

Cooperativity in the Folding of Helical *m*-Phenylene Ethynylene Oligomers Based upon the ‘Sergeants-and-Soldiers’ Principle

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Abstract: The ‘Sergeants-and-Soldiers’ principle has been examined in a series of *m*-phenylene ethynylene oligomers containing both chiral and achiral side chains. Circular dichroism (CD) spectroscopy was used to examine the twist sense bias of the helical conformation in the polar solvent acetonitrile. A nonlinear dependence of the CD signal on the amount of chiral side chains was

observed revealing cooperative interactions among the side chains through the backbone. On the other hand, the experiments indicate that in acetonitrile a

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full bias of the helicity cannot be accomplished by chiral side chains alone. Nevertheless, the folded oligomers are highly ordered since the placement of a single chiral side chain at the beginning of an oligomer results in the induction of a strong twist sense bias into the ordered helical conformation.

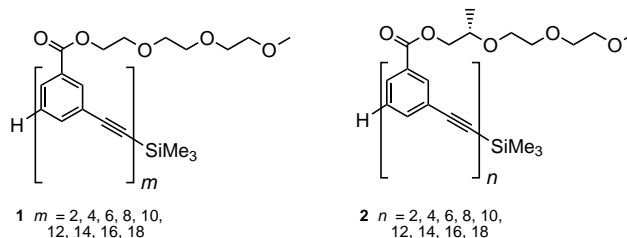
Introduction

Cooperative interactions in polymeric chains is an area of research that has provided a window to investigate weak interactions that cannot be deduced by standard methods.^[1–7] The work of Green and co-workers on polyisocyanates has been pioneering in this field, demonstrating the ‘Sergeants-and-Soldiers’ and ‘Majority Rules’ principles as experimental approaches to reveal cooperativity through the amplification of a biased main chain helicity.^[8–13] The cooperative effects among side chains through the backbone may result in a nonlinear relationship between the number of chiral side chains and the specific optical rotation in an intrinsically helical polymer. This phenomenon is referred to as the ‘Sergeants-and-Soldiers’ experiment,^[8] where the chiral units (sergeants) control the overall chirality of the structure

mediated through achiral units (soldiers). More recently, this behavior has been extended to the intermolecular association of discotic molecules in solution^[14–16] and in well-defined self-assemblies.^[17–19] In these situations, the overall chirality is due to an intrinsically chiral/helical packing of the molecules in the self-assembled architecture.

Results and Discussion

Random coil *m*-phenylene ethynylene oligomers (**1**) have been shown to fold via a cooperative transition into helices due to solvophobic forces.^[20, 21] The folding was determined to be chain length dependent and could be directed by additional programmed design elements in the oligomer.^[22, 23] The observation of a twist sense bias in the helically folded conformation of *m*-phenylene ethynylene oligomers series **2** has indicated the presence of cooperative interactions among the chiral side chains.^[24] For oligomer series **2**, all members



were fully substituted with chiral side chains, not allowing the cooperativity to be determined. To accomplish this task, oligomers with varying numbers of chiral side chains were

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synthesized. The synthesis was based on coupling of previously produced fragments containing achiral and chiral side chains^[20, 24, 25] (Scheme 1). The chemical purity and identity of the oligomers was determined by ¹H NMR, mass spectrometry, HPLC and size-exclusion chromatography (SEC). Four oligomers with both chiral and achiral side chains were synthesized; two tetradecamers with either one or two chiral side chains, a hexadecamer with four chiral side chains, and an octadecamer provided with six chiral side chains. For all of the compounds the chiral side chains were placed at the end of the oligomer.

By analogy to the fully chiral (**2**)^[24] and achiral (**1**)^[21] oligomers, the mixed side chain oligomers existed as a random coil in chloroform, and formed a helical conformation in acetonitrile as determined by UV/Vis spectroscopy. Circular dichroism (CD) measurements were performed to determine the extent of cooperative interactions among the side chains. Figure 1 shows the CD spectra of the four tetradecamers (**1** ($m = 14$), **8**, **9**, and **2** ($n = 14$)) with varying amounts of chiral

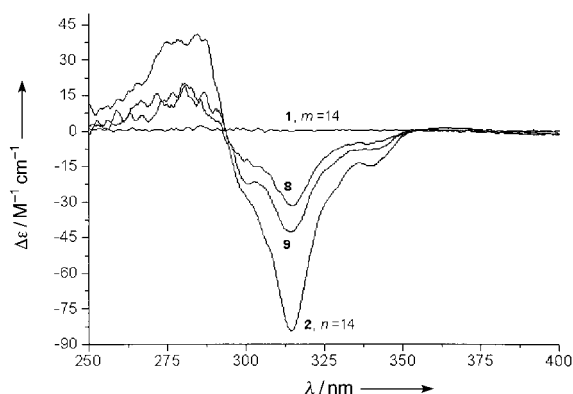


Figure 1. Plots of $\Delta\epsilon$ versus λ for tetradecamers with varying numbers of chiral side chains in acetonitrile, recorded at 20 °C at a concentration of 5 μM .

side chains. As expected, oligomer **1** ($m = 14$) without chiral side chains is optically inactive and tetradecamer **2** ($n = 14$) with all chiral side chains shows the largest Cotton effect. Surprisingly, the oligomer with one out of fourteen chiral side chains **8** displays a fairly strong Cotton effect, larger than expected on the basis of linearity. Furthermore, comparing the spectra of **2** ($n = 14$), **8**, and **9** reveals the presence of an isodichroic point at 295 nm, suggesting a similar helical

conformation to be adopted by all oligomers. Importantly, these result also indicate that overall, the helical conformation is highly ordered and there does not appear to be any “fraying” at the ends, since in oligomer **8** the only chiral side chain is located at the end/beginning of the helix.

The ability of the chiral side chain to transfer its chirality to the helical backbone was examined further by performing variable-temperature experiments (Figure 2a). It can be seen that in acetonitrile a modest twist sense bias is observed even at 70 °C and that the CD signal continues to increase as the temperature is lowered. The temperature denaturation of **8** (Figure 2b) shows a similar transition shape for the loss of optical activity as for the fully chiral oligomer **2** ($n = 14$).^[24]

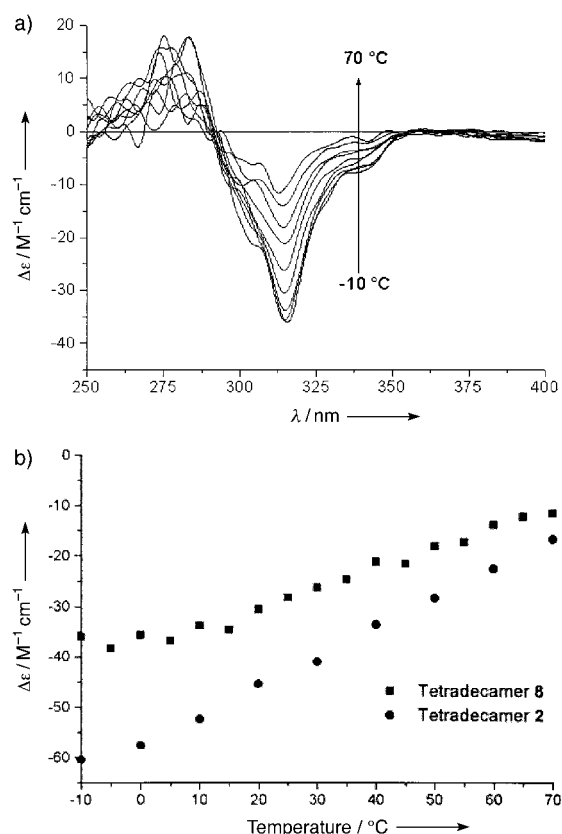
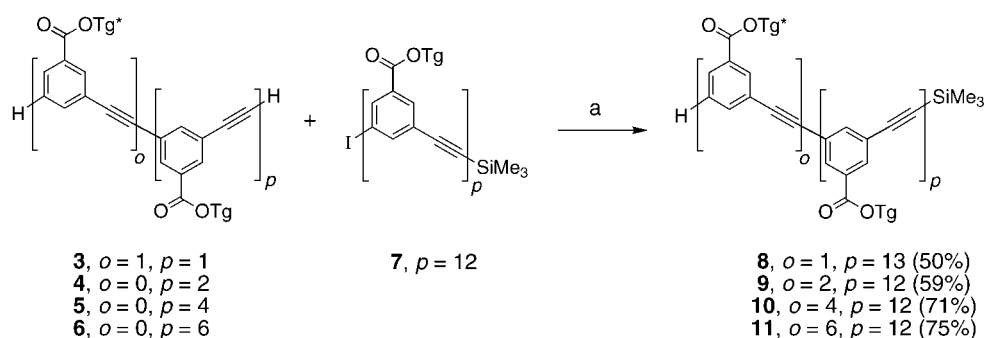


Figure 2. a) Variable-temperature CD spectra of tetradecamer **8** at various temperatures (70 \rightarrow -10 °C) in acetonitrile. b) Plot of CD intensity at 314 nm versus temperature for tetradecamer **8** (squares) and tetradecamer **2** ($n = 14$) (circles) in acetonitrile. All measurements are reversible; displayed spectra and data are equilibrium states.



Scheme 1. a) $[\text{Pd}_2(\text{dba})_3]$, CuI, PPh_3 , Et_3N , 70 °C. $\text{Tg} = -(\text{CH}_2\text{CH}_2\text{O})_3\text{CH}_3$; $\text{Tg}^* = -(\text{S})\text{-CH}_2\text{CH}(\text{CH}_3)\text{-O}-(\text{CH}_2\text{CH}_2\text{O})_2\text{CH}_3$; dba = *trans,trans*-dibenzylideneacetone.

The parallel temperature denaturation of the chiral helical conformations of **8** and **2** ($n=14$) implies that the helix stability is not affected by the number of chiral side chains and that the ratios of the diastereomeric excesses between **8** and **2** ($n=14$) are equal at all temperatures, even though the helix of **2** is biased to a greater extent.

The intramolecular transfer of chirality was also determined for the tetradecamer through octadecamer length oligomers (**1**, **2**, **8**, **9**, **10**, **11**). Figure 3 shows a plot of the normalized Cotton effect ($g_{\text{abs}}/g_{\text{max}}$) versus percent chiral side

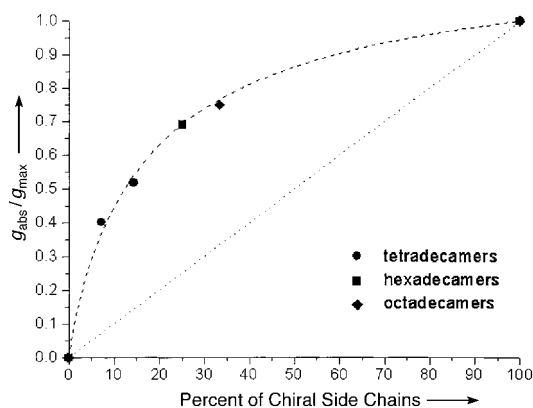


Figure 3. Plot of normalized $g_{\text{abs}}/g_{\text{max}}$ at 315 nm versus percent of chiral side chains for the mixed tetradecamers (**1** ($n=14$), **8**, **9** and **2** ($n=14$)), hexadecamers (**1** ($n=16$), **10** and **2** ($n=16$)) and octadecamers (**1** ($n=18$), **11** and **2** ($n=18$)) in acetonitrile at 20 °C. The dotted lines are meant to guide the eye, but do indicate that an asymptotic value is not reached.

chains. It can be seen that regardless of overall oligomer length, a positive nonlinear dependence of the optical activity on the percentage of chiral side chain is observed. This positive nonlinear effect strongly supports the cooperative nature of the folding process. The results further indicate that the twist sense bias is equally strong for every oligomer length, as the normalized Cotton effect versus percentage of chiral side chains seems to be independent on the oligomers length. The cooperativity as observed using the ‘Sergeants-and-Soldiers’ measurements is, however, not very strong. Around 15% chiral side chains is needed for obtaining half the intensity of the Cotton effect of the homochiral oligomers. This result contrasts with the cooperativity as observed for polyisocyanates^[8–12] and for helical columns of discotic molecules, which have been shown to become homochiral after addition of a small percentage of chiral seed molecules.^[14–16] In addition, the hand-drawn, curved line in Figure 3 seems to indicate that the induced Cotton effect does not reach an asymptotic value at higher percentages of chiral side chains, but increases up to 100% chiral side chains. This effect indicates that even for the oligomers fully substituted with chiral side chains, a 100 percent bias of the helicity is probably not reached. Apparently, the chiral side-chains do not account for a sufficient energy difference to move the equilibrium between *M* and *P* helices [Eq. (1)] to one side only.^[26]



Conclusion

In conclusion, intramolecular ‘Sergeants-and-Soldiers’ experiments indicate a nonlinear dependence of the CD signal on the amount of chiral side chains, revealing that there are cooperative interactions among the side chains and that they allow the chirality to be transferred to the backbone. On the other hand, the experiments indicate that in acetonitrile a full bias of the helicity cannot be accomplished by chiral side chains alone. Nevertheless, the folded oligomers are highly ordered as only one chiral side chain positioned at the end of an oligomer is capable of introducing a strong twist sense bias.

Experimental Section

General methods and materials: Unless otherwise noted, all starting materials were obtained from commercial suppliers and were used without further purification. Analytical thin layer chromatography (TLC) was performed on precoated sheets of silica gel 60, and silica gel column chromatography was carried out with silica gel 60 (230–400 mesh). Dry triethylamine and dry acetonitrile were obtained by vacuum transfer from calcium hydride. The ^1H NMR spectra were recorded at 500 or 400 MHz and ^{13}C NMR were recorded at 125 or 100 MHz. Chemical shifts are expressed in parts per million (δ) using residual solvent protons as internal standard. Chloroform ($\delta = 7.26$ for ^1H , $\delta = 77.0$ for ^{13}C) was used as an internal standard for $[\text{D}]$ chloroform and benzene ($\delta = 7.15$ for ^1H , $\delta = 128.0$ for ^{13}C) was used as an internal standard for $[\text{D}_6]$ benzene. Coupling constants, J , are reported in Hertz (Hz). Splitting patterns are designated as s, singlet; br s, broad singlet; d, doublet; t, triplet; q, quartet; dd, double doublet; ddd, double double doublet; dt, double triplet; m, multiplet; quin, quintet. Low-resolution mass spectra were obtained on either a Hewlett-Packard GC-MS equipped with a 30 m HP-1 capillary column operating at 70 eV or on a Finnigan-MAT CH5 spectrometer operating at 70 eV. High-resolution electron impact mass spectra were obtained on a Finnigan-MAT 731 spectrometer operating at 70 eV. Low- and high-resolution fast atom bombardment (FAB) mass spectra were obtained on VG ZAB-SE and VG 70-SE-4F spectrometers. Low-resolution matrix-assisted laser desorption ionization (MALDI) mass spectra were obtained by using 4-hydroxybenzylidenemalononitrile (4-HMBN) as the matrix. Elemental analyses were performed by the University of Illinois Micro Analytical Service Laboratory. Preparative size-exclusion chromatography (SEC) was performed by using Bio-Beads S-XI Beads (200–400 mesh) from Bio-Rad laboratories using toluene as the eluent. SEC analysis was performed by using a Waters 510 HPLC Pump, Waters 996 photodiode array, and a series of three Waters styragel HR 4E (7.8 \times 300 mm) columns which were calibrated with narrow molecular weight polystyrene standards. High performance liquid chromatography (HPLC) analysis was performed on a Rainin binary gradient system equipped with two SD-200 pumps, a Si 80–125-C5 analytical column (4.6 \times 250 mm), and a UV detector operating at 275 nm.

Absorbance and circular dichroism measurements: The UV absorption spectra were recorded on a Perkin-Elmer Lambda 900 spectrophotometer using 1-cm rectangular quartz cells. Circular dichroism spectra were recorded on a Jasco J-600 spectropolarimeter using 1-cm cylindrical quartz cells. UV/Vis and CD, variable-temperature spectra were obtained by equilibrating the sample at the desired temperature for 15 min with a temperature controllable cuvette holder.

Nomenclature of oligomers: All oligomers of dimer length and longer are named by using an abbreviated nomenclature system. The naming of the oligomers has the following generic naming pattern: X-A_n-B_n-Y. The X represents either a hydrogen (H) or an iodide group (I). The Y represents either a trimethylsilyl (TMS)-protected acetylene or a deprotected acetylene (H). A corresponds to a *meta*-substituted aromatic ring with a (2S)-2-[2-(2-methoxyethoxy)ethoxy]propan-1-ol side chain; B corresponds to a *meta*-substituted aromatic ring with a triethyleneglycol monomethyl ether side chain.

Synthesis

H-[A]₁-[B]₁-Br: To a solution of H-[A]₁-SiMe₃ (274 mg, 7.23 mmol) and THF (5 mL) was added a solution of tetrabutylammonium fluoride in wet THF (1.0 mL, 1.0 M). The solution was stirred for 1 min, filtered through silica (eluting with hexanes/EtOAc, 1/1), and the solvent was removed in vacuo to leave an orange oil. The crude acetylene was used without further purification. To a sealed tube fitted with a magnetic stirrer was added H-[A]₁-H (213 mg, 0.695 mmol), I-[B]₁-Br (449 mg, 0.950 mmol), [Pd₂(dba)₃] (14 mg, 0.02 mmol), CuI (8.0 mg, 0.04 mmol), PPh₃ (38 mg, 0.14 mmol), and dry triethylamine (5 mL). The mixture was evacuated and back-filled with nitrogen three times and heated at 55 °C for 16 h (during which time a white salt precipitate formed). The solution was diluted with EtOAc (20 mL), filtered to remove the precipitate and concentrated in vacuo leaving a brown residue. The crude product was purified by silica gel column chromatography (hexanes/EtOAc, 1/1, 1/2) to give analytically pure H-[A]₁-[B]₁-Br as a light yellow oil (425 mg, 0.652 mmol; 93 %). ¹H NMR (400 MHz, CDCl₃): δ = 8.20 (td, *J* = 1.69, 0.58 Hz, 1H), 8.15 (dd, *J* = 1.88, 1.56 Hz, 1H), 8.14 (t, *J* = 1.63 Hz, 1H), 8.04 (ddd, *J* = 7.73, 1.74, 1.19 Hz, 1H), 7.86 (dd, *J* = 1.87, 1.47 Hz, 1H), 7.71 (ddd, *J* = 7.80, 1.64, 1.32 Hz, 1H), 7.46 (td, *J* = 7.77, 0.77 Hz, 1H), 4.38–4.24 (m, 4H), 3.90–3.81 (m, 2H), 3.80–3.68 (m, 4H), 3.67–3.63 (m, 8H), 3.53–3.48 (m, 4H), 3.36 (s, 3H), 3.35 (s, 3H), 1.28 (d, *J* = 6.49 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ = 165.4, 164.5, 138.2, 135.8, 132.7, 132.4, 132.0, 131.3, 130.5, 129.8, 128.6, 125.0, 122.7, 122.2, 90.4, 87.6, 73.8, 71.8, 70.7, 70.5, 68.7, 68.6, 68.1, 67.9, 58.9, 17.0; MS (FAB): *m/z* (%): 653.2 (50), 651.2 (48), 154.1 (100), 136 (69); TLC: *R_f* = 0.10 (hexanes/EtOAc, 1/1); elemental analysis calcd (%) for C₃₁H₃₉O₁₀Br (651.55): C 57.15, H 6.03; found: C 56.91, H 5.99.

H-[A]₁-[B]₁-SiMe₃: To a sealed tube fitted with a magnetic stirrer was added H-[A]₁-[B]₁-Br (293 mg, 0.450 mmol), [Pd₂(dba)₃] (12 mg, 0.01 mmol), CuI (5.0 mg, 0.03 mmol), PPh₃ (31 mg, 0.12 mmol), and dry triethylamine (5 mL). The mixture was evacuated and back-filled with nitrogen three times and dry, degassed trimethylsilylacetylene (1.0 mL, 7.1 mmol) was added. The tube was sealed and stirred at 70 °C for 18 h (during which time a white precipitate formed). The solution was diluted with ethyl acetate (50 mL), filtered to remove the precipitate and concentrated in vacuo leaving a yellow residue. The crude product was purified by silica gel column chromatography (hexanes/EtOAc, 2/3, 2/5) to give analytically pure H-[A]₁-[B]₁-SiMe₃ as a colorless oil (275 mg, 0.411 mmol; 91 %). ¹H NMR (400 MHz, CDCl₃): δ = 8.20 (td, *J* = 1.70, 0.6 Hz, 1H), 8.14 (t, *J* = 1.6 Hz, 1H), 8.10 (t, *J* = 1.6 Hz, 1H), 8.04 (ddd, *J* = 8.0, 1.8, 1.2 Hz, 1H), 7.81 (t, *J* = 1.6 Hz, 1H), 7.71 (ddd, *J* = 7.77, 1.62, 1.34 Hz, 1H), 7.45 (td, *J* = 7.73, 0.75 Hz, 1H), 4.52–4.48 (m, 2H), 4.35–4.32 (m, 2H), 3.89–3.81 (m, 3H), 3.78–3.63 (m, 12H), 3.56–3.48 (m, 4H), 3.36 (s, 3H), 3.35 (s, 3H), 1.30 (d, *J* = 6.50 Hz, 3H), 0.26 (s, 9H); ¹³C NMR (100 MHz, CDCl₃): δ = 165.4, 165.0, 138.6, 135.7, 132.6, 132.5, 132.3, 130.6, 130.4, 129.6, 128.5, 123.9, 122.9, 102.7, 96.2, 89.5, 88.2, 73.7, 71.8, 70.7, 70.5, 70.48, 70.47, 70.45, 68.9, 68.6, 67.8, 64.3, 58.8, 17.0, -0.3; MS (FAB): *m/z* (%): 669 (50), 154.1 (100); TLC: *R_f* = 0.24 (hexanes/EtOAc, 1/2); elemental analysis calcd (%) for C₃₆H₄₈O₁₀Si (668.86): C 64.65, H 7.23; found: C 64.97, H 7.13.

H-[A]₁-[B]₁₃-SiMe₃ (8): To a solution of H-[A]₁-[B]₁-SiMe₃ (84 mg, 0.13 mmol) and THF (5 mL) was added a solution of tetrabutylammonium fluoride in wet THF (200 μL, 1.0 M). The solution was stirred for 1 min, filtered through silica (eluting with hexanes/EtOAc, 1/2), and the solvent was removed in vacuo to leave an orange oil. The crude acetylene was used without further purification. To a sealed tube fitted with a magnetic stirrer was added H-[A]₁-[B]₁-H (75 mg, 0.13 mmol), I-[B]₁₃-SiMe₃ (82 mg, 0.02 mmol), [Pd₂(dba)₃] (10 mg, 0.01 mmol), CuI (4.1 mg, 0.02 mmol), PPh₃ (21 mg, 0.08 mmol), dry triethylamine (1 mL), and dry acetonitrile (3 mL). The mixture was evacuated and back-filled with nitrogen three times and heated at 70 °C for 19 h. The solution was concentrated in vacuo leaving a brown residue. The crude product was purified by silica gel column chromatography (CHCl₃/acetone (1/0, 1/1); followed by CHCl₃/*i*PrOH (95/5, 94/6, 93/7, 91/9)) to give **8** (46 mg, 0.01 mmol; 50 %) as an off-white wax: ¹H NMR (400 MHz, CDCl₃): δ = 8.23–8.17 (m, 25H), 8.14 (t, *J* = 1.8 Hz, 1H), 8.11 (t, *J* = 1.6 Hz, 1H), 8.05 (ddd, *J* = 7.7, 1.7, 1.2 Hz, 1H), 7.92–7.90 (m, 11H), 7.88 (t, *J* = 1.6 Hz, 1H), 7.82 (t, *J* = 1.6 Hz, 1H), 7.73 (ddd, *J* = 7.7, 1.6, 1.3 Hz, 1H), 7.45 (td, *J* = 7.8, 0.6 Hz, 1H), 4.56–4.48 (m, 26H), 4.35–4.32 (m, 2H), 3.92–3.84 (m, 28H), 3.76–3.68 (m, 84H), 3.54–3.48 (m, 28H), 3.34 (s, 3H), 3.33 (s, 39H), 1.30 (d, *J* = 6.43 Hz, 1H), 0.27 (s,

9H); MS (MALDI): *m/z*: 4174.72 (calcd [*M* + Na]⁺ = 4175.69); TLC: *R_f* = 0.28 (CHCl₃/acetone, 2/1); GPC 3642 (*M_n*), 1.08 (*M_w*/*M_n*), 98.2 %.

H-[A]₂-[B]₁₂-SiMe₃ (9): To a solution of H-[A]₂-SiMe₃ (0.60 g, 0.88 mmol) and THF (6 mL) was added a solution of tetrabutylammonium fluoride in wet THF (1.1 mL, 1.0 M). The solution was stirred for 1 min, filtered through silica (eluting with hexanes/EtOAc, 1/2), and the solvent was removed in vacuo to leave a yellow oil. The crude product was used without further purification. To a sealed tube fitted with a magnetic stirrer was added H-[A]₂-H (38 mg, 0.06 mmol), I-[B]₁₂-SiMe₃ (70 mg, 0.02 mmol), [Pd₂(dba)₃] (9.3 mg, 0.01 mmol), CuI (3.7 mg, 0.02 mmol), PPh₃ (22 mg, 0.08 mmol), dry triethylamine (0.2 mL), and dry acetonitrile (2 mL). The mixture was evacuated and back-filled with nitrogen three times and heated at 70 °C for 35 h. The solution was concentrated in vacuo leaving a brown residue. The crude product was purified by silica gel column chromatography (CHCl₃/acetone (1/0, 2/1) followed by CHCl₃/*i*PrOH (95/5, 92/8)) to give **9** (47 mg, 0.01 mmol; 59 %) as an off-white wax: ¹H NMR (400 MHz, CDCl₃): δ = 8.23–8.17 (m, 25H), 8.14 (t, *J* = 1.8 Hz, 1H), 8.11 (t, *J* = 1.6 Hz, 1H), 8.05 (ddd, *J* = 7.7, 1.7, 1.2 Hz, 1H), 7.92–7.90 (m, 11H), 7.88 (t, *J* = 1.6 Hz, 1H), 7.82 (t, *J* = 1.6 Hz, 1H), 7.73 (ddd, *J* = 7.7, 1.6, 1.3 Hz, 1H), 7.45 (td, *J* = 7.8, 0.6 Hz, 1H), 4.56–4.48 (m, 24H), 4.35–4.32 (m, 4H), 3.92–3.84 (m, 26H), 3.76–3.68 (m, 84H), 3.54–3.48 (m, 28H), 3.34 (s, 3H), 3.33 (s, 39H), 1.30 (d, *J* = 6.5 Hz, 1H), 1.28 (d, *J* = 6.4 Hz, 1H), 0.27 (s, 9H); MS (MALDI): *m/z*: 4188.8 (calcd [*M* + Na]⁺ = 4186.7); TLC: *R_f* = 0.28 (CHCl₃/acetone, 2/1); GPC 4210 (*M_n*), 1.15 (*M_w*/*M_n*), 95 %.

H-[A]₄-[B]₁₂-SiMe₃ (10): To a solution of H-[A]₄-SiMe₃ (0.60 g, 0.88 mmol) and THF (6 mL) was added a solution of tetrabutylammonium fluoride in wet THF (1.1 mL, 1.0 M). The solution was stirred for 1 min, filtered through silica (eluting with hexanes/EtOAc, 1/2), and the solvent was removed in vacuo to leave a yellow oil. The crude product was used without further purification. To a sealed tube fitted with a magnetic stirrer was added H-[A]₄-H (44 mg, 0.04 mmol), I-[B]₁₂-SiMe₃ (76 mg, 0.02 mmol), [Pd₂(dba)₃] (7.0 mg, 0.01 mmol), CuI (3.4 mg, 0.18 mmol), PPh₃ (19 mg, 0.07 mmol), dry triethylamine (1 mL), and dry acetonitrile (6 mL). The mixture was evacuated and back-filled with nitrogen three times and heated at 70 °C for 19 h. The solution was concentrated in vacuo leaving a brown residue. The crude product was purified by silica gel column chromatography (CHCl₃/acetone (1/0, 1/1, 1/2) followed by CHCl₃/*i*PrOH (95/5, 94/6, 93/7, 91/9)) to give **10** (70 mg, 0.02 mmol; 71 %) as an off-white wax: ¹H NMR (400 MHz, CDCl₃): δ = 8.23–8.197 (m, 29H), 8.14 (t, *J* = 1.8 Hz, 1H), 8.11 (t, *J* = 1.6 Hz, 1H), 8.05 (ddd, *J* = 7.7, 1.7, 1.2 Hz, 1H), 7.92–7.90 (m, 13H), 7.88 (t, *J* = 1.6 Hz, 1H), 7.82 (t, *J* = 1.6 Hz, 1H), 7.73 (ddd, *J* = 7.7, 1.6, 1.3 Hz, 1H), 7.45 (td, *J* = 7.8, 0.6 Hz, 1H), 4.56–4.48 (m, 24H), 4.35–4.32 (m, 8H), 3.92–3.84 (m, 28H), 3.76–3.68 (m, 96H), 3.54–3.48 (m, 32H), 3.34 (s, 3H), 3.33 (s, 45H), 1.33–1.27 (m, 12H), 0.27 (s, 9H); MS (MALDI): *m/z*: 4795.55 (calcd [*M* + Na]⁺ = 4799.97); TLC: *R_f* = 0.25 (CHCl₃/*i*PrOH, 93/7); GPC 5603 (*M_n*), 1.15 (*M_w*/*M_n*), 97.5 %.

H-[A]₆-[B]₁₂-SiMe₃ (11): To a solution of H-[A]₆-SiMe₃ (516 mg, 0.27 mmol) and THF (8 mL) was added a solution of tetrabutylammonium fluoride in wet THF (0.4 mL, 1.0 M). The solution was stirred for 1 min, filtered through silica (eluting with CHCl₃/acetone, 2/1), and the solvent was removed in vacuo to leave a yellow oil. The crude product was used without further purification. To a sealed tube fitted with a magnetic stirrer was added H-[A]₆-H (51 mg, 0.03 mmol), I-[B]₁₂-SiMe₃ (70 mg, 0.02 mmol), [Pd₂(dba)₃] (8.0 mg, 0.01 mmol), CuI (3.6 mg, 0.02 mmol), PPh₃ (21 mg, 0.08 mmol), dry triethylamine (1 mL), and dry acetonitrile (3 mL). The mixture was evacuated and back-filled with nitrogen three times and heated at 70 °C for 10 h. The solution was concentrated in vacuo leaving a brown residue. The crude product was purified by silica gel column chromatography (CHCl₃/acetone (1/0, 1/1) followed by CHCl₃/*i*PrOH (95/5, 94/6, 93/7, 92/8)) to give **11** (76 mg, 0.01 mmol, 75 %) as an off-white wax: ¹H NMR (400 MHz, CDCl₃): δ = 8.23–8.197 (m, 33H), 8.14 (t, *J* = 1.8 Hz, 1H), 8.11 (t, *J* = 1.6 Hz, 1H), 8.05 (ddd, *J* = 7.7, 1.7, 1.2 Hz, 1H), 7.92–7.90 (m, 15H), 7.88 (t, *J* = 1.6 Hz, 1H), 7.82 (t, *J* = 1.6 Hz, 1H), 7.73 (ddd, *J* = 7.7, 1.6, 1.3 Hz, 1H), 7.45 (td, *J* = 7.8, 0.6 Hz, 1H), 4.56–4.48 (m, 24H), 4.35–4.32 (m, 30H), 3.92–3.84 (m, 28H), 3.76–3.68 (m, 108H), 3.54–3.48 (m, 36H), 3.34 (s, 3H), 3.33 (s, 51H), 1.33–1.27 (m, 18H), 0.27 (s, 9H); MS (MALDI): *m/z*: 5407.1 (calcd [*M* + Na]⁺ = 5406.2); TLC *R_f* = 0.25 (CHCl₃/*i*PrOH, 93/7); GPC 5931 (*M_n*), 1.16 (*M_w*/*M_n*), 100 %.

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- [26] It could also be argued that reversals of the helical twist sense occur within a single oligomer strand. However, this effect can be excluded since previous studies^[21] indicate that an analogous series of oligomers adopt a single helical conformation in solution absent of helical reversals.

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