ELECTRONIC SUPPLEMENTARY INFORMATION

The role of statistics and microenvironment for the photoresponse in multi-switch architectures: The case of photoswitchable oligoazobenzene foldamers

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**General Methods.** Compounds 1, 2, 5, 7, 8, 16, and 20 were prepared as described in the literature,[1] and the syntheses of oligomers 14, 12, and 10 were described in previously report.[1a] Toluene, diisopropylamine (DIPA), Et₃N, and CH₃CN were distilled prior to use under argon atmosphere over sodium and calcium hydride, respectively. All other chemical reagents were commercial and used as received. Column chromatography was carried out with 130-400 mesh silica gel. NMR spectra were recorded on a 400 MHz (100.6 MHz for ¹³C) Bruker AV 400 or on a 300 MHz Bruker DPX 300 spectrometer at 27 °C using residual protonated solvent signals as internal standard (¹H: δ(CHCl₃) = 7.26 ppm and ¹³C: δ(CHCl₃) = 77.16 ppm). 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 Q-TOF with a ISV of 950 V. MALDI-TOF mass spectra were obtained on Bruker-Apex III (365 nm laser wavelength), employing DCTB (10 mg/mL, 5/2 vol% with sample, sum of 3000 shots) as the matrix. GPC measurements were performed on a WGE Dr. Bures system using both UV (300 nm) and RI detection. The measurements were performed in THF at 30 °C on PSS columns using a flow rate of 1 mL/min. Calibration was done with several narrow polydispersity polystyrene samples, and 2,4-di-tert-butyl-4-methoxy-phenol was employed as internal standard to the samples.

**Optical Spectroscopy.** UV/vis absorption spectra were recorded in the given solvents (spectroscopic grade) using quartz cuvettes of 1 cm path length on a Cary 50 Spectrophotometer, equipped with Peltier thermostated cell holders (ΔT = ± 0.05 °C). Unless stated otherwise, all experiments were carried out at 25 ± 0.05 °C. For solvent titration

experiments, stock solutions (ca. $5 \times 10^{-5}$ M) in CHCl$_3$ and CH$_3$CN were used to prepare samples with varying solvent composition. Circular dichroism (CD) spectra were recorded on a JASCO 700 spectrometer using quartz cuvetts of 1 cm path length, equipped with Peltier thermostated cell holders, at $25 \pm 0.05 \, ^\circ\text{C}$. CD spectra, recorded as $\theta$ in millidegrees, were converted to $\Delta \varepsilon$ using the equation $\Delta \varepsilon = \theta / (33982 c l)$, where $\Delta \varepsilon$ is the difference in the molar absorptivity for oppositely polarized light in M$^{-1}$cm$^{-1}$, $c$ is the concentration in mol/L, and $l$ is the path length in cm.

**Irradiation Experiments.** Irradiation was performed using a LOT-Oriel 1000 W (900 W was chosen during irradiation) medium pressure Xe lamp, equipped with special filter-off filters $\lambda_{\text{max}} = 357 \, \text{nm} \at \text{T} = 35\%$ and $\text{FWHM} = 42 \, \text{nm}$ or cut-off filter $\lambda_{\text{max}} > 405 \, \text{nm} \at \text{T} = 65\%$, resulting in a narrow spectral window of UV-light and visible light, respectively.

**Analysis of the Composition of the Photostationary State (PSS).** All samples (ca. $10^{-3}$ M) were irradiated in acetonitrile until the PSS was reached (checking by UV/vis spectroscopy after dilution to ca. $10^{-6}$ M concentration). After evaporating the solvent quickly (ca. 10 min) in the dark under vacuo, samples were immediately dissolved in CDCl$_3$ to obtain $^1\text{H}$-NMR spectra. The Z-contents were derived by integrating the signals of $-\text{COOCH}^-$ or $-\text{COOCH}_2^-$, for chiral and achiral side chain, respectively (see Figure S13-15).

**Refolding Kinetics during Thermal Isomerization.** All samples were irradiated in acetonitrile until the PSS was reached (checking by combination of CD and UV/vis spectroscopies) and diluted to acetonitrile/H$_2$O solution (4/1, v/v), in which concentration is similar to the relevant $E \rightarrow Z$ isomerization experiment solution. The data of kinetic rate constants of refolding process plotted as $\ln[(k/T)]$ versus $1/T$ were fitted according to the
linear form of the Eyring equation:

$$\ln\left(\frac{k}{T}\right) = -\frac{\Delta H^*}{R} \cdot \frac{1}{T} + \frac{\Delta S^*}{R} - \ln\left(\frac{h}{k_B}\right)$$

where $T$ is the temperature, $R$ the gas constant ($1.987 \text{ cal} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$), $k_B$ the Boltzmann constant ($1.38 \times 10^{-23} \text{ J} \cdot \text{K}^{-1}$), and $h$ the Planck constant ($6.63 \times 10^{-34} \text{ J} \cdot \text{s}^{-1}$). According to the slope and intercept from the linear fitting, the enthalpy and entropy of activation for the refolding of foldamer during thermal isomerization can be determined (see Table 2 in the text).

**Electronic Spin Resonance (ESR) Spectroscopy.** The ESR spectra were recorded with a commercial X-Band (9.4 GHz) electron spin resonance spectrometer (Bruker, B-ER 420) which has been equipped with a new microwave bridge (Bruker, ECS 041 XK) and a new lock-in amplifier (Bruker, ER 023M) to improve the noise level of the machine. Cooling was done using a helium flow cryostat (Oxford ESR900). Spectra were taken in a TE$_{102}$ resonator at 20 K using a modulation amplitude of 1 G and a microwave power of 2 mW. These values were chosen such as to avoid overmodulation and saturation effects.

The samples of spin-labeled foldames for ESR spectra were diluted to approximate $10^{-7} \text{ M}$ from stock solution (approx. $10^{-5} \text{ M}$) to exclude the possibility of aggregation and the corresponding intermolecular spin-coupling interaction. The concentration was deduced from a concentration series of the singly labeled $11_4$-TEMPO oligomer in comparison with the spectrum of pure spin label in acetonitrile, where no indication of residual dipolar broadening can be observed.

The analysis of the data was done with a home-made program which utilizes a Fourier space analysis of the data. In particular, the spectrum of the uncoupled spin labels is convoluted with the appropriate sum of Pake-patterns to be generated from the distance.
distribution of the spin label.\textsuperscript{[2]} Two strategies were used to generate this distance distribution. On the one hand a distance distribution assuming two simple box like components whose width, height and position was determined using a least square fit scheme was used. On the other hand an algorithm using a Tichonov regularization scheme was used to generate a distance distribution.\textsuperscript{[3]} The error of amplitude ratio of $d_1/d_0$ in ESR spectra during the thermal isomerization of azobenzene was obtained from the average in a series measurement.

**Calculation of $\Delta G_{\text{nuc}}$ and $\Delta G_{\text{prop}}$ for 3 azos/turn Foldamer Series in Folding Process.**

Based on Zimm-Bragg two state helix-coil thermodynamic model, formation of OmPE foldamer includes helix nucleation and helix propagation. The Gibbs free energy change in this procedure follows this formula,\textsuperscript{[4]}

$$\Delta G = \Delta G_{\text{nuc}} + (n-N_i) \Delta G_{\text{prop}} = N_i k_B T \ln \omega + (n-N_i) (k_B T \ln \omega + \varepsilon)$$

where $n$ and $N_i$ is the total repeated units number and units number for nucleation, $\omega$ is the conformation of backbone chain, $\varepsilon$ is the energy getting from one unit interaction. In the formula, the first part, $N_i k_B T \ln \omega$, is the entropy cost due to nucleation formation, and the second part, $(k_B T \ln \omega + \varepsilon)$, is net enthalpy gain for one repeating unit joining to the helical structure. From the corresponding stabilization energies for foldamers 12\textsubscript{6} and 14\textsubscript{7}, the initial entropic cost, i.e. $\Delta G_{\text{nuc}}$, and the net enthalpic gain, i.e. $\Delta G_{\text{prop}}$, per added azobenzene unit can be obtained as 1.15 kcal/mol and -1.15 kcal/mol, respectively.


Synthesis

Syntheses of the oligomers were carried out by the following routes (Schemes S1, S2, S4 and S5):

Scheme S1. Synthetic route for oligomers 10, 14.4.
Scheme S2. Synthetic route for oligomers 114 and 145.
Scheme S3. Chemical structures of oligomers 10₃, 14₄, 11₄, 14₅, 10₅, 12₆, and 14₇.
Scheme S4. Synthetic route for oligomers 114-TEMPO$_{αβ}$ and 176-TEMPO$_{αβ}$. 
Scheme S5. Synthetic route for oligomers 114-TEMPO and 176-TEMPOα-γ.
**Compound 3**

In a dried flask flushed with argon, a mixture of 1 (180 mg, 0.2 mmol), 2 (136 mg, 0.2 mmol), Pd(PPh₃)₄ (22 mg, 0.02 mmol), CuI (4 mg, 0.02 mmol), and PPh₃ (11 mg, 0.04 mmol) was added together to a mixture of diisopropylamine (3 mL) and toluene (10 mL). After stirring for 16 h at 60 °C, the reaction mixture was concentrated in vacuo, and the crude compound was purified by column chromatography (DCM/acetone = 4:1) to yield compound 3 (195 mg, 0.13 mmol) in 65% yield as a bright orange oil. **¹H-NMR (300 MHz, CDCl₃):** δ (ppm) = 8.61 (t, ³J = 1.5, 1 H, Ar-H), 8.59 (t, ³J = 1.2, 1 H, Ar-H), 8.37 (t, ³J = 1.2, 1 H, Ar-H), 8.29 (m, 2 H, Ar-H), 8.24 (t, ³J = 1.5, 1 H, Ar-H), 8.21 (m, 2 H, Ar-H), 8.08 (t, ³J = 1.5, 1 H, Ar-H), 7.97 (t, ³J = 1.5, 1 H, Ar-H), 7.94 (t, ³J = 1.5, 1 H, Ar-H), 7.82 (t, ³J = 1.8, 1 H, Ar-H), 5.39 (m, 2 H, OCH), 4.57 (m, 4 H, OCH₂), 3.91 (m, 4 H, OCH₂), 3.84-3.60 (m, 40 H, OCH₂ and NCH₂), 3.55 (m, 8 H, OCH₂), 3.34 (s, 12 H, OCH₃), 1.43 (t, ³J = 1.8, 6 H, CCH₃), 1.29 (br, 6 H, NCCH₃), 0.30 (s, 9 H, Si(CH₃)₃). **¹³C-NMR (300 MHz, CDCl₃):** δ (ppm) = 164.13, 152.17, 151.98, 144.04, 138.51, 138.37, 135.48, 135.15, 132.83, 132.34, 131.96, 131.83, 131.57, 131.43, 129.56, 129.23, 128.65, 125.05, 124.83, 124.76, 124.09, 123.55, 123.40, 102.88, 96.78, 93.41, 89.53, 89.21, 89.11, 88.31, 73.88, 73.81, 71.87, 70.98, 69.11, 64.68, 64.60, 59.01, 48.37, 19.06, 16.74, 16.68, 0.17. **ESI-MS:** m/z = 1454.65 ([M+H]⁺) (calc. 1454.69 for C₇₅H₁₀₃N₅O₂₂Si+H⁺), 1476.62 ([M+Na]⁺) (calc. 1476.68 for C₇₅H₁₀₃N₅O₂₂Si+Na⁺), 738.82 ([M+Na+H]²⁺) (calc. 1477.68 for C₇₅H₁₀₃N₅O₂₂Si+Na⁺+H⁺).
**Compound 4**

To a dry and degassed sealed tube, 3 (290 mg, 0.2 mmol), iodine (51 mg, 0.2 mmol), and iodomethane (6 mL) were added. After stirring for 16 h at 110 °C, the remaining iodomethane was removed in vacuo to give a dark brown oily residue. The residue was purified by column chromatography (DCM/aceton=4:1) to yield the compound 4 (260 mg, 0.18 mmol) in 90 % yield as an orange oil. **¹H-NMR** (300 MHz, CDCl₃): δ (ppm) = 8.61 (t, ³J = 1.2, 1 H, Ar-H), 8.59 (t, ³J = 1.5, 1 H, Ar-H), 8.36 (t, ³J = 1.5, 1 H, Ar-H), 8.35 (t, ³J = 1.2, 1 H, Ar-H), 8.28 (m, 2 H, Ar-H), 8.24 (t, ³J = 1.2, 1 H, Ar-H), 8.22 (dd, ³J = 1.2, 2 H, Ar-H), 8.18 (t, ³J = 1.5, 1 H, Ar-H), 8.16 (t, ³J = 1.5, 1 H, Ar-H), 8.08 (t, ³J = 1.5, 1 H, Ar-H), 7.91 (t, ³J = 1.8, 1 H, Ar-H), 5.38 (m, 2 H, OCH), 4.55 (m, 4 H, OCH₂), 3.89 (m, 4 H, OCH₂), 3.80-3.60 (m, 36 H, OCH₂ and NCH₂), 3.53 (m, 8 H, OCH₂), 3.34 (s, 12 H, OCH₃), 1.39 (t, ³J = 2.4, 6 H, CCH₃), 0.30 (s, 9 H, Si(CH₃)₃). **¹³C-NMR** (300 MHz, CDCl₃): δ (ppm) = 164.13, 152.17, 151.98, 144.04, 138.51, 138.37, 135.48, 135.15, 132.83, 132.34, 131.96, 131.83, 131.57, 131.43, 129.56, 129.23, 128.65, 125.05, 124.83, 124.76, 124.09, 123.55, 123.40, 102.88, 96.78, 93.41, 89.53, 89.21, 89.11, 88.31, 73.88, 73.81, 71.87, 70.98, 69.11, 64.68, 64.60, 59.01, 48.37, 19.06, 16.74, 16.68, 0.17. **ESI-MS:** m/z = 1503.46 ([M+Na⁺]) (calc. 1476.68 for C₇₁H₉₃IN₂O₂₂Si+Na⁺), 763.25 ([M+2Na]²⁺) (calc. 1526.48 for C₇₁H₉₃IN₂O₂₂Si+2Na⁺).
Following the Sonogashira coupling protocol to compound 3, a mixture of 1 (273 mg, 0.4 mmol), 5 (185 mg, 0.2 mmol), Pd(PPh₃)₄ (45 mg, 0.04 mmol), CuI (8 mg, 0.04 mmol), and PPh₃ (22 mg, 0.08 mmol) was dissolved in a mixture of diisopropylamine (5 mL) and toluene (20 mL), and reacted for 20 h at 70 °C. The crude compound was purified by column chromatography (DCM/acetone = 3:1) to yield compound 6 (230 mg, 0.11 mmol) in 56 % yield as an orange wax. ¹H-NMR (300 MHz, CDCl₃): δ (ppm) = 8.61 (t, ³J = 1.5, 2H, Ar-H), 8.59 (t, ³J = 1.5, 2H, Ar-H), 8.37 (t, ³J = 1.5, 2H, Ar-H), 8.29 (m, 4H, Ar-H), 8.21 (m, 6H, Ar-H), 7.94 (t, ³J = 1.8, 2H, Ar-H), 5.40 (m, 2H, OCH), 4.54 (m, 8H, OCH₂), 3.89 (m, 8H, OCH₂), 3.81-3.60 (m, 48H, CH₂), 3.54 (m, 12H, CH₂), 3.33 (s, 18H, CH₃), 1.41 (dd, ³J = 1.8, 6H, CCH₃), 0.29 (s, 18H, Si(CH₃)₃). ESI-MS: m/z = 2037.12 ([M+H⁺]⁺) (calc. 2036.89 for C₁₀₆H₁₃₈N₄O₃₂Si₂+H⁺), 2059.43 ([M+Na⁺]⁺) (calc. 2058.88 for C₁₀₆H₁₃₈N₄O₃₂Si₂+Na⁺).
Oligomer 10₃

Following the Sonogashira coupling protocol to compound 3, a mixture of 4 (118 mg, 0.08 mmol), 7 (24 mg, 0.04 mmol), Pd(PPh₃)₄ (9 mg, 0.008 mmol), CuI (3 mg, 0.016 mmol), and PPh₃ (4 mg, 0.016 mmol) was added to a mixture of diisopropylamine (2 mL) and toluene (5 mL). After stirring the reaction mixture for 24 h at 70 °C, the crude compound was purified by column chromatography (DCM/acetone = 1:1) to give oligomer 10₃ (70 mg, 0.21 mmol) in 51 % yield as a bright orange wax. ¹H-NMR (300 MHz, CDCl₃): δ (ppm) = 8.63 (t, 3J = 1.2, 2 H, Ar-H), 8.61 (t, 3J = 1.5, 2 H, Ar-H), 8.57 (t, 3J = 1.6, 2 H, Ar-H), 8.39 (t, 3J = 1.6, 2 H, Ar-H), 8.37 (t, 3J = 1.5, 2 H, Ar-H), 8.32 (t, 3J = 1.2, 2 H, Ar-H), 8.29 (t, 3J = 1.2, 2 H, Ar-H), 8.27 (t, 3J = 1.2, 2 H, Ar-H), 8.22 (m, 10 H, Ar-H), 7.94 (dd, 3J = 1.2, 4 H, Ar-H), 5.40 (m, 4 H, OCH), 4.56 (m, 12 H, OCH₂), 3.90 (m, 12 H, OCH₂), 3.80-3.60 (m, 84 H, OCH₂), 3.55 (m, 20 H, OCH₂), 3.35 (s, 30 H, OCH₃), 1.42 (d, 3J = 12.8, 12 H, CCH₃), 0.29 (s, 18 H, Si(CH₃)₃).

MALDI-TOF MS (DCTB matrix): m/z = 3340.21 ([M+Na]+) (calc. 3340.43 for C₁₇₄H₂₂₂N₆O₅₅Si₂⁺Na⁺). GPC (THF, 30 °C): Mw = 4943, PDI (Mw/Mn) = 1.05.
**Oligomer 14**

To a solution of compound 6 (200 mg, 0.10 mmol) in THF (30 ml) was added a solution of tetrabutylammonium fluoride (TBAF) in THF (0.25 mL, 1 M). After stirring for 1 min, the reaction was stopped and filtered through a short silica gel column using aceton as the eluent solution. Organic solvent was removed in vacuo, and the orange residue was purified by column chromatography (DCM/acetone = 2:1) to produce di-acetylenic compound (100 mg, 0.05 mmol) in 52% yield. The product was used directly without characterization. In the Sonogashira coupling process, to a dried and degassed schlenk tube, a mixture of diacetylenic compound (76 mg, 0.04 mmol), 4 (118 mg, 0.08 mmol), Pd(PPh3)4 (9 mg, 0.008 mmol), CuI (3 mg, 0.016 mmol), and PPh3 (4 mg, 0.016 mmol) was added together to a mixture of diisopropylamine (3 mL) and toluene (5 mL). After stirring for 22 h at 70 °C, the reaction mixture was concentrated in vacuo, and the crude compound was purified by column chromatography (DCM/acetone = 1:2) to yield oligomer 14 (230 mg, 0.022 mmol) in 56% yield as an orange wax. **1H-NMR** (300 MHz, CDCl3): δ (ppm) = 8.64 (t, 3J = 1.2, 4H, Ar-H), 8.61 (t, 3J = 1.6, 2H, Ar-H), 8.58 (t, 3J = 1.6, 2H, Ar-H), 8.39 (m, 6H, Ar-H), 8.34 (m, 4H, Ar-H), 8.30 (t, 3J = 1.5, 2H, Ar-H), 8.28 (t, 3J = 1.5, 2H, Ar-H), 8.22 (m, 14H, Ar-H), 7.95 (m, 6H, Ar-H), 5.41 (m, 6H, OCH), 4.57 (m, 16H, OCH2), 3.89 (m, 16H, OCH2), 3.68 (m, 12OH, CH2), 3.55 (m, 28H, CH2), 3.34 (s, 42H, CH3), 1.43 (dd, 3J = 12.4, 18H, CCH3), 0.28 (s, 18 H, Si(CH3)3). MALDI-TOF MS (DCTB matrix): m/z = 4622.24 ([(M+Na]+) (calc. 4622.19 for C242H306N8O76Si2+Na+). GPC (THF, 30 °C): Mw = 5295, PDI (Mw/Mn) = 1.04.
Compounds 9 and 13

To a dried and degassed flask, a mixture of 1 (682 mg, 1.0 mmol), 8 (540 mg, 1.0 mmol), Pd(PPh₃)₄ (116 mg, 0.1 mmol), CuI (19 mg, 0.1 mmol), and PPh₃ (54 mg, 0.01 mmol) was added to a mixture of diisopropylamine (4 mL) and toluene (20 mL). After reacting for 14 h at 70 °C, the crude compounds were purified by column chromatography (DCM/acetone = 4:1, and then DCM/acetone = 3:1) to yield compounds 9 (430 mg, 0.38 mmol) and 13 (520 mg, 0.31 mmol) in 38% and 31% yields, respectively, as bright orange oils.

For compound 9: ¹H-NMR (300 MHz, CDCl₃): δ (ppm) = 8.62 (t, 3J = 1.5, 1H, Ar-H), 8.58 (t, 3J = 1.5, 1H, Ar-H), 8.36 (dd, 3J = 1.2, 2H, Ar-H), 8.28 (dd, 3J = 1.2, 2H, Ar-H), 8.23 (t, 3J = 1.5, 1H, Ar-H), 8.20 (t, 3J = 1.5, 1H, Ar-H), 8.11 (t, 3J = 1.8, 1H, Ar-H), 5.37 (m, 1H, OCH), 4.56 (m, 4H, OCH₂), 3.89 (m, 4H, OCH₂), 3.74 (m, 24H, CH₂), 3.66 (m, 6H, CH₂), 3.35 (s, 9H, CH₃), 1.39 (d, 3J = 1.8, 3H, CCH₃), 0.26 (s, 9H, Si(CH₃)₃). ¹³C-NMR (300 MHz, CDCl₃): δ (ppm) = 165.1, 164.5, 152.9, 152.0, 151.8, 135.6, 135.4, 134.9, 132.9, 131.6, 129.5, 128.5, 124.9, 124.8, 124.7, 124.6, 123.2, 102.9, 102.8, 96.8, 96.7, 71.9, 70.6, 69.1, 64.8, 64.6, 59.0, 0.2. ESI-MS: m/z = 1133.31 ([M+H⁺]) (calc. 1133.35 for C₅₂H₆₉N₂O₁₆Si+H⁺), 1155.27 ([M+Na⁺]) (calc. 1155.34 for C₅₂H₆₉N₂O₁₆Si+Na⁺).

For compound 13: ¹H-NMR (300 MHz, CDCl₃): δ (ppm) = 8.62 (t, 3J = 1.4, 2 H, Ar-H), 8.58 (t, 3J = 1.2, 2 H, Ar-H), 8.38 (t, 3J = 1.2, 2 H, Ar-H), 8.31 (t, 3J = 1.5, 2 H, Ar-H), 8.29 (t, 3J = 1.5, 2 H, Ar-H), 8.24 (m, 4 H, Ar-H), 7.97 (t, 3J = 1.8, 1 H, Ar-H), 5.42 (m, 1H, OCH), 4.54 (m, 8 H, OCH₂), 3.91 (m, 8 H, OCH₂), 3.80-3.60 (m, 36 H, OCH₂), 3.54 (m, 10 H, OCH₂), 3.36 (s, 15 H, OCH₃), 1.39 (d, 3J = 1.8, 3H, CCH₃), 0.30 (s, 18 H, Si(CH₃)₃). ¹³C-NMR (300 MHz, CDCl₃):
MHz, CDCl₃): δ (ppm) = 165.1, 164.5, 152.9, 152.0, 151.8, 135.6, 135.4, 134.9, 132.9, 131.6, 129.5, 128.5, 124.9, 124.8, 124.7, 124.6, 123.2, 102.9, 102.8, 96.8, 96.7, 71.9, 70.6, 69.1, 64.8, 64.6, 59.0, 0.2. **ESI-MS:** m/z = 1688.84 ([M+H]^+) (calc. 1689.04 for C₈₇H₁₁₄N₄O₂₆Si₂+H⁺), 1709.83 ([M+Na]^+) (calc. 1709.72 for C₈₇H₁₁₄N₄O₂₆Si₂+Na⁺).
Following the Sonogashira coupling protocol to compound 3, a mixture of 7 (60 mg, 0.10 mmol), 9 (220 mg, 0.20 mmol), Pd(PPh₃)₄ (22 mg, 0.02 mmol), CuI (2 mg, 0.02 mmol), and PPh₃ (6 mg, 0.04 mmol) was added to a mixture solvent of diisopropylamine (2 mL) and toluene (8 mL). After stirring for 22 h at 70 °C, the mixture was concentrated in vacuo and purified by column chromatography (DCM/acetone = 2:1) to yield compound 15 (180 mg, 0.068 mmol) as an orange wax in 68 % yield. ¹H-NMR (300 MHz, CDCl₃): δ (ppm) = 8.66 (t, ³J = 1.5, 2H, Ar-H), 8.62 (t, ³J = 1.2, 2H, Ar-H), 8.59 (t, ³J = 1.2, 2 H, Ar-H), 8.41 (t, ³J = 1.5, 2H, Ar-H), 8.39 (t, ³J = 1.5, 2H, Ar-H), 8.34 (t, ³J = 1.5, 2H, Ar-H), 8.31 (t, ³J = 1.4, 2H, Ar- H), 8.29 (t, ³J = 1.6, 2H, Ar-H), 8.24 (m, 6H, Ar-H), 7.97 (t, ³J = 1.8, 2H, Ar-H), 5.42 (m, 2H, OCH), 4.56 (m, 12H, OCH₂), 3.89 (m, 12H, OCH₂), 3.74 (m, 60H, CH₂), 3.52 (m, 16H, CH₂), 3.32 (s, 24H, CH₃), 1.41 (d, ³J = 1.8, 6H, CCH₃), 0.28 (s, 18 H, Si(CH₃)₃). ESI-MS: m/z = 1333.05 ([M+2Na]²⁺) (calc. 2666.10 for C₁₃₆H₁₇₄N₆O₄₂Si₂+2Na²⁺).
Electronic Supplementary Information

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Oligomer 114

Following synthesis protocol to oligomer 14, TMS protecting group on compound 13 (422 mg, 0.25 mmol) was removed by TBAF in THF (50 mL) to produce di-acetylenic compound (150 mg, 0.10 mmol) in 41% yield. To a dried and degassed schlenk tube, a mixture of di-acetylenic compound (124 mg, 0.08 mmol), 9 (181 mg, 0.16 mmol), Pd(PPh₃)₄ (18 mg, 0.016 mmol), CuI (3 mg, 0.016 mmol), and PPh₃ (9 mg, 0.032 mmol) was added together with a mixture of diisopropylamine (4 mL) and toluene (10 mL). After stirring for 23 h at 70 °C, the reaction mixture was concentrated in vacuo, and the crude compound was purified by column chromatography (DCM/acetone = 1:1, 1:2) to yield oligomer 11 (120 mg, 0.034 mmol) in 42% yield as an orange wax. ¹H-NMR (300 MHz, CDCl₃): δ (ppm) = 8.62 (m, 4 H, Ar-H), 8.57 (m, 4 H, Ar-H), 8.40-8.20 (m, 22 H, Ar-H), 7.95-8.00 (m, 3 H, Ar-H), 5.44 (m, 3H, OCH), 4.59 (m, 16 H, OCH₂), 3.93 (m, 16 H, OCH₂), 3.79-3.62 (m, 84 H, OCH₂), 3.55 (m, 22 H, OCH₂), 3.36 (m, 33 H, OCH₃), 1.43 (d, J = 1.8, 9H, CCH₃), 0.30 (s, 18 H, Si(CH₃)₃). MALDI-TOF MS (DCTB matrix): m/z = 3575.94 ([M+Na]+) (calc. 3575.56 for C₁₈₅H₂₃₄N₈O₅₈Si₂Na⁺). GPC (THF, 30 °C): Mw = 3885, PDI (Mw/Mn) = 1.03.
**Oligomer 14₅**

Following protocol to oligomer 14₄, TMS protecting group on compound 15 (150 mg, 0.06 mmol) was removed by TBAF in THF (30 mL) to produce di-acetylenic compound (85 mg, 0.034 mmol) in 56% yield. To a dried and degassed schlenk tube, a mixture of di-acetylenic compound (74 mg, 0.030 mmol), 9 (68 mg, 0.060 mmol), Pd(PPh₃)₄ (7 mg, 0.006 mmol), CuI (2 mg, 0.012 mmol), and PPh₃ (3 mg, 0.012 mmol) was added together with a mixture of diisopropylamine (4 mL) and toluene (10 mL). After stirring for 22 h at 70 °C, the reaction mixture was concentrated in vacuo, and the crude compound was purified by column chromatography (DCM/acetone = 1:2) to yield oligomer 14₅ (54 mg, 0.012 mmol) in 40% yield as an orange wax. ¹H-NMR (300 MHz, CDCl₃): δ (ppm) = 8.63-8.56 (m, 10H, Ar-H), 8.39-8.22 (m, 28 H, Ar-H), 7.96 (m, 4H, Ar-H), 5.41 (m, 4H, OCH), 4.56 (m, 18H, OCH₂), 3.89 (m, 18H, OCH₂), 3.68 (m, 112H, CH₂), 3.54 (m, 27H, CH₂), 3.34 (m, 42H, CH₃), 1.42 (d, J = 2.4, 12H, CCH₃), 0.30 (s, 18 H, Si(CH₃)₃. MALDI-TOF MS (DCTB matrix): m/z = 4509.96 ([M+Na]+) (calc. 4510.02 for C₂₃₄H₂₉₄N₁₀O₇₄Si₂⁺Na⁺), 4526.03 ([M+K]+) (calc. 4526.13 for C₂₃₄H₂₉₄N₁₀O₇₄Si₂⁺K⁺). GPC (THF, 30 °C): M_w = 4598, PDI (M_w/M_n) = 1.02.
Compounds 18 and 19.

Following to synthesis protocol to compounds 9 and 13, a mixture of 8 (460 mg, 0.8 mmol), 16 (640 mg, 0.8 mmol), Pd(PPh₃)₄ (92 mg, 0.16 mmol), CuI (30 mg, 0.16 mmol), and PPh₃ (43 mg, 0.26 mmol) was added to a mixture of diisopropylamine (5 mL) and toluene (30 mL). After reacting for 14 h at 70 °C, the crude compounds were purified by column chromatography (DCM/acetone = 4:1, and then DCM/acetone = 3:1) to yield compounds 18 (310 mg, 0.25 mmol) and 19 (400 mg, 0.29 mmol) in 31 % and 36% yields, respectively, as bright orange oils.

For compound 18: ¹H-NMR (300 MHz, CDCl₃): δ (ppm) = 8.63 (t, 3J = 1.5, 1H, Ar-H), 8.57 (t, 3J = 1.5, 1H, Ar-H), 8.35 (dd, 3J = 1.2, 2H, Ar-H), 8.28 (dd, 3J = 1.2, 2H, Ar-H), 8.26 (t, 3J 1.2, 1H, Ar-H), 8.20 (t, 3J = 1.5, 1H, Ar-H), 8.07 (t, 3J = 1.8, 1H, Ar-H), 5.36 (m, 3H, OCH), 3.68 (m, 36H, CH₂), 3.66 (m, 6H, CH₂), 3.35 (s, 9H, CH₃), 1.39 (d, 3J = 1.8, 9H, CCH₃), 0.26 (s, 9 H, Si(CH₃)₃). ¹³C-NMR (300 MHz, CDCl₃): δ (ppm) = 165.1, 164.5, 152.9, 152.0, 151.8, 135.6, 135.4, 134.9, 132.9, 131.6, 129.5, 128.5, 124.9, 124.8, 124.7, 124.6, 123.2, 102.9, 102.8, 96.8, 96.7, 71.9, 70.6, 69.1, 64.8, 64.6, 59.0, 0.2. ESI-MS: m/z = 1249.62 ([M+H⁺]) (calc. 1249.44 for C₅₈H₇₁N₂O₁₅SiH⁺), 1271.64 ([M+Na⁺]) (calc. 1271.42 for C₅₈H₇₁N₂O₁₅Si+Na⁺).

For compound 19: ¹H-NMR (300 MHz, CDCl₃): δ (ppm) = 8.64 (t, 3J = 1.5, 2 H, Ar-H), 8.60 (t, 3J = 1.5, 2 H, Ar-H), 8.42 (t, 3J = 1.2, 2 H, Ar-H), 8.40 (t, 3J = 1.2, 2 H, Ar-H), 8.32 (t, 3J = 1.2, 2 H, Ar-H), 8.24 (m, 4 H, Ar-H), 7.97 (t, 3J = 1.8, 1 H, Ar-H), 5.44 (m, 5H, OCH), 3.82-3.60 (m, 60 H, OCH₂), 3.52 (m, 10 H, OCH₂), 3.38 (s, 15 H, OCH₃), 1.42 (d, 3J = 2.1, 15H,
CCH₃), 0.29 (s, 18 H, Si(CH₃)₃). ¹³C-NMR (300 MHz, CDCl₃): δ (ppm) = 165.2, 164.6, 153.2, 152.2, 151.6, 135.4, 135.3, 135.0, 132.8, 131.2, 129.4, 128.9, 125.9, 124.9, 124.6, 124.5, 122.9, 101.9, 101.8, 96.9, 96.7, 71.8, 70.7, 69.5, 64.5, 64.0, 59.1, 0.2. ESI-MS: m/z = 1920.04 ([M+H]+) (calc. 1919.90 for C₉₀H₁₃₈N₄O₃₀Si₂+H⁺), 1941.92 ([M+Na]+) (calc. 1941.88 for C₉₀H₁₃₈N₄O₃₀Si₂+Na⁺).
Compounds 21 and 22.

Following to synthesis protocol to compounds 9 and 13, a mixture of 1 (615 mg, 0.9 mmol), 20 (470 mg, 0.8 mmol), Pd(PPh₃)₄ (208 mg, 0.18 mmol), CuI (34 mg, 0.18 mmol), and PPh₃ (48 mg, 0.18 mmol) was added to a mixture of diisopropylamine (5 mL) and toluene (30 mL). After reacting for 14 h at 70 °C, the crude compounds were purified by column chromatography (DCM/acetone = 6:1, and then DCM/acetone = 4:1) to yield compounds 21 (290 mg, 0.27 mmol) and 22 (410 mg, 0.25 mmol) in 30 % and 27% yields as orange oil and wax, respectively.

For compound 21: ESI-MS: m/z = 1083.42 ([M+2H]⁺) (calc. 1083.36 for C₅₁H₆₇N₄O₁₂Si+2H⁺), 1105.40 ([M+H+Na]⁺) (calc. 1105.34 for C₅₁H₆₇N₄O₁₂Si +H⁺+Na⁺). GPC peak area: 99.0%.

For compound 22: ESI-MS: m/z = 1637.86 ([M+2H]⁺) (calc. 1637.74 for C₈₆H₁₁₁N₆O₂₂Si₂+2H⁺), 1659.90 ([M+H+Na]⁺) (calc. 1659.72 for C₈₆H₁₁₁N₆O₂₂Si₂+H⁺+Na⁺). GPC peak area: 98.5%.
**Oligomer 11TEMPO**

Following protocol to oligomer 14, TMS protecting group on compound 19 (150 mg, 0.06 mmol) was removed by TBAF in THF (30 mL) to produce di-acetylenic compound (85 mg, 0.034 mmol) in 56% yield. To a dried and degassed Schlenk tube, a mixture of di-acetylenic compound (107 mg, 0.06 mmol), 21 (162 mg, 0.15 mmol), Pd(PPh₃)₄ (14 mg, 0.012 mmol), CuI (2 mg, 0.012 mmol), and PPh₃ (3 mg, 0.012 mmol) was added together with a mixture of diisopropylamine (3 mL) and toluene (10 mL). After stirring for 22 h at 70 °C, the reaction mixture was concentrated in vacuo, and the crude compound was purified by column chromatography (DCM/acetone = 2:1) to yield oligomer 11TEMPO (88 mg, 0.024 mmol) in 40% yield as an orange wax. MALDI-TOF MS (DCTB matrix): m/z = 3684.92 ([M+2H]⁺) (calc. 3684.70 for C₁₉₅H₂₅₂N₁₂O₅₄Si₂+2H⁺), 3706.88 ([M+H+Na]⁺) (calc. 3706.68 for C₁₉₅H₂₅₂N₁₂O₅₄Si₂+H+Na⁺). GPC (THF, 30 °C): M_w = 4238, PDI (M_w/M_n) = 1.03.
Compound 23

Following protocol to oligomer 14, TMS protecting group on compound 19 (300 mg, 0.16 mmol) was removed by TBAF in THF (50 mL) to yield di-acetylenic compound (170 mg, 0.10 mmol) in 60% yield. To a dried and degassed Schlenk tube, a mixture of di-acetylenic compound (140 mg, 0.08 mmol), 20 (160 mg, 0.32 mmol), Pd(PPh₃)₄ (18 mg, 0.016 mmol), CuI (3 mg, 0.016 mmol), and PPh₃ (4 mg, 0.016 mmol) was added together to a mixture of diisopropylamine (2 mL) and toluene (10 mL). After stirring for 22 h at 70 °C, the reaction mixture was concentrated in vacuo, and the crude compound was purified by column chromatography (DCM/acetone = 3:1) to yield compound 23 (80 mg, 0.032 mmol) in 43% yield as an orange wax. **ESI-MS:** m/z = 2576.02 ([M+3H]+) (calc. 2575.94 for C₁₂₅H₁₆₂I₂N₈O₃₄+3H⁺), 2599.02 ([M+2H+Na]+) (calc. 2598.92 for C₁₂₅H₁₆₂I₂N₈O₃₄+2H+Na⁺).

GPC peak area: 99.0%.
**Compound 24**

![Diagram of Compound 24](image)

Compound 13 (250 g, 0.15 mmol) was dissolved in a solvent mixture of THF (60 mL) and water (7 mL). Then, a solution of TBAF (0.2 mL, 1 M in THF) dissolved in THF (25 mL) was added dropwise to the solution slowly. Conversion was monitored by TLC and the reaction was stopped after 1.5 h, filtered through a short silica gel column using acetone as the eluent. After the organic solvent was removed in vacuo, the crude compound was purified by column chromatography (DCM/acetone = 3:1) to get compound 24 (95 mg, 0.06%) in the yield of 40% as a red oil. **1H-NMR** (300 MHz, CDCl₃): δ (ppm) = 8.61 (t, 3J = 1.2, 2 H, Ar-H), 8.54 (t, 3J = 1.2, 2 H, Ar-H), 8.32 (t, 3J = 1.2, 2 H, Ar-H), 8.30 (t, 3J = 1.5, 2 H, Ar-H), 8.25 (t, 3J = 1.5, 2 H, Ar-H), 8.15 (m, 4 H, Ar-H), 7.94 (t, 3J = 1.8, 1 H, Ar-H), 5.38 (m, 1H, OCH), 4.52 (m, 8 H, OCH₂), 3.92 (m, 8 H, OCH₂), 3.83-3.60 (m, 36 H, OCH₂), 3.53 (m, 10 H, OCH₂), 3.36 (s, 15 H, OCH₃), 3.28 (s, 1 H, C≡CH), 1.39 (d, 3J = 1.8, 3H, CCH₃), 0.30 (s, 9 H, Si(CH₃)₃). **13C-NMR** (300 MHz, CDCl₃): δ (ppm) = 165.2, 164.6, 152.9, 152.2, 151.9, 151.8, 135.6, 135.4, 134.9, 132.9, 131.6, 129.5, 128.5, 124.9, 124.8, 124.7, 124.6, 123.2, 102.9, 102.8, 96.8, 96.7, 71.9, 70.6, 69.1, 64.8, 64.6, 59.0, 0.2. **ESI-MS**: m/z = 1615.82 ([M+H]+) (calc. 1615.69 for C₈₄H₁₅₆N₄O₂₆Si+H⁺), 1637.80 ([M+Na]+) (calc. 1637.68 for C₈₄H₁₅₆N₄O₂₆Si+Na⁺).
Oligomer \textit{17}_β-\textit{TEMPO}_{α,β}

Following the Sonogashira coupling protocol to compound 3, a mixture of 23 (60 mg, 0.025 mmol), 24 (80 mg, 0.05 mmol), Pd(PPh₃)₄ (6 mg, 0.005 mmol), CuI (1 mg, 0.005 mmol), and PPh₃ (2 mg, 0.005 mmol) was added to a mixture solvent of diisopropylamine (1 mL) and toluene (8 mL). After stirring for 18 h at 65 °C, the mixture was concentrated in vacuo and purified by column chromatography (DCM/acetone = 1:2) to yield Oligomer \textit{17}_β-\textit{TEMPO}_{α,β} (72 mg, 0.013 mmol) as an orange wax in 52 % yield. MALDI-TOF MS (DCTB matrix): \(m/z = 5575.40\) ([M+2H+Na]+) (calc. 5575.48 for C$_{293}$H$_{372}$N$_{16}$O$_8$Si$_2$+2H+Na$^+$), 5590.89 ([M+2H+K]$^+$) (calc. 5590.45 for C$_{195}$H$_{252}$N$_{12}$O$_{54}$Si$_2$+2H+K$^+$). GPC (THF, 30 °C): \(M_w = 5392\), PDI (M$_w$/M$_n$) = 1.09.
Oligomer 11ₜ-TEMPO

Following protocol to oligomer 14ₜ, TMS protecting group on compound 22 (250 mg, 0.15 mmol) was removed by TBAF in THF (50 mL) to yield di-acetylenic compound (104 mg, 0.07 mmol) in 46% yield. To a dried and degassed schlenk tube, a mixture of di-acetylenic compound (60 mg, 0.04 mmol), 18 (150 mg, 0.12 mmol), Pd(PPh₃)₄ (9 mg, 0.008 mmol), CuI (2 mg, 0.008 mmol), and PPh₃ (2 mg, 0.008 mmol) was added together with a mixture of diisopropylamine (2 mL) and toluene (8 mL). After stirring for 18 h at 70 °C, the reaction mixture was concentrated in vacuo, and the crude compound was purified by column chromatography (DCM/acetone = 1:1) to yield oligomer 11ₜ-TEMPO (60 mg, 0.016 mmol) in 42% yield as an orange wax. MALDI-TOF MS (DCTB matrix): m/z = 3759.01 ([M+H+Na]⁺) (calc. 3758.68 for C₁₉₆H₂₅₅N₁₀O₅₈Si₂+H+Na⁺), 3773.10 ([M+H+K]⁺) (calc. 3773.65 for C₁₉₆H₂₅₅N₁₀O₅₈Si₂+H+K⁺). GPC (THF, 30 °C): Mₘ = 4344, PDI (Mₘ/Mₙ) = 1.03.
Following protocol to compound 23, to a dried and degassed schlenk tube, a mixture of the TMS-deprotection compound 19 (100 mg, 0.055 mmol), 20 (190 mg, 0.33 mmol), Pd(PPh₃)₄ (13 mg, 0.011 mmol), CuI (2 mg, 0.011 mmol), and PPh₃ (3 mg, 0.011 mmol) was added together to a mixture of diisopropylamine (2 mL) and toluene (10 mL). After stirring for 16 h at 60 °C, the reaction mixture was concentrated in vacuo, and the crude compound was purified by column chromatography (DCM/acetone = 2:1) to yield compound 25 (90 mg, 0.035 mmol) in 63 % yield as an orange wax. ¹H-NMR (300 MHz, CDCl₃): δ (ppm) = 8.61 (t, 3J = 1.2, 4 H, Ar-H), 8.39-8.30 (m, 10 H, Ar-H), 8.28 (t, 3J = 1.2, 2 H, Ar-H), 8.22 (t, 3J = 1.5, 2 H, Ar-H), 8.17 (t, 3J = 1.5, 2 H, Ar-H), 8.10 (m, 4 H, Ar-H), 7.96 (t, 3J = 1.8, 1 H, Ar-H), 7.54 (m, 7H, OCH), 3.78-3.53 (m, 98 H, OCH₂), 3.39 (s, 21 H, OCH₃), 1.38 (d, 3J = 1.8, 21H, CCH₃). ¹³C-NMR (300 MHz, CDCl₃): δ (ppm) = 166.1, 165.1, 165.0, 164.3, 152.2, 144.1, 135.3, 135.2, 132.4, 132.3, 132.0, 129.2, 129.0, 128.7, 125.3, 125.1, 125.0, 124.7, 124.1, 123.2, 102.9, 102.8, 93.5, 89.2, 88.5, 74.0, 71.7, 70.5, 70.4, 70.3, 59.2, 48.3, 18.9, 16.7. ESI-MS: m/z = 2676.86 ([M+H]^+) (calc. 2676.93 for C₁₂₇H₁₆₈I₂N₄O₄₂⁺H⁺), 2698.80 ([M+Na]^+) (calc. 2698.92 for C₁₂₇H₁₆₈I₂N₄O₄₂⁺Na⁺).
Compound 26

Compound 22 (320 mg, 0.2 mmol) was dissolved in a solvent mixture of THF (60 mL) and water (7 mL). Then, a solution of TBAF (0.2 mL, 1 M in THF) dissolved in THF (25 mL) was added dropwise to the solution slowly. Conversion was monitored by TLC and the reaction was stopped after 2 h, filtered through a short silica gel column using acetone as the eluent. After the organic solvent was removed in vacuo, the crude compound was purified by column chromatography (DCM/acetone = 3:1) to get compound 26 (110 mg, 0.07 mmol) in 35% yield as an orange wax. ESI-MS: m/z = 1564.72 ([M+2H]^+) (calc. 1564.69 for C_{83}H_{103}N_{6}O_{22}Si+2H^+), 1586.86 ([M+H+Na]^+) (calc. 1586.68 for C_{83}H_{103}N_{6}O_{22}Si+H+Na^+). GPC peak area: 99.0%.
Following the Sonogashira coupling protocol to compound 3, a mixture of 25 (80 mg, 0.03 mmol), 26 (94 mg, 0.06 mmol), Pd(PPh₃)₄ (7 mg, 0.06 mmol), CuI (1 mg, 0.06 mmol), and PPh₃ (2 mg, 0.06 mmol) was added to a mixture solvent of diisopropylamine (1 mL) and toluene (5 mL). After stirring for 20 h at 70 °C, the mixture was concentrated in vacuo and purified by column chromatography (DCM/acetone = 1:2) to yield oligomer 17₆-TEMPOᵦᵣ (83 mg, 0.015 mmol) in 51 % yield as an orange wax. MALDI-TOF MS (DCTB matrix): m/z = 5553.87 ([M+3H]⁺) (calc. 5553.49 for C₂₉₃H₇₇₂N₁₆O₈₆Si₂+3H⁺), 5575.77 ([M+2H+Na]⁺) (calc. 5575.53 for C₂₉₃H₇₇₂N₁₆O₈₆Si₂+2H+K⁺). GPC (THF, 30 °C): Mw = 5775, PDI (Mw/Mn) = 1.05.
Figures and captions

Figure S1. MALDI-TOF mass spectra of oligomers 10₃, 14₄, 11₄, and 14₅.
Figure S2. MALDI-TOF mass spectra of spin-labeled oligomers 11_4-TEMPO_α,β, 17_6-TEMPO_α,β, 17_6-TEMPO_α,γ, and 11_4-TEMPO.
Figure S3. Overlay of GPC traces of oligomers $10_3$, $14_4$, $11_4$, and $14_5$. 
**Figure S4.** Overlay of GPC traces of spin-labeled oligomers 11₄-TEMPOₐ,β, 17₆-TEMPOₐ,β, 17₆-TEMPOₐ,γ, and 11₄-TEMPO.
Figure S5. $^1$H NMR spectrum of oligomer 14$_4$ (CDCl$_3$, 25 °C).

Figure S6. $^1$H NMR spectrum of oligomer 10$_3$ (CDCl$_3$, 25 °C).
Figure S7. $^1$H NMR spectrum of oligomer 14$_5$ (CDCl$_3$, 25 °C).

Figure S8. $^1$H NMR spectrum of oligomer 11$_4$ (CDCl$_3$, 25 °C).
**Figure S9.** UV/vis absorption (left) and CD (right) spectra of oligomer 11₄ for solvent titration experiments (CH₃CN → CHCl₃ with 5 vol% increments) at 25 °C.

**Figure S10.** Solvent titration curves (fraction unfolded vs solvent composition) for the oligomers 11₄, 12₆, 14₄, 14₅, and 14₇.
Figure S11. Helix stabilization energy (Gibbs free energy) of foldamers 11₄, 12₆, 14₄, 14₅, and 14₇ in CH₃CN at 25 °C.

Figure S12. UV/vis absorption (left) and CD (right) spectra of photochemical $E \rightarrow Z$ isomerization of oligomer 11₄ during the course of irradiation at $\lambda_{irr} = 358$ nm in CH₃CN at 25 °C. The insets in the UV/vis absorption spectra show a magnification of the increasing n→π* absorption band of the azobenzene units.
Figure S13. $^1$H-NMR spectrum of oligomer 14$_4$ (ca. $5 \times 10^{-4}$) in PSS showing amounts and location of Z-azobenzene in CDCl$_3$ at 25 °C (magenta peaks denote Azo$\text{core}$ and Azo$\text{term}$ and blue peaks denote Azo$\text{term}$).
Figure S14. $^1$H-NMR spectrum of oligomer 14s (ca. $5 \times 10^{-4}$) in PSS showing amounts and location of Z-azobenzene in CDCl$_3$ at 25 °C (green peaks denote $Azo_{\text{inter}}$-1 and $Azo_{\text{core}}$, magenta peaks denote $Azo_{\text{inter}}$-2 and $Azo_{\text{term}}$, and blue peaks denote $Azo_{\text{term}}$).
Figure S15. $^1$H-NMR spectrum of oligomer 11$_4$ (ca. $3 \times 10^{-3}$) in PSS showing amounts and location of Z-azobenzene in CD$_3$CN at 25 °C (red peaks denote $Azo_{core}$ and blue peaks denote $Azo_{term}$).
Figure S16. Graphic illustration of the statistics of the photoinduced processes of the tetradecameric foldamers 14₄, 14₅, and 14₇. Top: Comparison of the kinetic rate constants of the individual isomerization events of azobenzene units (left) and the denaturation of foldamers (right). Bottom: the resulting level of the average number of Z-azobenzene (left) and the unfolded state of the foldamers (right).
Figure S17. CD spectra of foldamer 14 in acetonitrile/H$_2$O (4/1, v/v) solution during the thermal isomerization of azobenzene starting from the PSS reached in acetonitrile solution at various temperature, i.e. 15 °C (top), 25 °C (center), and 35 °C (bottom).
Figure S18. CD spectra of foldamer 14s in acetonitrile/H₂O (4/1, v/v) solution during the thermal isomerization of azobenzene starting from the PSS reached in acetonitrile solution at various temperature, i.e. 15 °C (top), 25 °C (center), and 35 °C (bottom).
Figure S19. CD spectra of foldamer 14 in acetonitrile/H₂O (4/1, v/v) solution during the thermal isomerization of azobenzene starting from the PSS reached in acetonitrile solution at various temperature, i.e. 15 °C (top), 25 °C (center), and 35 °C (bottom).
**Figure S20.** CD spectra of foldamer 126 in acetonitrile/H₂O (4/1, v/v) solution during the thermal isomerization of azobenzene starting from the PSS reached in acetonitrile solution at 25 °C.

**Figure S21.** CD spectra of foldamer 147 in acetonitrile/H₂O (4/1, v/v) solution during the thermal isomerization of azobenzene starting from the PSS reached in chloroform solution at 25 °C.
**Figure S22.** CD spectra of foldamer 14s in acetonitrile/H$_2$O (4/1, v/v) solution during the thermal isomerization of azobenzene starting from the PSS reached in chloroform solution at 25 °C.

**Figure S23.** CD spectra of foldamer 14s in acetonitrile/H$_2$O (4/1, v/v) solution during the thermal isomerization of azobenzene starting from the PSS reached in chloroform solution at 25 °C.
Figure S24. Kinetic rate constants of the refolding process of foldamer 147 in acetonitrile/H₂O (4/1, v/v) solution during the thermal isomerization of azobenzene starting from the PSS reached in acetonitrile solution.

Figure S25. Kinetic rate constants of the refolding process of foldamer 145 in acetonitrile/H₂O (4/1, v/v) solution during the thermal isomerization of azobenzene starting from the PSS reached in acetonitrile solution.
**Figure S26.** Kinetic rate constants of the refolding process of foldamer 14, in acetonitrile/H₂O (4/1, v/v) solution during the thermal isomerization of azobenzene starting from the PSS reached in acetonitrile solution.
**Figure S27.** Eyring plots for the refolding process of tetradecameric foldamers during the thermal isomerization of azobenzene in acetonitrile/H$_2$O (4/1, v/v) solution. All the linear fittings are obtained with high correlation coefficients (R>0.99).

**Figure S28.** The isokinetic plots of tetradecameric foldamers 14$_4$, 14$_5$, and 14$_7$ and single azobenzene.
Figure S29. UV/vis absorption (top) and CD (bottom) spectra of oligomers $11_4$-TEMPO$_{\alpha\beta}$ and $17_6$-TEMPO$_{\alpha\beta}$ for solvent titration experiments (CH$_3$CN $\rightarrow$ CHCl$_3$ with 5 vol% increments) at 25 °C.
**Figure S30.** Solvent titration curves (fraction unfolded vs solvent composition) for the oligomers 11_4-TEMPO_{\alpha\beta} and 17_6-TEMPO_{\alpha\beta}.

**Figure S31.** Helix stabilization energy (Gibbs free energy) of foldamers 11_4-TEMPO_{\alpha\beta} and 17_6-TEMPO_{\alpha\beta} in CH_3CN at 25 °C.
Figure S32. UV/vis absorption spectra of photochemical $E \rightarrow Z$ isomerization of oligomers $11_{4}$-TEMPO$_{αβ}$ and $17_{6}$-TEMPO$_{αβ}$ during the course of irradiation at $λ_{irr} = 358$ nm in CH$_3$CN at 25 °C. The insets in the UV/vis spectra show a magnification of the increasing $n\rightarrow\pi^*$ absorption band of the azobenzene units.

Figure S33. CD spectra of photochemical $E \rightarrow Z$ isomerization of oligomers $11_{4}$-TEMPO$_{αβ}$ and $17_{6}$-TEMPO$_{αβ}$ during the course of irradiation at $λ_{irr} = 358$ nm in CH$_3$CN at 25 °C.
Table S2. Folding and photoswitching behavior of oligomers 11₄-TEMPOₐ,β and 17₆-TEMPOₐ,β in CH₃CN at 25 °C.

<table>
<thead>
<tr>
<th></th>
<th>ΔG (CH₃CN) [kcal mol⁻¹]</th>
<th>k (E → Z) [×10² s⁻¹]</th>
<th>k (unfolding) [×10² s⁻¹]</th>
<th>Photoinduced [unfolding]%</th>
</tr>
</thead>
<tbody>
<tr>
<td>11₄-TEMPOₐ,β</td>
<td>2.41 ± 0.13</td>
<td>1.72 ± 0.02</td>
<td>2.56 ± 0.08</td>
<td>85.6%</td>
</tr>
<tr>
<td>17₆-TEMPOₐ,β</td>
<td>3.79 ± 0.34</td>
<td>1.44 ± 0.02</td>
<td>1.73 ± 0.03</td>
<td>56.4%</td>
</tr>
</tbody>
</table>

*a* derived from UV/vis spectra; *b* derived from CD spectra.

Figure S34. ESR spectrum of singly spin-labeled foldamer 11₄-TEMPO in acetonitrile at 20 K, which was used as the background of no intermolecular spin-coupling interaction.