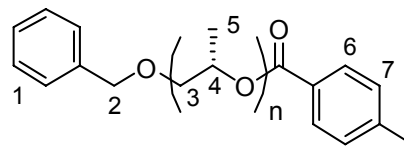
GPC (30 °C, THF): Mn (PDI) = 8300 (1.10).

Mn ( $^1\text{H-NMR}$  endgroup analysis) = 2900, Mn (theory): 2000.

### PPO-(*para*-iodobenzoate)

*General procedure for coupling para-iodobenzoic acid chloride to hydroxyl-terminated PPOs:*

A dry Schlenk tube was loaded with PPO **81**, dry  $\text{CH}_2\text{Cl}_2$ , and dry  $\text{Et}_3\text{N}$ . The solution was cooled to 0 °C and a solution of 10-fold excess acid chloride **28** in  $\text{CH}_2\text{Cl}_2$  was



slowly, followed by DMAP. The beige suspension was

stirred for 1 h at 0 - 5 °C and then left overnight to warm up to rt. The suspension was diluted with  $\text{CH}_2\text{Cl}_2$ , filtered, and the obtained clear filtrate washed subsequently with sat. aq.  $\text{NH}_4\text{Cl}$ , sat. aq.  $\text{NaHCO}_3$ , and sat. aq.  $\text{NaCl}$ . The organic phase was dried over  $\text{MgSO}_4$ , filtered, concentrated, and dried in vacuo. The obtained solid was recrystallized from acetone at -20 °C, isolated and redissolved in  $\text{CH}_2\text{Cl}_2$  and residual solids consisting of hydrolyzed acid chloride filtered off. The solution was concentrated, dried by wrapping with benzene, and finally dried in vacuo over prolonged time.

### 82a (5k)

Used reagents: PPO **81a** 1.000 g (0.20 mmol), iodobenzoic acid chloride **28** 0.533 g (2.00 mmol), DMAP 0.012 g (0.10 mmol),  $\text{Et}_3\text{N}$  (0.30 mL),  $\text{CH}_2\text{Cl}_2$  (6 mL). Yield: 0.61 g (58 %).

$^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta(\text{ppm}) = 7.75$  (d,  $^3\text{J}(\text{H,H}) = 8.7$  Hz, 2H, H-7), 7.70 (d,  $^3\text{J}(\text{H,H}) = 8.7$  Hz, 2H, H-6), 7.30 (d,  $^3\text{J}(\text{H,H}) = 4.3$  Hz, 4H, H-1<sub>o,m</sub>), 5.20 (m, 1H, H-4<sub>end</sub>), 4.51 (s, 2H, H-2), 3.50 (m, 217H, H-3), 3.37 (m, 110H, H-4), 1.31 (d,  $^3\text{J}(\text{H,H}) = \text{xx}$  Hz, 3H, H-5<sub>end</sub>), 1.09 (d,  $^3\text{J}(\text{H,H}) = 6.2$  Hz, 338H, H-5).

GPC (40 °C, THF): Mn (PDI) = 14100 (1.13).

### 82b (10k)

Used reagents: PPO **81b** 1.000 g (0.1 mmol), iodobenzoic acid chloride **28** 0.266 g (1.00 mmol), DMAP 0.006 g (0.05 mmol),  $\text{Et}_3\text{N}$  (0.15 mL),  $\text{CH}_2\text{Cl}_2$  (3 mL). Yield: 1.02 g (quantitative).

$^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta(\text{ppm}) = 7.74$  (d,  $^3\text{J}(\text{H,H}) = 8.7$  Hz, 2H, H-7),  $7.70$  (d,  $^3\text{J}(\text{H,H}) = 8.7$  Hz, 2H, H-6),  $7.28$  (d,  $^3\text{J}(\text{H,H}) = 4.6$  Hz, 4H, H-1<sub>o,m</sub>),  $5.19$  (m, 1H, H-4<sub>end</sub>),  $4.51$  (s, 2H, H-2),  $3.50$  (m, 452H, H-3),  $3.37$  (m, 228H, H-4),  $1.30$  (d,  $^3\text{J}(\text{H,H}) = 6.4$  Hz, 3H, H-5<sub>end</sub>),  $1.09$  (d,  $^3\text{J}(\text{H,H}) = 6.2$  Hz, 676H, H-5).

GPC (40 °C, THF): Mn (PDI) = 31200 (1.13).

### 82c (20k)

Used reagents: PPO **81c** 1.000 g (0.05 mmol), iodobenzoic acid chloride **28** 0.133 g (0.50 mmol), DMAP 0.003 g (0.03 mmol),  $\text{Et}_3\text{N}$  (0.07 mL),  $\text{CH}_2\text{Cl}_2$  (1.5 mL). Yield: 0.99 g (98 %).

$^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta(\text{ppm}) = 7.75$  (d,  $^3\text{J}(\text{H,H}) = 8.2$  Hz, 2H, H-6),  $7.70$  (d,  $^3\text{J}(\text{H,H}) = 8.2$  Hz, 2H, H-7),  $7.30$  (d,  $^3\text{J}(\text{H,H}) = \text{xx}$  Hz, 4H, H-1<sub>o,m</sub>),  $4.51$  (s, 2H, H-2),  $5.20$  (m, 1H, H-4<sub>end</sub>),  $3.50$  (m, 1118H, H-3),  $3.37$  (m, 567H, H-4),  $1.30$  (d,  $^3\text{J}(\text{H,H}) = 6.5$  Hz, 3H, H-5<sub>end</sub>),  $1.10$  (d,  $^3\text{J}(\text{H,H}) = 5.9$  Hz, 1692H, H-5).

GPC (40 °C, THF): Mn (PDI) = 49500 (1.22).

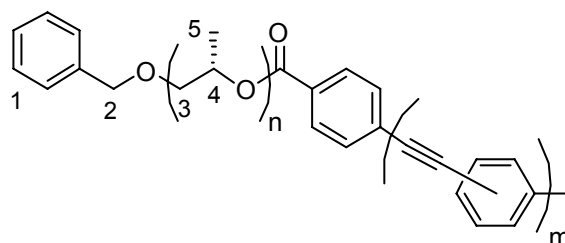
### PPO-block-PpPE and PPO-block-PmPE copolymers

*General procedure for polymerization of para-ethynyl-iodobenzene or meta-ethynyl-iodobenzene to activated PPOs of different lengths:*

A flame dried Schlenk tube was loaded with activated PPO **82**, PE monomer **78** or **83**, respectively and catalysts  $\text{Pd}(\text{PPh}_3)_4$  and  $\text{CuI}$ .

Finally a solvent mixture of pre-degassed THF,  $\text{Et}_3\text{N}$ , and MeCN was added. The reaction flask

was covered with aluminum and stirred at rt for 3 d. The heavy suspension was diluted with  $\text{CH}_2\text{Cl}_2$  and washed subsequently with sat. aq.  $\text{NH}_4\text{Cl}$ , sat. aq.  $\text{NaHCO}_3$ , and sat. aq.  $\text{NaCl}$  before continuing with individual purification procedures.



*Poly(propylene oxide)-block-poly(para-phenylene ethynylene)s:*

### 84a (5k)

Used reagents: activated PPO **82a** 0.100 g (0.02 mmol), 1-ethynyl-4-iodobenzene **83** 0.412 g (1.81 mmol),  $\text{Pd}(\text{PPh}_3)_4$  0.191 g (0.166 mmol),  $\text{CuI}$  0.028 g (0.150 mmol), THF (3.0 mL),  $\text{Et}_3\text{N}$  (3.0 mL), MeCN (0.3 mL). Yield: 53 %

$^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta(\text{ppm}) = 8.02 - 7.25$  (m, 32H, H<sub>Ar</sub>),  $4.53$  (s, 2H, H-2),  $3.52$  (m, 167H, H-3),  $3.39$  (m, 85H, H-4),  $1.12$  (d,  $^3\text{J}(\text{H,H}) = 6.1$  Hz, 270H, H-5).

**84b (10k)**

Used reagents: activated PPO **82b** 0.100 g (0.01 mmol), 1-ethynyl-4-iodobenzene **83** 0.171 g (0.75 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> 0.090 g (0.078 mmol), CuI 0.014 g (0.075 mmol), THF (1.5 mL), Et<sub>3</sub>N (1.5 mL), MeCN (0.2 mL). Yield: 45 %

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): δ(ppm) = 8.06 - 7.26 (m, 53H, H<sub>Ar</sub>), 5.25 (b, 1H, H-4<sub>end</sub>), 4.53 (s, 2H, H-2), 3.52 (m, 570H, H-3), 3.40 (m, 285H, H-4), 1.12 (d, <sup>3</sup>J(H,H) = 6.1 Hz, 861H, H-5).

GPC (30 °C, THF): Mn (PDI) = 15600 (2.68).

**84c (20k)**

Used reagents: activated PPO **82c** 0.100 g (0.005 mmol), 1-ethynyl-4-iodobenzene **83** 0.114 g (0.50 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> 0.049 g (0.043 mmol), CuI 0.007 g (0.038 mmol), THF (0.75 mL), Et<sub>3</sub>N (0.75 mL), MeCN (0.1 mL). Yield: 38 %

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): δ(ppm) = 8.02 - 7.26 (m, 64H, H<sub>Ar</sub>), 5.25 (b, 1H, H-4<sub>end</sub>), 4.52 (s, 2H, H-2), 3.51 (m, 1075H, H-3), 3.38 (m, 545H, H-4), 1.10 (d, <sup>3</sup>J(H,H) = 6.0 Hz, 1589H, H-5).

*Poly(propylene oxide)-block-poly(meta-phenylene ethynylene)s:*

**91a (5k)**

Used reagents: activated PPO **82a** 0.100 g (0.02 mmol), 1-ethynyl-3-iodobenzene **78** 0.456 g (2.00 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> 0.256 g (0.22 mmol), CuI 0.038 g (0.20 mmol), THF (3.0 mL), Et<sub>3</sub>N (3.0 mL), MeCN (0.35 mL).

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): δ(ppm) = 8.02 - 7.26 (m, 49H, H<sub>Ar</sub>), 5.23 (m, 1H, H-4<sub>end</sub>), 4.52 (s, 1H, H-2), 3.51 (m, 273H, H-3), 3.39 (m, 136H, H-4), 1.34 (d, <sup>3</sup>J(H,H) = 6.4 Hz, 3H, H-5<sub>end</sub>), 1.10 (d, <sup>3</sup>J(H,H) = 6.2 Hz, 440H, H-5).

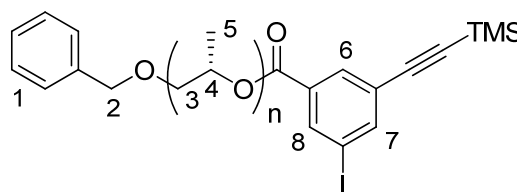
**91b (20k)**

Used reagents: activated PPO **82b** 0.100 g (0.01 mmol), 1-ethynyl-3-iodobenzene **78** 0.228 g (1.00 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> 0.127 g (0.11 mmol), CuI 0.019 g (0.10 mmol), THF (1.5 mL), Et<sub>3</sub>N (1.5 mL), MeCN (0.2 mL).

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): δ(ppm) = 8.01 - 7.26 (m, 35H, H<sub>Ar</sub>), 5.23 (m, 1H, H-4<sub>end</sub>), 4.52 (s, 2H, H-2), 3.51 (m, 465H, H-3), 3.38 (m, 236H, H-4), 1.33 (d, <sup>3</sup>J(H,H) = 6.4 Hz, 3H, H-5<sub>end</sub>), 1.10 (d, <sup>3</sup>J(H,H) = 6.1 Hz, 717H, H-5).

*Graft Copolymer.***PPO-(3-iodo-5-(TMS-ethynyl)benzoate) 94**

A flame-dried flask was loaded under argon with 3-iodo-5-(TMS-ethynyl)benzoic acid **93** (0.034 g, 0.10 mmol), PPO **81b** (0.200 g, 0.02 mmol), DPTS (0.009 g, 0.03 mmol), and 0.2 mL dry CH<sub>2</sub>Cl<sub>2</sub>. The



mixture was cooled to 0 °C and a solution of DIC (0.019 g, 0.12 mmol) in 0.1 mL CH<sub>2</sub>Cl<sub>2</sub> was added dropwise. The suspension was stirred for 5 d at rt, filtered, the filtrate concentrated. The residue was suspended in toluene, the generated urea filtered off, and the filtrate concentrated. The crude product was recrystallized from acetone at -20 °C (0.186 g, 90 %).

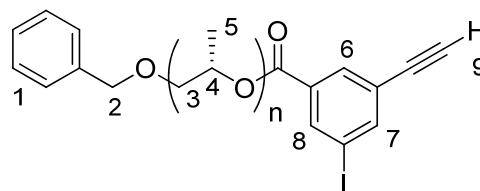
<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): δ(ppm) = 8.23 (s, 1H, H-6), 8.01 (s, 1H, H-8), 7.91 (s, 1H, H-7), 7.29 (d, <sup>3</sup>J(H,H) = 4.8 Hz, 4H, H-1<sub>o,m</sub>), 5.20 (m, 1H, H-4<sub>end</sub>), 4.50 (s, 2H, H-2), 3.50 (m, 463H, H-3), 3.37 (m, 235H, H-4), 1.29 (d, <sup>3</sup>J(H,H) = 6.4 Hz, 3H, H-5<sub>end</sub>), 1.09 (d, <sup>3</sup>J(H,H) = 6.1 Hz, 694H, H-5), 0.20 (s, 9H, TMS).

<sup>13</sup>C-NMR (100.6 MHz, CDCl<sub>3</sub>): δ(ppm) = 144.4, 138.2, 132.4, 128.3, 127.4, 75.5, 73.4, 17.4, -0.3.

GPC (30 °C, THF): Mn (PDI) = 30600 (1.16).

**PPO-(3-iodo-5-ethynylbenzoate) 95**

TMS-protected macromonomer **94** (0.090 g, 0.009 mmol) was dissolved in 0.15 mL THF. A 1 molar solution of TBAF in THF (0.013 mL, 0.013 mmol) was added together with a drop of distilled water. The reaction mixture was stirred for 1 h, diluted with



CH<sub>2</sub>Cl<sub>2</sub>, and filtered through a short silica gel plug. The solution was concentrated and recrystallized from acetone at -20 °C yielding a white crystalline solid (0.092 g, quantitative).

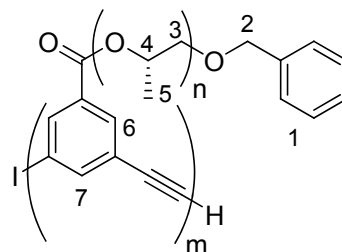
<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): δ(ppm) = 8.28 (t, <sup>4</sup>J(H,H) = 1.5 Hz, 1H, H-6), 8.05 (t, <sup>4</sup>J(H,H) = 1.3 Hz, 1H, H-8), 7.94 (t, <sup>4</sup>J(H,H) = 1.4 Hz, 1H, H-7), 7.30 (d, <sup>3</sup>J(H,H) = 4.3 Hz, 4H, H-1<sub>o,m</sub>), 5.21 (m, 1H, H-4<sub>end</sub>), 4.51 (s, 2H, H-2), 3.49 (m, 510H, H-3), 3.37 (m, 262H, H-4), 3.15 (s, 1H, H-9), 1.30 (d, <sup>3</sup>J(H,H) = 6.4 Hz, 3H, H-5<sub>end</sub>), 1.09 (d, <sup>3</sup>J(H,H) = 6.4 Hz, 791H, H-5).

<sup>13</sup>C-NMR (100.6 MHz, CDCl<sub>3</sub>): δ(ppm) = 144.4, 138.6, 132.3, 128.3, 127.5, 93.1, 75.5, 73.6, 17.3.

GPC (30 °C, THF): Mn (PDI) = 22900 (1.60).

**PPO-graft-PmPE copolymer 96**

A flame-dried flask was loaded with desilylated macromonomer **95** (0.088 g, 0.009 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (2 mg, 1.3 μmol), and CuI (0.2 mg, 0.9 μmol). A pre-degassed solvent mixture of 0.15 mL THF, 0.15 mL Et<sub>3</sub>N, and 0.05 mL MeCN was added, the reaction mixture submitted to a freeze-pump-thaw cycle, and stirred at rt for 3 d. The mixture was diluted with CH<sub>2</sub>Cl<sub>2</sub>, washed with aq.



sat. NH<sub>4</sub>Cl, aq. sat. NaHCO<sub>3</sub>, and aq. sat. NaCl. The organic phase was dried over MgSO<sub>4</sub>, concentrated, and the obtained solid recrystallized from acetone at -20 °C (0.063 g, 71 %).

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): δ(ppm) = 8.15 (b, 2H, H-6), 7.85 (b, 1H, H-7), 7.30 (d, <sup>3</sup>J(H,H) = 4.4 Hz, 4H, H-1<sub>o,m</sub>), 4.51 (s, 2H, H-2), 3.51 (m, 435H, H-3), 3.38 (m, 218H, H-4), 1.35 (d, <sup>3</sup>J(H,H) = 4.6 Hz, 3H, H-5<sub>end</sub>), 1.10 (d, <sup>3</sup>J(H,H) = 6.0 Hz, 660H, H-5).

<sup>13</sup>C-NMR (100.6 MHz, CDCl<sub>3</sub>): δ(ppm) = 128.3, 127.5, 75.5, 73.4, 17.4.

GPC (30 °C, THF): Mn (PDI) = 123500 (1.16).

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