Electronic Supplementary Information

Helix stabilization through pyridinium-π interactions

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General. Unless otherwise noted, all starting materials were obtained from commercial suppliers and were used without further purification. All air- or moisture-sensitive reactions were done under an atmosphere of dry argon. Flash column chromatography was carried out with silica gel 60 (230-400 mesh) from EM Science. Dry triethylamine and acetonitrile were obtained using a solvent-purification system from Anhydrous Engineering.

The ^{1}H and ^{13}C NMR spectra were recorded on a Varian Unity 400, Varian Unity 500, or Varian Narrow Bore 500 spectrometer. Chemical shifts are expressed in parts per million (δ) using residual solvent protons as internal standard (δ 7.26 ppm for $CHCl_3$). Coupling constants, *J*, are reported in Hertz (Hz), and splitting patterns are designated as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), br (broad), and app (apparent). Mass spectra were obtained through the Mass Spectrometry Facility, School of Chemical Sciences, Universtiy of Illinois. Low resolution matrix assisted laser desorption (MALDI) mass spectra were obtained using a Applied Biosystems Voyager-DE STR spectrometer. High pressure liquid chromatography (HPLC) analysis was performed with a Rainin Dynamax solvent delivery system, model SD-200, using a Microsorb Si-80-125-C5 silica column and a UV detector operating at 290 nm.

Measurement of $\Delta G(CH_3CN)$. The UV absorption spectra were recorded on a Shimadzu (model UV-2501) spectrophotometer using 1-cm quartz cells and thermostated to 25 ± 0.2 °C. Samples were prepared using spectrophotometric grade acetonitrile or chloroform purchased from Fisher. For the titration experiments, two stock solutions (c = 1.0-3.0 μM) of the appropriate oligomer were prepared such that the A_{289} of each solution was approximately 0.75. Mixed solvent compositions from 0-100% $CHCl_3$ were prepared by adding the appropriate volume of each stock solution to a scintillation vial. The UV spectrum was measured for each sample. For each solvent composition, the data shown in Figure S1 is an average of two different solutions.

By analogy to the solvent denaturation of proteins and peptide secondary structures, the free energy change between the folded and unfolded oligomer conformations was assumed to depend linearly on solvent composition (eq. 1).[1]

$$\Delta G = \Delta G(CH_3CN) - m[CHCl_3] \quad (1)$$

$\Delta G(CH_3CN)$ in eq. 1 represents the free energy difference between the folded and unfolded conformations in pure acetonitrile and the value of *m* describes how rapidly the free energy of the transition changes with solvent composition. The intercept of a plot of ΔG versus $[CHCl_3]$ thus provides $\Delta G(CH_3CN)$. The concentration of denaturant required to reach the midpoint of the transition $[CHCl_3]_{1/2}$ is given by $\Delta G(CH_3CN)/m$.

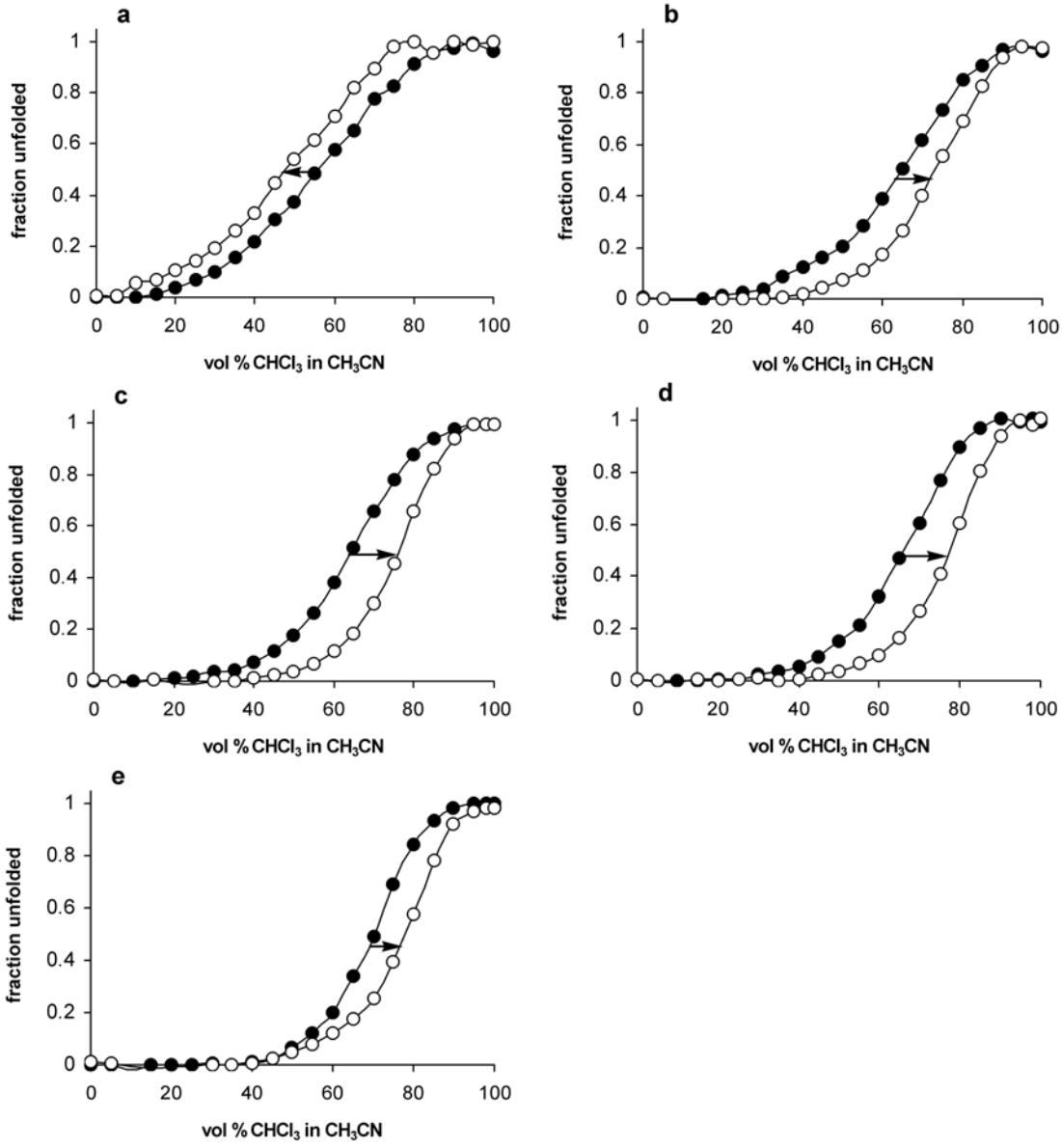
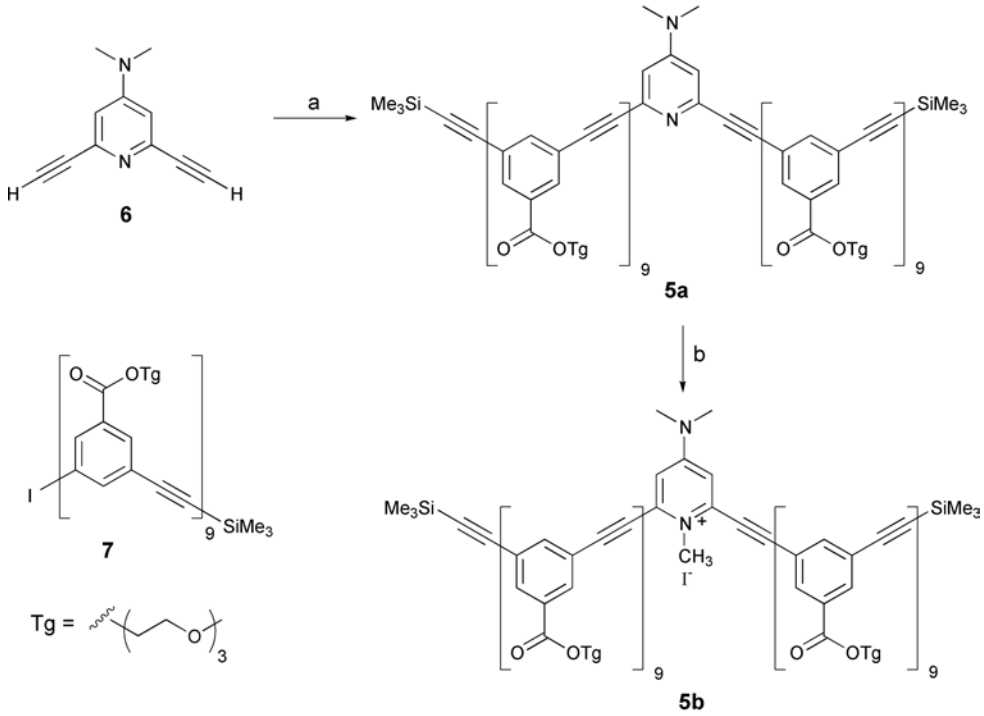


Figure S1. Solvent denaturation curves of oligomer sereis **a** (●) and series **b** (○), for (a) **1**, (b) **2**, (c) **3**, (d) **4**, (e) **5**. The arrows show the midpoint shift of denaturation upon methylation.

Reaction procedures. Synthesis of oligomers **1a-4a** and **1b-4b** has been reported previously.[2] Synthesis of olgiomers **5a** and **5b** is outlined in Scheme S1. Pd-catalyzed cross-coupling of *N,N*-dimethylaminopyridine monomer **6**,[2] with 2 equiv of iodide-terminated PE oligomer **7** provided oligomer **5a** in 42% yield. Reaction of **5a** with methyl iodide yielded **5b** in 95% yield.

Scheme S1. Synthesis of pyridine-containing oligomers



Nomenclature of Oligomers. All oligomers are named using an abbreviated nomenclature system. All oligomers follow the naming pattern: **X-[A]$_n$-Y-[A]$_n$-X** where **X** represents a trimethylsilylacetylene (TMS), iodide (I), or *N,N*-diethyltriazene (N_3Et_2) capping group, **A** represents a phenyl ring with a triethyleneglycol monomethyl ether (Tg) sidechain, and **Y** represents a *N,N*-dimethylaminopyridine monomer or the corresponding methyl pyridinium monomer.

TMS-[A]$_9$-N$_3$Et$_2$. A vial was charged with **TMS-[A]$_4$-N$_3$Et$_2$**[1] (0.0421 g, 0.0315 mmol), AcOH (0.0019 mL, 0.033 mmol), and THF (0.5 mL). A solution of TBAF in THF (1.0 M, 0.033 mL) was added, and the reaction mixture stirred for 1 min. The solution was filtered through a plug of silica gel with 2:1 CH_2Cl_2:acetone, and evaporated to give an dark yellow oil. To a 4 mL sealed tube was added $Pd_2(dba)_3$ (0.650 mg, 0.710 μmol), CuI (0.137 mg, 0.719 μmol), and PPh_3 (0.852 mg, 3.25 μmol). The contents of the sealed tube were degassed by alternating three times between vacuum and argon, then deprotected **TMS-[A]$_4$-N$_3$Et$_2$**[1] transferred via syringe with 3 x 0.25 mL portions of CH_3CN and **TMS-[A]$_5$-I**[2] (0.0516 g, 0.0312 mmol) transferred via syringe with 3 x 0.25 mL portions of CH_3CN. Triethylamine (0.5 mL) was

added to the sealed tube, the solution degassed, the tube sealed under an atmosphere of argon, and the reaction mixture stirred in an oil bath at 60°C for 26 h. The solvents were evaporated to give a pale yellow wax, which was purified by silica gel chromatography (3:97, 8:92 $CHCl_3$:*i*PrOH) to give 0.0710 g of pale yellow wax (81%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.21-8.18 (m, 15H), 8.15 (t, *J* = 1.6 Hz, 1H), 8.11 (t, *J* = 1.6 Hz, 1H), 8.06 (br s, 1H), 7.91-7.90 (m, 7H), 7.88 (t, *J* = 1.5 Hz, 1H), 7.82 (t, *J* = 1.6 Hz, 1H), 4.54-4.49 (m, 18H), 3.89-3.84 (m, 22H), 3.75-3.64 (m, 54H), 3.54-3.52 (m, 18H), 3.36-3.34 (m, 27H), 1.42-1.34 (m, 6H), 0.27 (s, 9H). MS (MALDI) *m/z* 2810.21 (calcd $[M + Na]^+$ = 2809.12). HPLC (1.0 mL/min, 4% *i*PrOH/$CHCl_3$ for 30 min, retention time 13.3 min) indicated >99% purity.

TMS-[A]$_9$-I (7). To a 4 mL sealed tube was added **TMS-[A]$_9$-N$_3$Et$_2$** (0.0485 g, 0.0174 mmol) and 1 mL CH_3I. The tube was sealed under an atmosphere of argon, and heated in an oil bath at 110 °C for 15 h. The solvent was removed under vacuum to give a yellow wax, which was purified by silica gel chromatography (3:97, 8:92 $CHCl_3$:*i*PrOH) to give 0.0440 g of white wax (90%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.36 (t, *J* = 1.5 Hz, 1H), 8.21-8.17 (m, 15H), 8.15 (t, *J* = 1.5 Hz, 1H), 8.11 (t, *J* = 1.5 Hz, 1H), 8.07 (t, *J* = 1.5 Hz, 1H), 7.91-7.88 (m, 7H), 7.82 (t, *J* = 1.5 Hz, 1H), 4.54-4.49 (m, 18H), 3.89-3.84 (m, 18H), 3.75-3.65 (m, 54H), 3.55-3.52 (m, 18H), 3.36-3.35 (m, 27H), 0.27 (s, 9H). MS (MALDI) *m/z* 2834.43 (calcd $[M + Na]^+$ = 2835.88). HPLC (1.0 mL/min, 4.5% *i*PrOH/$CHCl_3$ for 30 min, retention time 11.0 min) indicated >99% purity.

TMS-[A]$_9$-[DMAP]-[A]$_9$-TMS (5a). To a 4 mL sealed tube was added **6** (1.02 mg, 5.99 μmol), $Pd_2(dba)_3$ (0.375 mg, 0.410 μmol), CuI (0.129 mg, 0.677 μmol), and PPh_3 (0.476 mg, 1.81 μmol). The contents of the sealed tube were degassed by alternating three times between vacuum and Ar, then **7** (0.0343 g, 12.2 μmol) transferred via syringe with 3 x 0.3 mL portions of CH_3CN. Triethylamine (0.3 mL) was added to the sealed tube, the solution degassed, the tube sealed under an atmosphere of Ar, and the reaction mixture stirred in an oil bath at 60°C for 24 h. The solvents were evaporated to give a brown wax, which was purified by silica gel chromatography (95:5, 90:10 $CHCl_3$:*i*PrOH) to give 0.0141 g of pale yellow wax (42%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.30-8.09 (m, 36H), 7.96-7.80 (m, 18H), 6.71 (br s, 2H), 4.54-4.49 (m, 36H), 3.88-3.85 (m, 36H), 3.74-3.64 (m, 108H), 3.53-3.50 (m, 362H), 3.35-3.34 (m, 54H), 3.16 (br s, 6H), 0.26 (s, 18H). MS (MALDI) *m/z* 5565.80 (calcd $[M + Na]^+$ 5563.15). HPLC (1.0 mL/min, 5% *i*PrOH/$CHCl_3$ w/ 0.02% Et_3N 30 min, retention time 8.8 min) indicated >98% purity.

TMS-[A]$_9$-[DMAP$^+$-MeI$^-$]-[A]$_9$-TMS (5b). A scintillation vial was charged with **5a** (0.0070 g, 1.3 μmol) and CH_3I (2 mL). The reaction mixture was stirred for 1 h, then the solvent removed under vacuum to give 0.0070 g of yellow wax (95%). ^{1}HNMR (500 MHz, $CDCl_3$) δ 8.28-8.10 (m, 36H), 7.93-7.82 (m, 18H), 4.52 (br s, 39H), 3.87-3.84 (m, 36H), 3.74-3.65 (m, 108H), 3.54-3.52 (m, 42 H), 3.35-3.34 (m, 54H), 0.26 (s, 18H). MS (MALDI) *m/z* 5555.62 (calcd $[M]^+$ 5555.21).

[1] R. B. Prince, J. G. Saven, P. G. Wolynes and J. S. Moore, *J. Am. Chem. Soc*., 1999, **121**, 3114.
[2] J. M. Heemstra and J. S. Moore, *J. Am. Chem. Soc.*, 2004, **126**, 1648.