



Supporting Information

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Helicity Inversion in Novel Responsive Foldamers Induced by Achiral Halide Anions

Robert M. Meudtner and Stefan Hecht*

Department of Chemistry, Humboldt-Universität zu Berlin

Brook-Taylor-Str. 2, 12489 Berlin, Germany

Fax: (+49) 30 2093-6940; E-mail: sh@chemie.hu-berlin.de

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General Methods. Solvents and starting materials were used as received. 3,6,9-Trioxadecan-1-ol (triethyleneglycol monomethyl ether), 3,5-dinitrobenzoic acid and 3-nitrobenzoic acid are commercially available as bulk chemical and were used without further purification. Tetrahydrofuran (THF) was distilled under an inert gas (Ar) atmosphere from sodium/benzophenone prior to use for the reactions requiring absolute THF. The chiral side chain (2S)-4,7,10,13-tetraoxatetradecan-2-ol,^[1] AA' monomer 6-ethynyl-2-[(triisopropylsilyl)ethynyl]-4-(3,6,9-trioxadec-1-yloxy)pyridine **1**,^[2] and esterification catalyst 4-dimethylaminopyridinium *p*-toluenesulfonate (DPTS)^[3] were prepared using previously published procedures. Pd(PPh₃)₄ was freshly prepared.^[4] All reactions requiring inert gas were performed under Ar atmosphere. The Cu-catalyzed cycloaddition reactions were performed in the dark under argon atmosphere, solid sodium ascorbate and concentrated aqueous CuSO₄ stock solutions (10 mg CuSO₄/0.3 mL of H₂O) were used as *in-situ* Cu(I)-source. An aqueous EDTA-disodium salt solution (16 g/L Na₂-EDTA), adjusted to a pH ~ 8-9, was used to remove Cu-ions in aqueous extraction steps. Column chromatography was carried out with 130 – 400 mesh silica gel using the eluents specified (PE = petroleum ether, EtOAc = ethyl acetate). NMR spectra were recorded on a 300 MHz (75.6 MHz for ¹³C) Bruker DPX 300 spectrometer or a 300 MHz Bruker Avance II spectrometer at 23 °C using residual protonated solvent signals as internal standard (¹H: δ(CHCl₃) = 7.26 ppm and ¹³C: δ(CHCl₃) = 77.11 ppm). Assignments are based on chemical shifts (Ar is used as abbreviation for assigning both aromatic as well as triazole moieties). Mass spectrometry was performed on Thermo LTQ FT instrument (ESI, ESI-HRMS; additives of mixtures of MeOH/H₂O 75/25 + 0.5 % formic acid) and MSI Concept 1H (EI, 70 eV ionization) as well as on a QSTARXL Applied Biosystems ESI Q-TOF with a ISV of 950 V. HPLC separations were performed with Shimadzu LC-10A systems equipped with a photodiode array detector (PAD or DAD; mixtures of water/MeOH as eluent) or with Waters Alliance systems (mixtures and gradient mixtures of acetonitrile/water) equipped with 150 x 2 mm Luna columns (3 μm, phenyl-hexyl material). The Waters systems consisted of a Waters Separations Module 2695, a Waters Diode Array detector 996 and a Waters Mass Detector ZQ 2000. Conditions are specified when describing the corresponding substances. Signals have been detected by UV between 200-400 nm

[1] A. Khan, C. Kaiser, S. Hecht, *Angew. Chem.* **2006**, *118*, 1912-1915; *Angew. Chem. Int. Ed.* **2006**, *45*, 1878- 1881.

[2] R. M. Meudtner, M. Ostermeier, R. Goddard, C. Limberg, S. Hecht *Chem. Eur. J.* **2007**, *13*, 9834-9840.

[3] J. S. Moore, S. I. Stupp, *Macromolecules* **1990**, *23*, 65-70.

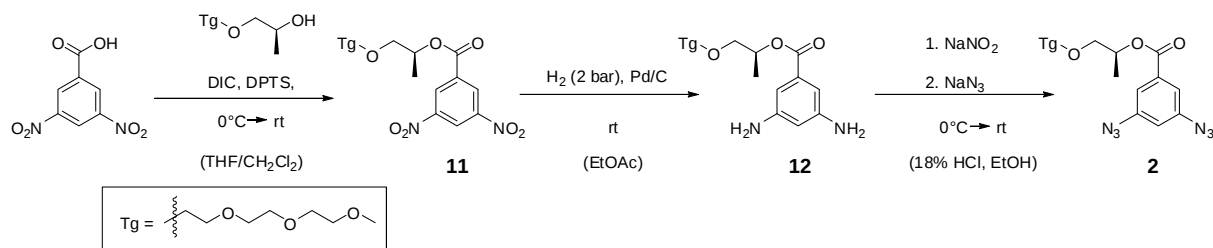
[4] D. R. Coulson, *Inorg. Syn.* **1971**, *13*, 121-124.

(MaxPlot). GPC measurements were performed on a WGE Dr. Bures system equipped with three 300 x 8 mm SDV columns (50 Å 5 µ PSS, 500 Å 5 µ PSS, 1000 Å 5 µ PSS) and one 50 x 8 mm SDV column using both UV (300 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.

UV-visible absorption and fluorescence emission spectra were recorded in quartz cuvettes of 1 cm path length on a Cary 50 Spectrophotometer and a Cary Eclipse Fluorimeter, respectively, each equipped with a Peltier thermostated cell holder at 25 ± 0.05 °C using spectrophotometric grade solvents. Emission spectra were corrected for variations in photomultiplier response and lamp intensity over wavelength using correction curves generated on the instrument, followed by normalization considering the optical density of the sample at the excitation wavelength. The samples were excited at $\lambda = 265$ nm, slit widths were set to 10 nm bandpass for excitation and 10 nm bandpass for emission. Optical response experiments of oligomer **10** towards halide anions were performed in solvent mixtures of 75 vol% water in acetonitrile at 25 °C and a halide anion concentration of $7.5 \cdot 10^{-2}$ M. Note that due to the low concentrations, necessary to avoid aggregation and for analytical reasons (CD spectroscopy), large excess of halide anions had to be employed to achieve binding and therefore titration experiments to deduce binding stoichiometry were not possible. Circular dichroism spectra were recorded on a JASCO J-710 spectropolarimeter using quartz cuvettes of 1 cm path length at 25 ± 1 °C. In some cases circular dichroism spectra recorded as θ in millidegrees, were converted in $\Delta\epsilon$ using the equation $\Delta\epsilon = \theta/32980 \cdot c \cdot l$, where $\Delta\epsilon$ is the molar circular-dichroism absorption in $\text{M}^{-1} \text{cm}^{-1}$, c is the concentration in mol/L, and l is the path length of the cuvette ($= 1$ cm). Temperature dependent CD measurements were performed over a temperature range starting at 5 °C up to 75 °C by heating the sample in temperature intervals of 10 K, allowing the sample to equilibrate for 40 min at each temperature (until the CD signal intensity remained constant). The influence of 18-crown-6 on the folding behavior of oligomer **10** in the presence of potassium halides was analyzed by using an aqueous 0.22 M 18-crown-6 solution, which was mixed with an aqueous 0.20 M KBr solution, stirred at rt for 30 min, and after addition of an acetonitrile solution containing oligomer **10** CD spectra were recorded in an overall 75 vol% water in acetonitrile solution.

The molecular model of heptadecamer **10** (MS Figure 1) was generated via semiempirical PM3 geometry optimization of a “rational” model, which was constructed from DFT-optimized BTP segments joined in a reasonable geometry. Note that due to the projected exhausting calculation times appropriate higher level calculations have not been attended.

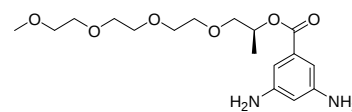
Synthesis of the chiral diazido benzoate building block



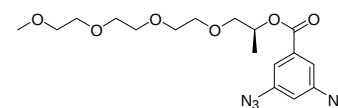
In a two-necked flask 18.01 g 3,5-dinitrobenzoic acid (84.9 mmol, 1.15 equiv.) and 16.4 g (2S)-4,7,10,13-tetraoxatetradecan-2-ol (73.8 mmol, 1 equiv.) were dissolved in 50 mL of dry THF at rt and after cooling the mixture down to 0 °C under argon atmosphere a mixture of 5.44 g DPTS (18.5 mmol, 0.25 equiv.) dissolved in CH₂Cl₂ was added. 13.8 mL of *N,N'*-diisopropylcarbodiimide (88.6 mmol, 1.2 equiv.) were added drop wise in the counterflow of argon using a syringe whereupon a colorless precipitate appeared immediately and the mixture became viscous. After 10 min the mixture was allowed to reach rt and stirred over night at rt under argon. After consumption of all starting material indicated by TLC monitoring the reaction was quenched with 100 mL of water and stirred for ½ h. The solvent was removed in *vacuo* and the residue was dried in oil pump *vacuo* for 1 h, toluene added and the colorless solid was filtered off. After standing in the fridge for 4 h the mixture was filtered again, the solvent removed in *vacuo* and the title compound was isolated as pale yellow oil using column chromatography (PE/EtOAc 7/3 → EtOAc) in 85-95% yield. **TLC** (PE/EtOAc 2/8) R_f = 0.44. **¹H-NMR** (300 MHz, CDCl₃): δ (ppm) = 9.18 (t, J⁴ = 2.1 Hz, 1H, Ar-*H*), 9.12 (d, J⁴ = 2.1 Hz, 2H, Ar-*H*), 5.46 – 5.36 (m, 1H, CHCH₃), 3.76 – 3.55 (m, 12H, OCH₂), 3.51 – 3.47 (m, 2H, OCH₂), 3.32 (s, 3H, OCH₃), 1.40 (d, J³ = 6.6 Hz, 3H, CHCH₃). **¹³C-NMR** (75 MHz, CDCl₃): δ (ppm) = 162.03 (-CO₂-), 148.57 (NO₂C_{Ar}), 134.26 (C_{Ar}), 129.47 (CH_{Ar}), 122.24 (CH_{Ar}), 73.36 (OCH₂), 72.46 (CHCH₃), 71.85 (OCH₂), 70.74 (OCH₂), 70.56 (OCH₂), 70.54 (OCH₂), 70.45 (OCH₂), 58.95 (OCH₃), 16.54 (CHCH₃). **MS** (ESI): *m/z* = 417.1 ([M + H]⁺), 434.1 ([M + NH₄]⁺), 439.1 ([M + Na]⁺), 455.1 ([M + K]⁺). **HRMS** (ESI): *m/z* = 439.1324 (calcd 439.1323 for [M + Na]⁺). **HPLC** (CH₃CN/H₂O 4/6 → 95/5, t_R = 11.3 min.): 99.9 area %.

(2S)-4,7,10,13-tetraoxatetradecan-2-yl 3,5-diaminobenzoate 12

1.053 g (2.53 mmol, 1 equiv.) **11** were treated with 0.11 g Pd on activated carbon (10% wt) in 10 mL of ethyl acetate and the mixture was evacuated and flushed with H₂ repeatedly (3 cycles) and afterwards stirred under H₂ atmosphere (2 bar) for 6 h to give 898 mg of the title compound as a brown oil (quantitative yield). **TLC** (CH₂Cl₂/acetone 8/2 + 0.1 % TEA) R_f = 0.12. **¹H-NMR** (300 MHz, CDCl₃): δ (ppm) = 6.80 (d, J⁴ = 2.1 Hz, 2H, ArH), 6.21 (t, J⁴ = 2.0 Hz, 1H, ArH), 5.31 – 5.21 (m, 1H, CHCH₃), 3.73 – 3.51 (m, 14H, OCH₂), 3.37 (s, 3H, OCH₃), 1.33 (d, J³ = 6.5 Hz, 3H, CHCH₃). **¹³C-NMR** (75 MHz, CDCl₃): δ (ppm) = 166.36 (-CO₂-), 147.21 (NH₂C_{Ar}), 132.50 (CO₂C_{Ar}), 107.38 (HC_{Ar}), 105.97 (HC_{Ar}), 73.83 (OCH₂), 71.99 (OCH₂), 70.93 (CHCH₃), 70.74 (OCH₂), 70.68 (OCH₂), 70.57 (OCH₂), 69.94 (OCH₂), 59.11 (OCH₃), 16.81 (CHCH₃). **MS** (EI T = 155 °C): m/z = 356 ([M]⁺), 193 ([M - C₇H₁₅O₃]⁺), 152, 135 ([C₁₀H₁₃N₂O₂]⁺), 107, 80, 59 ([C₃H₇O]⁺), 45 ([C₂H₅O]⁺). **HRMS** (ESI): m/z = 379.1833 (calcd 379.1839 for [M + Na]⁺). **HPLC** (CH₃CN/H₂O 4/6 → 95/5, t_R = 2.6 min.): 99.9 area %.

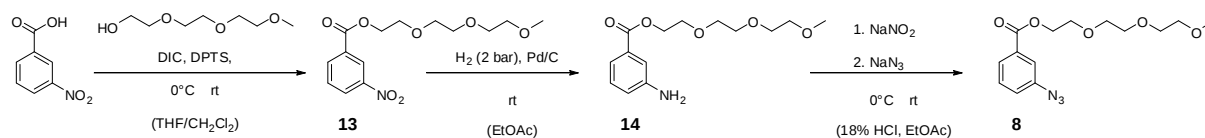
**(2S)-4,7,10,13-tetraoxatetradecan-2-yl 3,5-diazidobenzoate 2**

0.906 g **12** (2.543 mmol, 1 equiv.) were dissolved in 50 ml of 37 % HCl, cooled down to 0 °C and treated successively with small portions of 0.597 g NaNO₂ (8.646 mmol, 3.4 equiv.) and after stirring for 20 min at 0 °C 0.562 g NaN₃ (8.646 mmol, 3.4 equiv.) were added gradually. Stirring was continued for 15 min. at 0 °C and afterwards the mixture was allowed to reach rt and after stirring at rt for 20 min it was poured into 150 mL of ice cold water, transferred into a separation funnel and the aqueous phase was extracted with ethyl acetate (4 x). The combined organic phases were washed with water (1 x), sat. NaHCO₃ solution (1 x) and aqueous sat. NaCl solution. After drying over MgSO₄ the solvent was removed *in vacuo*. 0.78 g of the title compound were obtained as an orange oil after purification by column chromatography (gradient of CH₂Cl₂/MeOH 96/4 → 94/6) (yields ranging from 75-90%). **TLC** (CH₂Cl₂/acetone 8/2) R_f = 0.42. **¹H-NMR** (300 MHz, CDCl₃): δ (ppm) = 7.47 (d, J⁴ = 2.1 Hz, 2H, ArH), 6.8 (t, J⁴ = 2.1 Hz, 1H, ArH), 5.33 - 5.31 (m, 1H, CHCH₃), 3.76 - 3.53 (m, 14H, OCH₂), 3.37 (s, 3H, OCH₃), 1.37 (d, J³ = 6.4 Hz, 3H, CHCH₃). **¹³C-NMR** (75 MHz, CDCl₃): δ (ppm) = 164.10 (-CO₂), 141.87 (N₃C_{Ar}), 133.46 (CO₂C_{Ar}), 116.10 (HC_{Ar}), 113.42 (HC_{Ar}), 73.31 (OCH₂), 71.67 (OCH₂), 70.80 (CHCH₃), 70.59 (OCH₂), 70.37 (OCH₂), 70.26 (OCH₂), 58.74 (OCH₃), 16.51 (CHCH₃). **HRMS** (ESI): m/z = 431.1649 (calcd 431.1644 for [M + Na]⁺). **HPLC** (125 mm



Nucleodur 100-5-C₁₈, 4.0 mm i.D., MeOH/H₂O 75/25, 0.8 ml/min, 7.2 MPa, 308 K, det. UV 254 nm, $t_R = 7.0$ min.): 99.7 area %.

Synthesis of the aryl azide terminating building block

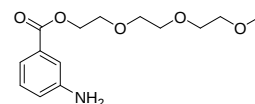


(3,6,9-trioxadec-1-yl) 3-nitrobenzoate 13

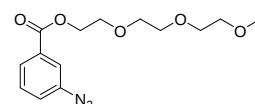
In a two-necked flask 13.37 g 3-nitrobenzoic acid (80.0 mmol, 1.0 equiv.) and 17.45 g 3,6,9-trioxadecan-1-ol (72.0 mmol, 0.9 equiv.) were dissolved in 25 mL of dry THF at rt and after cooling the mixture down to 0 °C under argon atmosphere a mixture of 4.71 g DPTS (16.0 mmol, 0.2 equiv.) dissolved in CH₂Cl₂ were added. 13.7 mL of *N,N'*-diisopropylcarbodiimide (88.0 mmol, 1.1 equiv.) were added dropwise in the counterflow of argon using a syringe whereupon a colorless precipitate appeared immediately and the mixture became viscous. After 10 min the mixture was allowed to reach rt and stirred over night at rt under argon. After consumption of all starting material indicated by TLC monitoring the reaction was quenched with 220 mL of water and stirred for 20 min. The solvent was removed in *vacuo* and the residue was dried in *vacuo* (oil pump) for 2 h, toluene added and the colorless solid was filtered off. After standing in the fridge for 4 h the mixture was filtered again, the solvent removed in *vacuo* and the title compound was isolated as yellow oil (20.5 g, 91%) using column chromatography (PE/EtOAc 1/1 → 1/2). **TLC** (EtOAc/PE 1/1) $R_f = 0.18$. **¹H-NMR** (300 MHz, CDCl₃): δ (ppm) = 8.80 – 8.79 (m, 1H, ArH), 8.38 – 8.31 (m, 2H, ArH), 7.61 (t, $J^3 = 8.1$ Hz, 1H, ArH), 4.50 – 4.47 (m, 2H, OCH₂), 3.83 – 3.80 (m, 2H, OCH₂), 3.69 – 3.58 (m, 6H, OCH₂), 3.49 – 3.46 (m, 2H, OCH₂), 3.30 (s, 3H, OCH₃). **¹³C-NMR** (75 MHz, CDCl₃): δ (ppm) = 164.39 (-CO₂-), 148.19 (C_{Ar}NO₂), 135.37 (HC_{Ar}), 131.84 (C_{Ar}CO₂-), 129.62 (HC_{Ar}), 127.39 (HC_{Ar}), 124.59 (HC_{Ar}), 71.86 (OCH₂), 70.64 (OCH₂), 70.59 (OCH₂), 70.55 (OCH₂), 68.92 (OCH₂), 64.90 (OCH₂), 58.96 (OCH₃). **MS** (ESI): $m/z = 314.1$ ([M + H]⁺), 331.2 ([M + NH₄]⁺), 336.2 ([M + Na]⁺), 352.1 ([M + K]⁺). **HRMS** (ESI): $m/z = 314.1231$ (calcd 314.1234 for [M + H]⁺). **HPLC** (CH₃CN/H₂O 4/6 → 95/5, $t_R = 7.6$ min): 99 area %.

(3,6,9-trioxadec-1-yl) 3-aminobenzoate 14

In a one necked flask 4.3 g **13** (13.74 mmol, 1 equiv.) were dissolved in 15 mL of ethyl acetate, 0.4 g Pd on charcoal (10% wt) were added, the stirred mixture was degassed *in vacuo* and flushed with H₂ (3 cycles). After stirring for 18 h at rt in H₂ atmosphere (2 bar) the mixture was filtered through a celite pad and the solvent was removed *in vacuo* to give the title compound as yellow oil (3.88 g, quant. yield). **TLC** (PE/EtOAc 3/7) R_f = 0.22. **¹H-NMR** (300 MHz, CDCl₃): δ (ppm) = 7.39 – 7.36 (m, 1H, ArH), 7.32 – 7.30 (m, 1H, ArH), 7.14 (t, J³ = 8.1 Hz, 1H, ArH), 6.82 – 6.78 (m, 1H, ArH), 4.42 – 4.38 (m, 2H, OCH₂), 3.86 (br s, 2H, NH₂), 3.79 – 3.75 (m, 2H, OCH₂), 3.69 – 3.59 (m, 6H, OCH₂), 3.50 – 3.47 (m, 2H, OCH₂), 3.32 (s, 3H, OCH₃). **¹³C-NMR** (75 MHz, CDCl₃): δ (ppm) = 166.67 (-CO₂-), 146.66 (C_{Ar}NH₂), 130.91 (C_{Ar}CO₂-), 129.11 (C_{Ar}H), 119.47 (HC_{Ar}), 119.31 (HC_{Ar}), 115.66 (HC_{Ar}), 71.86 (OCH₂), 70.60 (OCH₂), 70.51 (OCH₂), 70.48 (OCH₂), 69.13 (OCH₂), 63.95 (OCH₂), 58.90 (OCH₃). **MS** (ESI): m/z = 284.1 ([M + H]⁺), 301.0 ([M + NH₄]⁺), 306.2 ([M + Na]⁺), 322.1 ([M + K]⁺), 567.3 ([2M + H]⁺), 589.3 ([2M + Na]⁺), 605.2 ([2M + K]⁺). **HRMS** (ESI): m/z = 284.1495 (calcd 284.1492 for [M + H]⁺). **HPLC** (CH₃CN/H₂O 7/3 → CH₃CN, t_R = 2.9 min): 99.7 area %.

**(3,6,9-trioxadec-1-yl) 3-azidobenzoate 8**

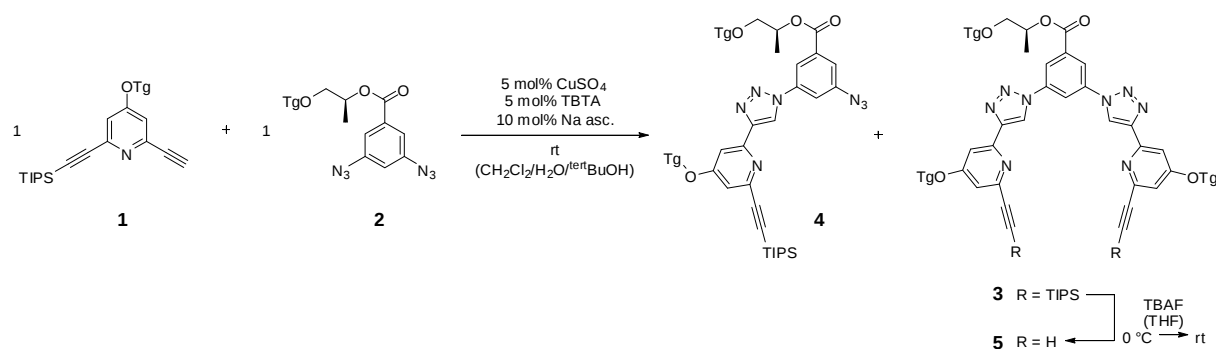
8.7 g **14** (30.74 mmol, 1 equiv.) were dissolved in 100 mL of 17 % HCl under help of gentle warming and addition of EtOH. The mixture was cooled down to 0 °C, 2.33 g NaNO₂ (33.81 mmol, 1.1 equiv.) were added in small portions and after stirring for 15 min. at 0 °C 2.4 g NaN₃ (36.89 mmol, 1.2 equiv.) were added gradually. Stirring was continued for 15 min. at 0 °C and afterwards the mixture was allowed to reach rt and after stirring at rt for 15 min it was poured into 300 mL of ice cold water, transferred into a separation funnel and the aqueous phase was extracted with ethyl acetate (4 x). The combined organic phases were washed with water (1 x), sat. NaHCO₃ solution (1 x) and aqueous sat. NaCl solution. After drying over MgSO₄ the solvent was removed *in vacuo* and the title compound was isolated as yellow oil (8.36 g, 88 %) by column chromatography (PE/EtOAc 1/1). **TLC** (PE/EtOAc 1/1) R_f = 0.26. **¹H-NMR** (300 MHz, CDCl₃): δ (ppm) = 7.80 – 7.78 (m, 1H, ArH), 7.72 – 7.70 (m, 1H, ArH), 7.44 – 7.39 (t, J³ = 7.9 Hz, 1H, ArH), 7.22 – 7.18 (m, 1H, ArH), 4.50 – 4.46 (m, 2H, OCH₂), 3.85 – 3.82 (m, 2H, OCH₂), 3.73 – 3.63 (m, 6H, OCH₂), 3.55 – 3.51 (m, 2H, OCH₂), 3.36 (s, 3H, OCH₃). **¹³C-NMR** (75 MHz, CDCl₃): δ (ppm) = 165.74 (-CO₂-), 140.60 (C_{Ar}N₃), 131.95 (C_{Ar}CO₂-), 129.87 (C_{Ar}H), 126.20 (HC_{Ar}), 123.51 (HC_{Ar}), 120.15 (HC_{Ar}), 71.99 (OCH₂), 70.78 (OCH₂), 70.72 (OCH₂), 70.68



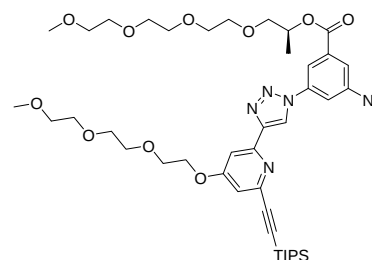
(OCH₂), 69.20 (OCH₂), 64.53 (OCH₂), 59.12 (OCH₃). **MS** (EI, 60 °C – 100 °C): m/z = 309.1 ([M]⁺), 249.1, 206.1 ([C₉H₈N₃O₃]⁺), 193.1, 179.1, 163.1 ([C₇H₁₅O₄]⁺), 146.0 ([C₅H₅Cl₂N]⁺), 119, 90.0 ([C₄H₁₀O₂]⁺), 59.1 ([C₃H₇O]⁺, 100%), 45.0 ([C₂H₅O]⁺). **HRMS** (EI, 60 °C – 100 °C): m/z = 309.1325 (calcd 309.1325 for [M]⁺). **HPLC** (CH₃CN/H₂O 4/6 → 95/5, t_R = 8.9 min): 100 area %.

General procedure of the copper catalyzed 1,3-dipolar cycloaddition

In a three necked flask the bisacetylene component (1 equiv.), the aryl azide component (if not noted: 2.4 equiv. per mol bisacetylene) were dissolved in CH₂Cl₂ and the solvent mixture of H₂O/^{tert}BuOH (1/2) was added. Sodium ascorbate (0.4 equiv.) and TBTA (0.15 equiv.) were added. The flask was evacuated and flushed with argon repeatedly (3 cycles). CuSO₄ (0.15 equiv., stock solution, 10 mg CuSO₄ per 0.3 mL of water) was added in the counterflow of argon and the mixture was vigorously stirred at rt in the dark for the period of time as noted. In case of an appearing precipitate additional CH₂Cl₂ was added. The reaction course was monitored by taking small samples for HPLC or GPC analysis and in case of a sluggish getting reaction rate additional sodium ascorbate (0.4 equiv.) was added. After the acetylene starting material was consumed the mixture was diluted with CH₂Cl₂ and transferred into a separation funnel. The organic phase was washed with aqueous Na₂-EDTA solution (1 x), the aqueous phase was extracted with CH₂Cl₂ (3 x), and afterwards the combined organic phases were washed again with aqueous Na₂-EDTA solution (2 x) and once with aqueous sat. NaCl solution. After drying over MgSO₄, filtration, and removal of the solvent *in vacuo* the corresponding products were isolated by column chromatography (CH₂Cl₂/acetone or CH₂Cl₂/MeOH).



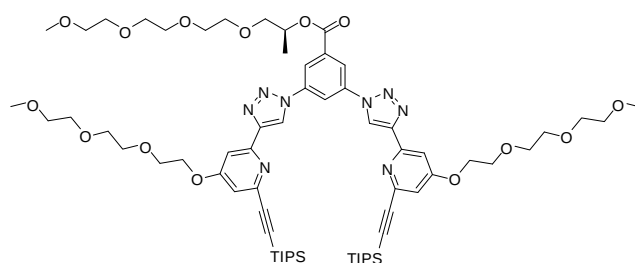
3-Azido-5-(4-{4-(3,6,9-trioxadec-1-yloxy)})-6-[(triisopropylsilyl)ethynyl]-pyridin-2-yl-[1,2,3]-triazole-1-yl)-benzoic acid (2S)-4,7,10,13-tetraoxatetradecan-2-yl ester 4



The reaction was performed with **1** (1 equiv.) and **2** (1 equiv.) following the general “Click reaction” protocol using the amount of 5 mol% CuSO₄, 5 mol% TBTA and 20 mol% sodium ascorbate under argon atmosphere and the reaction was stirred for 4 d. Products have been isolated using column chromatography (gradient CH₂Cl₂ → CH₂Cl₂/acetone 8/2) to give the title compound as yellow oil (26-35%). **TLC** (CH₂Cl₂/acetone 85/15) R_f = 0.6. **¹H-NMR** (300 MHz, CDCl₃): δ (ppm) = 8.76 (s, 1H, ArH), 8.16 (t, J⁴ = 1.6 Hz, 1H, ArH), 7.74 (t, J⁴ = 1.8 Hz, 3H, ArH), 7.0 (d, J⁴ = 2.4 Hz, 1H, ArH), 5.42 – 5.32 (m, 1H, CHCH₃), 4.28 (t, J³ = 4.8 Hz, 2H, OCH₂), 3.89 (t, J³ = 4.9 Hz, 2H, OCH₂), 3.75 – 3.47 (m, 22H, OCH₂), 3.35 (s, 3H, OCH₃), 3.32 (s, 3H, OCH₃), 1.38 (d, J³ = 6.5 Hz, 3H, CHCH₃), 1.14, 1.13 (s, s, 21H, SiCHCH₃). **¹³C-NMR** (75 MHz, CDCl₃): δ (ppm) = 165.62 (-CO₂-), 163.93 (-CO₂-), 151.29 (C_{Ar}), 148.73 (C_{Ar}), 144.18 (C_{Ar}), 142.50 (C_{Ar}), 138.13 (C_{Ar}), 133.93 (C_{Ar}), 120.95 (C_{Ar}), 119.96 (C_{Ar}), 117.07 (C_{Ar}), 115.03 (C_{Ar}), 114.96 (C_{Ar}), 105.84 (C_{Ar}), 105.72 (C≡C), 91.57 (C≡C), 73.53 (OCH₂), 71.91 (OCH₂), 71.88 (OCH₂), 71.38 (OCH₂), 71.31 (OCH₂), 70.92 (OCH₂), 70.77 (OCH₂), 70.62 (OCH₂), 70.60 (CHCH₃), 70.56 (OCH₂), 70.44 (OCH₂), 69.24 (OCH₂), 67.81 (OCH₂), 58.99 (OCH₃), 58.93 (OCH₃), 18.66 (Si-CH-CH₃), 16.69 (CHCH₃), 11.26 (Si-CH). **MS** (ESI): *m/z* = 854 ([M + H]⁺), 876 ([M + Na]⁺), 892 ([M + K]⁺). **HRMS** (ESI): *m/z* = 876.4293 (calcd 876.4297 for [M + Na]⁺). **HPLC** (CH₃CN/H₂O 85/15, t_R = 5.7 min): 98 area %.

(S)-2,5,8,11-tetraoxatetradecan-13-yl 3,5-bis(-4-(4-(3,6,9-trioxadec-1-yloxy)-6-((triisopropylsilyl)ethynyl)pyridin-2-yl)-1H-1,2,3-triazol-1-yl)benzoate 3

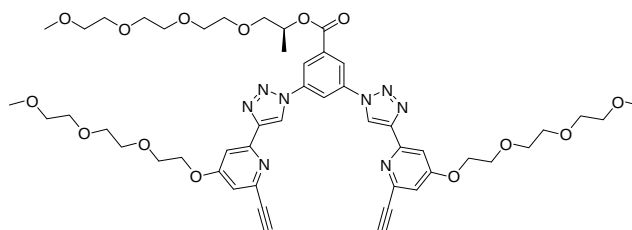
In the reaction **1** (1 equiv.) was reacted with **2** (1 equiv.) following the general “Click reaction” protocol using the amount of 5 mol% CuSO₄, 5 mol% TBTA and 20 mol% sodium ascorbate under



argon atmosphere for 4 d. The title compound has been isolated as colorless oil (28-35% yield) using column chromatography (gradient CH₂Cl₂ → CH₂Cl₂/acetone 8/2). **TLC** (CH₂Cl₂/acetone 85/15) R_f = 0.28. **¹H-NMR** (300 MHz, CDCl₃): δ (ppm) = 8.89 (s, 2H, ArH), 8.74 (t, J⁴ = 2.0 Hz, 1H, ArH), 8.54 (d, J⁴ = 2.0 Hz, 2H, ArH), 7.79 (d, J⁴ = 2.4 Hz, 2H, ArH), 7.04 (d, J⁴ = 2.4 Hz, 2H, ArH), 5.51 – 5.41 (m, 1H, CHCH₃), 4.32 (t, J³ = 4.9 Hz, 4H, OCH₂),

3.92 (t, $J^3 = 4.9$ Hz, 4H, OCH_2), 3.82 – 3.48 (m, 30H, OCH_2), 3.38 (s, 6H, OCH_3), 3.33 (s, 3H, OCH_3), 1.45 (d, $J^3 = 6.5$ Hz, 3H, CHCH_3), 1.13 (s, s, 42H, SiCHCH_3). **^{13}C -NMR** (75 MHz, CDCl_3): δ (ppm) = 165.35 (OC_{Ar}), 163.43 ($-\text{CO}_2-$), 151.32 (C_{Ar}), 148.66 (C_{Ar}), 144.04 (C_{Ar}), 137.99 (C_{Ar}), 133.84 (C_{Ar}), 121.25 (C_{Ar}), 120.36 (C_{Ar}), 115.57 (C_{Ar}), 114.73 (C_{Ar}), 105.94 (C_{Ar}), 105.67 ($\text{C}\equiv\text{C}$), 90.70 ($\text{C}\equiv\text{C}$), 73.43 (OCH_2), 71.74 (OCH_2), 71.69 (CHCH_3), 71.38 (OCH_2), 70.77 (OCH_2), 70.64 (OCH_2), 70.47 (OCH_2), 70.44 (OCH_2), 70.38 (OCH_2), 70.22 (OCH_2), 69.12 (OCH_2), 67.70 (OCH_2), 58.74 (OCH_3), 58.67 (OCH_3), 18.57 (Si-CH-CH_3), 16.60 (CHCH_3), 11.12 (Si-CH). **MS** (ESI): m/z = 1299 ($[\text{M} + \text{H}]^+$), 1321 ($[\text{M} + \text{Na}]^+$). **HRMS** (ESI): m/z = 1321.6953 (calcd 1321.6946 for $[\text{M} + \text{Na}]^+$). **HPLC** (125 mm Nucleodur 100-5- C_{18} , 4.0 mm i.D., MeOH/ H_2O 95/5, 0.8 ml/min, 7.5 MPa, 308 K, det. UV 220 nm, t_R = 13.6 min.): 99.5 area %.

**(S)-2,5,8,11-tetraoxatetradecan-13-yl
3,5-bis(4-((3,6,9-trioxadec-1-yloxy)-6-
ethynylpyridin-2-yl)-1H-1,2,3-triazol-1-
yl)benzoate 5**

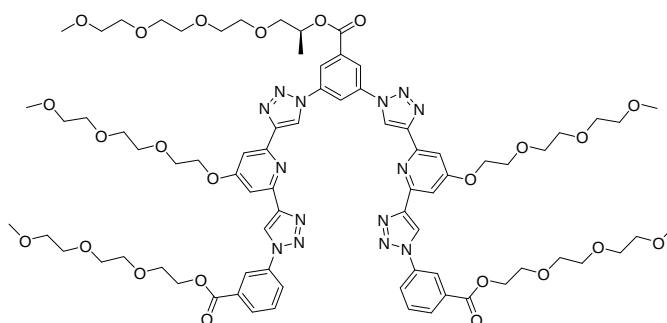


3 (743 mg, 0.57 mmol, 1 equiv.) was dissolved in 50 mL of THF and cooled down to 0 °C. Under stirring 1.7 mL of a 1 M TBAF-THF solution was added drop by drop (3 equiv.) and the mixture was allowed to reach rt within 10 min. After consumption of all starting material indicated by TLC monitoring (CH_2Cl_2 /acetone 8/2) the mixture was filtered through a silica gel plug and the product washed down with THF. Removal of the solvent *in vacuo* followed by isolation of the title compound using column chromatography ($\text{CH}_2\text{Cl}_2 \rightarrow \text{CH}_2\text{Cl}_2 + 4\%$ MeOH) gave a yellow oil (533 mg, 94%). **TLC** (CH_2Cl_2 /MeOH 96/4) R_f = 0.14. **^1H -NMR** (300 MHz, CDCl_3): δ (ppm) = 8.85 (s, 2H, ArH), 8.68 (t, $J^4 = 2.0$ Hz, 1H, ArH), 8.43 (d, $J^4 = 2.0$ Hz, 2H, ArH), 7.71 (d, $J^4 = 2.3$ Hz, 2H, ArH), 6.94 (d, $J^4 = 2.3$ Hz, 2H, ArH), 5.51 – 5.41 (m, 1H, CHCH_3), 4.24 (t, $J^3 = 4.8$ Hz, 4H, OCH_2), 3.85 (t, $J^3 = 4.7$ Hz, 4H, OCH_2), 3.75 – 3.41 (m, 30H, OCH_2), 3.29 (s, 6H, OCH_3), 3.25 (s, 3H, OCH_3), 3.16 (s, 2H, $\text{C}\equiv\text{CH}$), 1.38 (d, $J^3 = 6.5$ Hz, 3H, CHCH_3). **^{13}C -NMR** (75 MHz, CDCl_3): δ (ppm) = 165.34 (OC_{Ar}), 163.15 ($-\text{CO}_2-$), 150.99 (C_{Ar}), 148.30 (C_{Ar}), 142.78 (C_{Ar}), 137.66 (C_{Ar}), 133.78 (C_{Ar}), 120.59 (C_{Ar}), 119.70 (C_{Ar}), 114.93 (C_{Ar}), 114.05 (C_{Ar}), 105.94 (C_{Ar}), 82.38 ($\text{C}\equiv\text{C}$), 76.97 ($\text{C}\equiv\text{C}$), 73.22 (OCH_2), 71.56 (OCH_2), 71.52 (OCH_2), 71.23 (CHCH_3), 70.58 (OCH_2), 70.44 (OCH_2), 70.29 (OCH_2), 70.25 (OCH_2), 70.21 (OCH_2), 70.07 (OCH_2), 68.90 (OCH_2), 67.63 (OCH_2), 58.64 (OCH_3), 58.58 (OCH_3), 16.50 (CHCH_3). **MS** (ESI): m/z = 987.5 ($[\text{M} + \text{H}]^+$), 1009.5 ($[\text{M} +$

$\text{Na}]^+$). **HRMS** (ESI): $m/z = 987.4459$ (calcd 987.4458 for $[\text{M} + \text{H}]^+$). **HPLC** ($\text{CH}_3\text{CN}/\text{H}_2\text{O}$ 4/6 $\rightarrow$ 95/5, $t_R = 14.5$ min): 100 area %.

(S)-Bis(2-(2-(2-methoxyethoxy)ethoxy)ethyl) 3,3'-(4,4'-(6,6'-(1,1'-(5-(3-methyl-2,5,8,11,14-pentaoxapentadecan-1-oyl)-1,3-phenylene)bis(1H-1,2,3-triazole-4,1-diyl))bis(4-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)pyridine-6,2-diyl))bis(1H-1,2,3-triazole-4,1-diyl))dibenzoate 9

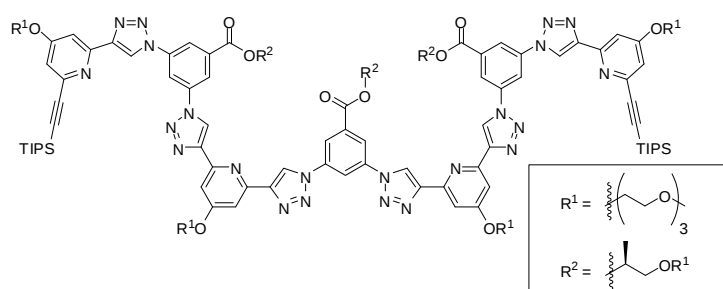
Following the general click reaction procedure the reaction was stirred for 5 d and the title compound was isolated as colorless wax (115 mg, 90%) using column chromatography



($\text{CH}_2\text{Cl}_2 + 30\%$ acetone $\rightarrow$ $\text{CH}_2\text{Cl}_2 \rightarrow \text{CH}_2\text{Cl}_2 + 4\%$ MeOH). **TLC** ($\text{CH}_2\text{Cl}_2/\text{MeOH}$ 97/3) $R_f = 0.18$. **$^1\text{H-NMR}$** (300 MHz, CDCl_3): δ (ppm) = 8.94 (br s, 2H, ArH), 8.82 (br s, 2H, ArH), 8.69-8.67 (m, 1H, ArH), 8.60-8.59 (m, 2H, ArH), 8.49-8.48 (m, 2H, ArH), 8.12-8.07 (m, 4H, ArH), 7.77 (br s, 4H, ArH), 7.61 (t, $J^3 = 7.9$ Hz, 2H, ArH), 5.50-5.40 (m, 1H, CHCH_3), 4.48 (t, $J^3 = 4.8$ Hz, 4H, OCH_2), 4.39 (m, 4H, OCH_2), 3.97 (t, $J^3 = 4.1$ Hz, 4H, OCH_2), 3.85-3.45 (m, 50H, OCH_2), 3.37 (s, 6H, OCH_3), 3.31 (s, 6H, OCH_3), 3.30 (s, 3H, OCH_3), 1.44 (d, $J^3 = 6.5$ Hz, 3H, CHCH_3). **$^{13}\text{C-NMR}$** (75 MHz, CDCl_3): δ (ppm) = 166.65, 165.15, 163.74, 151.18, 150.66, 149.28, 148.80, 138.13, 137.02, 134.22, 131.89, 129.95, 129.8, 129.16, 128.87, 128.06, 124.59, 121.27, 120.6, 115.44, 106.61, 106.33, 73.56, 71.94, 71.87, 71.72, 70.99, 70.85, 70.68, 70.6, 70.55, 70.44, 69.32, 69.03, 68.0, 64.66, 59.03, 58.96, 16.78. **HRMS** (ESI): $m/z = 803.3537$ (calcd 803.3590 for $([\text{M} + 2\text{H}]^{2+}/2)$). **HPLC** ($\text{CH}_3\text{CN}/\text{H}_2\text{O}$ 7/3 $\rightarrow$ CH_3CN , $t_R = 6.0$ min): 98 area %. **GPC** (THF, RI signal): $M_w = 1.65 \cdot 10^3$ g/mol, $M_n = 1.65 \cdot 10^3$ g/mol, PDI = 1.00.

Oligomer 6

Following the general “Click reaction” procedure compound 5 (1 equiv.) was stirred with compound 4 (2.2 equiv. per mol bisacetylene) for 5 d under argon

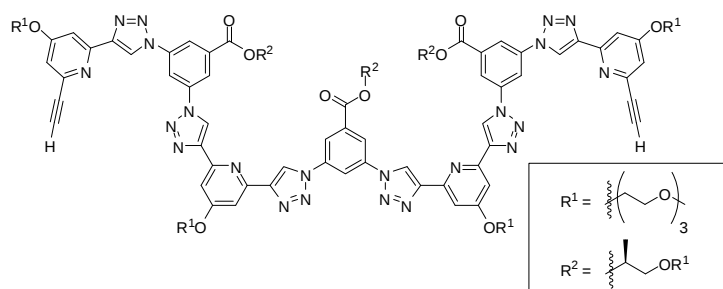


and after consumption of all acetylene starting material monitored by HPLC the reaction was

worked up as described above. Purification using column chromatography ($\text{CH}_2\text{Cl}_2 + 25\%$ acetone $\rightarrow \text{CH}_2\text{Cl}_2 \rightarrow \text{CH}_2\text{Cl}_2 + 4\%$ MeOH) gave the title compound as slightly yellow wax (182 mg, 85%). **TLC** ($\text{CH}_2\text{Cl}_2/\text{MeOH}$ 97/3) $R_f = 0.14$. **$^1\text{H-NMR}$** (300 MHz, CDCl_3): δ (ppm) = 9.0-8.49 (m, 15H, ArH), 7.81-7.73 (m, 6H, ArH), 7.0 (br s, 2H, ArH), 5.50-5.36 (m, 3H, CHCH_3), 4.48 (br s, 4H, OCH_2), 4.20 (br s, 4H, OCH_2), 4.04-3.43 (m, 82H, OCH_2), 3.37 (s, 12H, OCH_3), 3.29 (s, 9H, OCH_3), 1.44-1.40 (m, 9H, CHCH_3), 1.12 (s, 42H, SiHCH_3 , SiHCH_3). **$^{13}\text{C-NMR}$** (75 MHz, CDCl_3): δ (ppm) = 166.23, 165.39, 163.78, 163.56, 151.08, 150.95, 148.92, 148.82, 144.04, 138.16, 137.85, 133.87, 121.10, 120.44, 116.09, 115.45, 114.34, 106.07, 105.44, 91.36, 73.54, 73.46, 71.84, 71.82, 71.77, 71.70, 71.44, 71.38, 70.80, 70.50, 70.37, 70.28, 69.10, 67.85, 67.58, 58.94, 58.85, 58.79, 18.47, 16.80, 16.66, 11.06. **MS** (ESI-TOF): $m/z = 899.1$ (calcd 898.8 for $([\text{M} + 3\text{H}]^{3+}/3)$, 906.1 (calcd 906.1 for $([\text{M} + 2\text{H} + \text{Na}]^{3+}/3)$, 913.7 (calcd 913.4 for $([\text{M} + 2\text{Na} + \text{H}]^{3+}/3)$, 1348.1 (calcd 1347.7 for $([\text{M} + 2\text{H}]^{2+}/2)$, 1359.1 (calcd 1358.6 for $([\text{M} + \text{H} + \text{Na}]^{2+}/2)$, 1368.6 (calcd 1369.6 for $([\text{M} + 2\text{Na}]^{2+}/2)$. **HPLC** ($\text{CH}_3\text{CN}/\text{H}_2\text{O}$ 7/3 $\rightarrow \text{CH}_3\text{CN}$, $t_R = 18.3$ min): 98.6 area %.

Oligomer 7

Compound **6** (171 mg, 0.64 mmol, 1 equiv.) was dissolved in 40 mL of THF and cooled down to 0 °C. Under stirring 0.25 mL of a 1 M TBAF-THF solution (0.25 mmol,

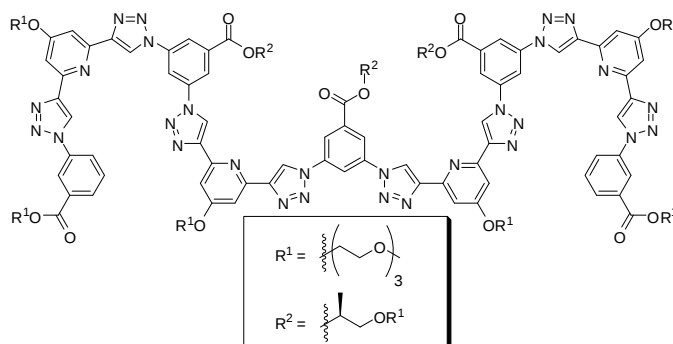


3 equiv.) were added drop by drop and the mixture was stirred at 0 °C for 10 min., allowed to reach rt and stirred at rt for 25 min. After consumption of all starting material indicated by TLC monitoring ($\text{CH}_2\text{Cl}_2 + 5\%$ MeOH) the mixture was filtered through a silica gel plug and the product washed down with THF containing 5 % MeOH. Removal of the solvent *in vacuo* followed by isolation of the title compound using column chromatography ($\text{CH}_2\text{Cl}_2 + 5\%$ MeOH) gave a colorless wax (139 mg, 92%). **TLC** ($\text{CH}_2\text{Cl}_2/\text{MeOH}$ 95/5) $R_f = 0.12$. **$^1\text{H-NMR}$** (300 MHz, CDCl_3): δ (ppm) = 9.20-8.37 (m, 15H, ArH), 7.89-7.63 (m, 6H, ArH), 6.99 (br s, 2H, ArH), 5.53-5.32 (m, 3H, CHCH_3), 4.38 (br s, 4H, OCH_2), 4.27 (br s, 4H, OCH_2), 4.05-3.42 (m, 82H, OCH_2), 3.34, 3.35 (s, s, 12H, OCH_3), 3.31 (s, 9H, OCH_3), 3.16 (br s, 2H, $\text{C}\equiv\text{CH}$), 1.45-1.41 (m, 9H, CHCH_3). **HRMS** (ESI-TOF): $m/z = 794.6824$ (calcd 794.6915 for $([\text{M} + 3\text{H}]^{3+}/3)$, 802.0134 (calcd 802.0188 for $([\text{M} + 2\text{H} + \text{Na}]^{3+}/3)$, 809.3365 (calcd 809.3462 for $([\text{M} + 2\text{Na} + \text{H}]^{3+}/3)$, 816.6608 (calcd 816.6734 for $([\text{M} + 3\text{Na}]^{3+}/3)$, 1192.0378 (calcd 1191.5337 for $([\text{M} + 2\text{H}]^{2+}/2)$, 1203.0344 (calcd 1202.5246 for $([\text{M} + \text{Na} + \text{H}]^{2+}/2)$, 1214.0071

(calcd 1213.5156 for $[M + 2Na]^{2+}/2$). **MS** (High-resolution ESI-MS): $m/z = 1191.5370$ (calcd 1191.5337 for $[M + 2H]^{2+}/2$). **HPLC** (CH_3CN/H_2O 7/3 $\rightarrow$ CH_3CN , $t_R = 6.8$ min): 99.6 area %.

Oligomer 10

Following the general click reaction procedure compound **7** (1 equiv.) was stirred with compound **4** (2.4 equiv. per mol **7**) the reaction was stirred for 10 d and the title compound was isolated as yellow wax (75 mg, 86%) using



column chromatography ($CH_2Cl_2 + 1\%$ MeOH $\rightarrow$ $CH_2Cl_2 + 8\%$ MeOH) followed by preparative TLC ($CH_2Cl_2 + 7\%$ MeOH). **TLC** (CH_2Cl_2 /MeOH 95/5) $R_f = 0.16$. **1H -NMR** (300 MHz, $CDCl_3$): δ (ppm) = 9.41-6.72 (m, 33H, ArH), 5.59-5.19 (m, 3H, CHCH₃), 4.67-2.88 (m, 141H, OCH₂, OCH₃), 1.68-1.38 (m, 9H, CHCH₃). **HRMS** (ESI-TOF): $m/z = 1001.0893$ (calcd 1000.7798 for $[M + 3H]^{3+}/3$), 1008.4095 (calcd 1008.1071 for $[M + 2H + Na]^{3+}/3$), 1501.6212 (calcd 1500.6661 for $[M + 2H]^{2+}/2$). **GPC** (THF, UV 254 nm): $M_w = 2.18 \cdot 10^3$ g/mol, $M_n = 1.85 \cdot 10^3$ g/mol, PDI = 1.17.

Optical Spectroscopy Figures

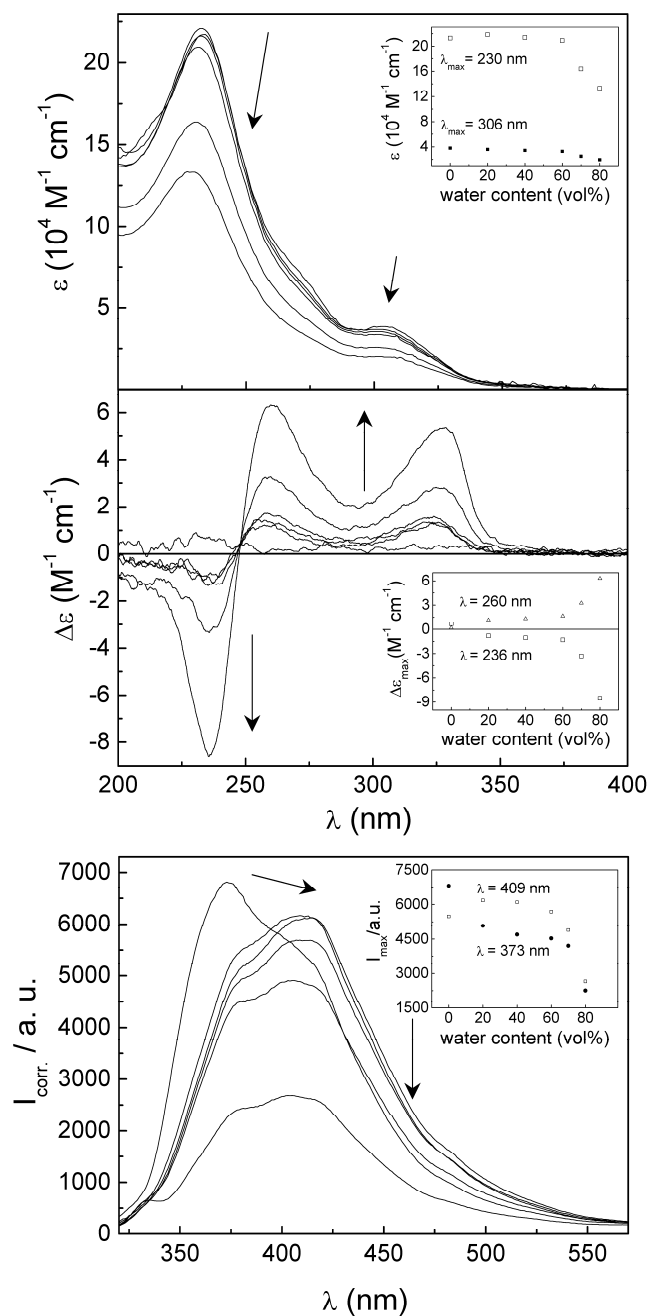


Figure 1. Optical spectra of clickamer **10** in acetonitrile with increasing water content at 25 °C. Top (MS Figure 2): UV/vis absorption spectra ($5 \cdot 10^{-6}$ M). Middle (MS Figure 2): CD spectra ($5 \cdot 10^{-6}$ M). Bottom: Corrected normalized fluorescence spectra ($2 \cdot 10^{-6}$ M).

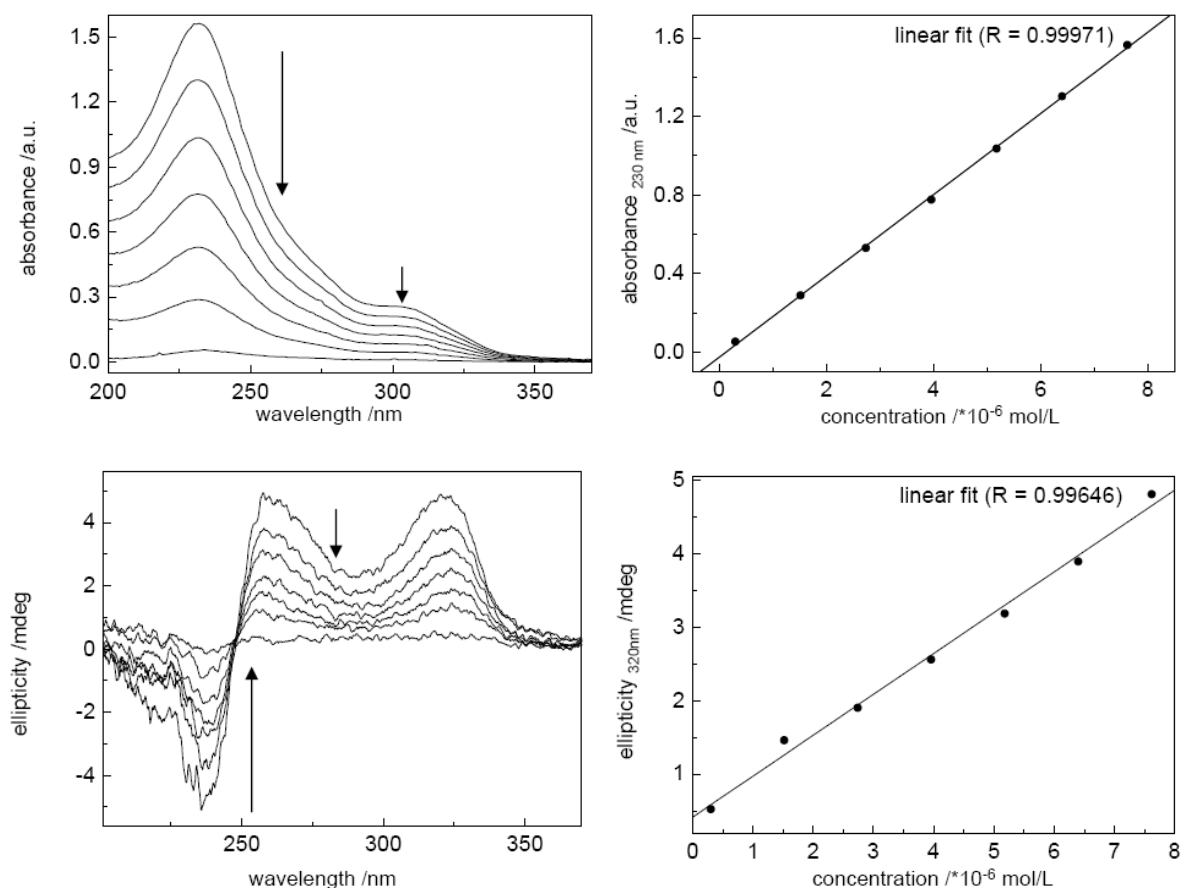


Figure 2. UV/vis spectra and CD spectra of the dilution series of oligomer **10** at a concentration of 10^{-6} mol/L in acetonitrile containing 40 vol% water show a linear dependency. (In preliminary dynamic light scattering experiments employing identical concentrations and solvent composition, no aggregation was detected.)

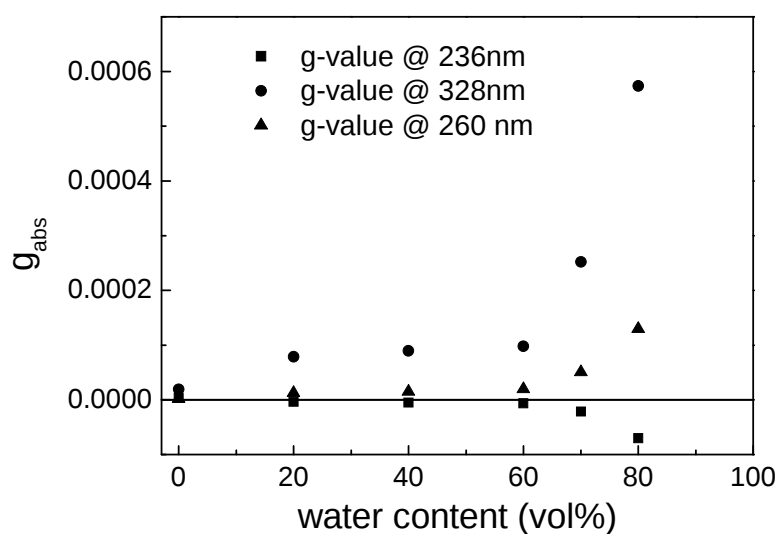


Figure 3. The chiral anisotropy factor $g = (\Delta\epsilon/\epsilon)$ shown at various wavelengths 236 nm, 260 nm, and 328 nm.

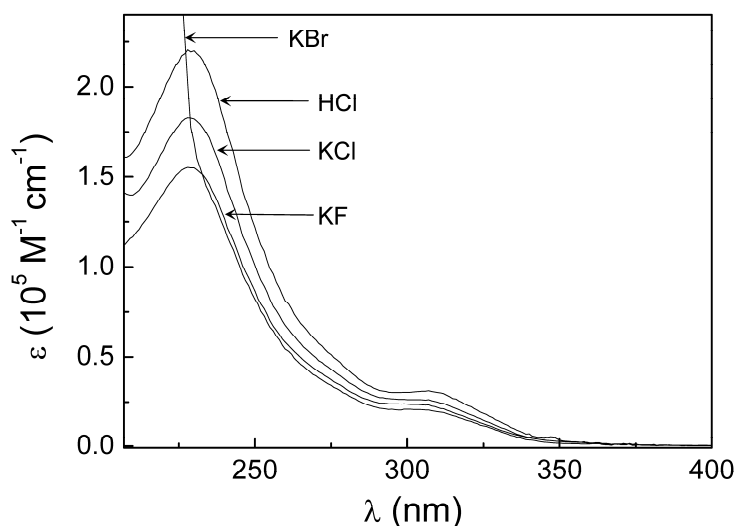


Figure 4. The UV/vis absorption spectra corresponding to Figure 3 in the manuscript illustrating the response of oligomer **10** ($8 \cdot 10^{-6} \text{ M}$, 75 vol% water in acetonitrile, 25 °C) to various halide anions constituted either as potassium salts or as acid; KCl, KBr, KF and HCl.

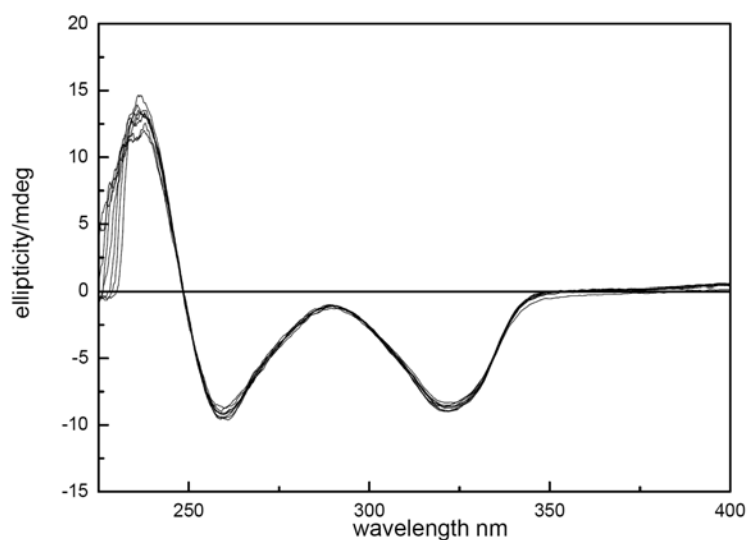


Figure 5. CD spectra of clickamer **10** ($8 \cdot 10^{-6} \text{ M}$) and KBr ($75 \cdot 10^{-3} \text{ M}$) in 75 vol% water in acetonitrile recorded over a temperature range spanning 5 – 75 °C with temperature intervals of 10 K each and appropriate sample equilibration show practically temperature independent behavior.

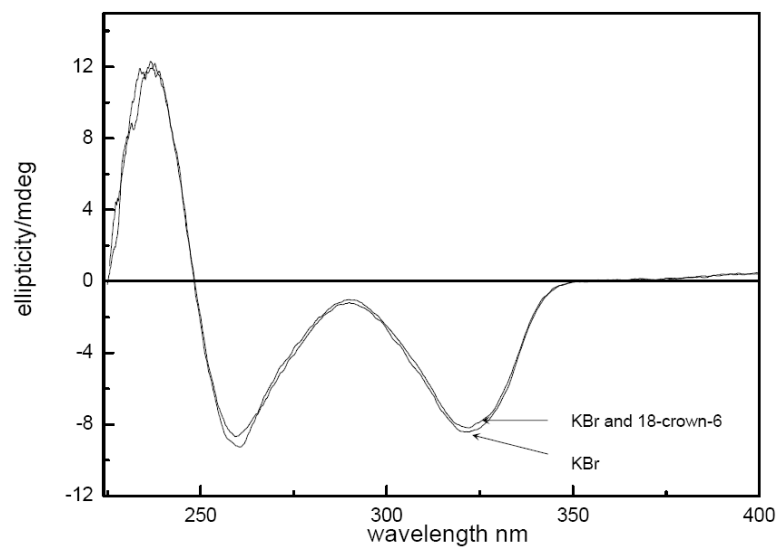


Figure 6. CD spectra of oligomer **10** ($8 \cdot 10^{-6}$ M) and KBr ($37.5 \cdot 10^{-3}$ M) in the absence and presence of 18-crown-6 ($112.5 \cdot 10^{-3}$ M, 3-fold excess corresponding to K^{+}) in 75 vol% water in acetonitrile at 25 °C.

COCCOCCOCCOCCOC[C@H](C)OC(=O)c1cc([N+](=O)[O-])ccc1[N+](=O)[O-]