Supplementary Material (ESI) for New Journal of Chemistry

Extending Helicity – Capturing the Helical Character of Longer *ortho* Phenylene Ethynylene Oligomers

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Supporting Information

I. Synthetic procedures

Measurements. ^{1}H, and ^{13}C NMR spectra for general analysis were obtained at 400 MHz with a Bruker DPX-400 NMR spectrometer and analyzed with the Bruker XWIN NMR program. ^{1}H, and ^{13}C NMR data for the solvent titrations and temperature studies were obtained with a 600 MHz Bruker spectrometer and analyzed mass spectral data were obtained at the University of Massachusetts Amherst mass spec facility, which is supported in part by the National Science Foundation.

Materials. Reagent grade tetrahydrofuran (THF) was distilled under nitrogen from sodium benzophenone. All other solvents were used as received. 3-nitro-4-iodophenol **(1)** was purchased from Aldrich and used without further purification. Trans dichlorobis (triphenylphosphine) palladium ($Pd(P\phi_3)_2Cl_2$) was purchased from Strem Chemical. Tri-ethylene glycol monomethyl ether was purchased from Aldrich and used after solvation in dichloromethane, and passing through a pipette of silica and subsequent evaporation. The compound was then evaporated and dried under vacuum. Trimethylsilyl acetylene was purchased from GFS chemicals. Methyl iodide was purchased from Alfa Aesar and used without further purification. All other reagents were purchased from Alfa Aesar or Aldrich Chemical Co. and all were used as received.

Purification. All column chromatography was performed on an ISCO Companion using the column sizes and solvent gradients as indicated.

Abbreviations used: DCM (dichloromethane), TBAF (Tetra butyl ammonium fluoride), EtOAc (ethyl acetate), TEA (triethylamine), TMS (trimethylsilyl).

General TMS Deprotection Procedure (TBAF). One equivalent of the TMS protected compound was dissolved in dry THF and cooled to 0°C in a round bottom flask with stirbar. 1.2 equivalents of TBAF in 1 M THF solution with 5% H_2O content were added, and the reaction was stirred for 5 minutes. Enough hexane was then added to bring the reaction to a 1:1 THF/hexane ratio, precipitating most excess TBAF and t-butyl ammonium hydroxide, and the reaction was stirred for an additional 10 minutes. The reaction mixture was injected directly, without evaporation, onto either a silica-packed pipette or a flash chromatography column for purification.

General Triazene Activation Procedure. This procedure was performed by microwave synthesis in Biotage 2-5 mL vials. Each vial was filled with 250 mg of triazene protected compound 0.05 eq of I_2 and of MeI ≈130 eq, a stirbar was added, and a septum crimped on. Microwave heat was applied to each tube, at a temperature of 150°C for a time of one hour. After all reactions had completed, the tubes were opened, combined, filtered

through a Celite pad and washed with ethyl ether, and evaporated under a N_2 stream, and purified by flash chromatography.

General Sonogashira Coupling Procedure. A schlenk flask with stirbar was flame dried under vacuum and backfilled with N_2 three times. To this flask were added 0.05-0.1 equivalents (based on the acetylene compound) of $Pd(P\phi_3)_2Cl_2$ and 0.1-0.2 equivalents of CuI. The 1-1.1 equivalents of the acetylene compound to 1 equivalent iodide were dissolved in separate flasks in TEA and transferred via syringe to the schlenk flask under N_2. The schlenk flask was gently degassed for 30 seconds then backfilled with N_2. The flask sealed and placed in an oil bath at 55°C for at least 6-18 hours and checked by TLC for completeness. A precipitate should form. Once done, the reaction solution was diluted with ether, filtered through a pad of Celite and concentrated. The residue was then purified using Silica flash chromatography using the solvents indicated.

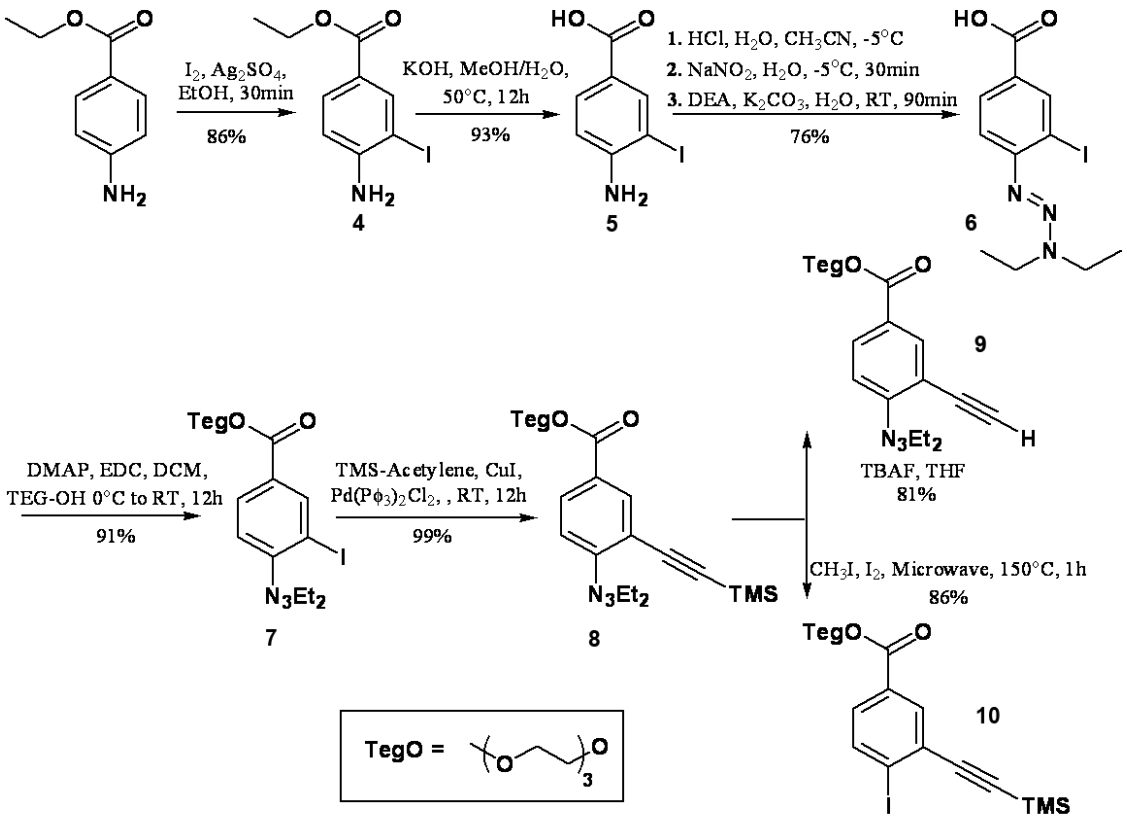
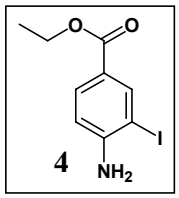
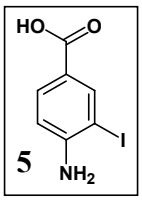


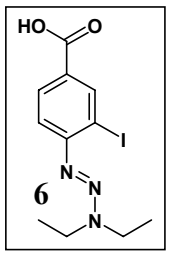
Figure S1: Synthetic scheme for Teg-Ester monomer



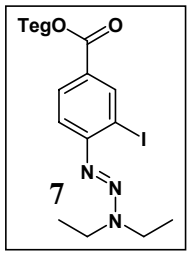
4-Amino-3-iodo-benzoic acid ethyl ester (4) l3.8 g of I_2 (54.5 µmol, 1.0 mol eq.), and 17.0 g of Ag_2SO_4 (54.5 µmol, 1.0 mol eq.) were added to 300 mL of 95% EtOH with rapid stirring. 9.00 g of 4-amino benzoic acid ethyl ester (54.5 µmol, 1.0 mol eq.) was dissolved in another 100 mL EtOH and added to the reaction, which was stirred at room temperature for 30 minutes. Mixture was filtered through frit to remove salts and the EtOH was removed by rotary evaporation. Residue was partitioned between 300 mL DCM and 150 mL 5% aqueous NaOH. The organic layer was washed again with another 150 mL 5% aqueous NaOH, followed by washes with 2 150 mL portions of 5% aqueous Na_2SO_3, dried over $MgSO_4$, and evaporated. After purification by flash chromatography (85->100% DCM: Hexanes) a tan solid was obtained (13.6 g, 86%). ^{1}H NMR (DMSO-d_6): δ 8.102 (d, 1H, phenyl H, J = 2.0), 7.652 (dd, 1H, phenyl H, J_1 = 2.0, J_2 = 8.4), 6.743 (d, 1H, phenyl H, J = 8.4), 6.065 (s, 2H, NH_2), 4.207 (q, 2H, J = 7.2, CH_2), 1.267 (t, 3H, J = 7.2, CH_3) ppm. ^{13}C NMR (DMSO-d_6): δ 164.53, 152.94, 140.25, 130.50, 118.45, 112.92, 81.07, 60.00, 14.29 ppm. MS *m/z* = 291 (m + H^+).



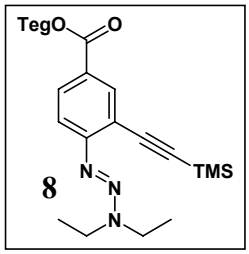
4-Amino-3-iodo-benzoic acid (5) A solution of 13.0 g KOH (232 mmol , 5.0 eq) in 700 mL 3:1 MeOH/H_2O was made, and 13.6 g of **4** (46.7 mmol, 1.0 eq) was added. The mixture was stirred at 50°C overnight. Methanol was removed by rotary evaporation, and the mixture was brought to pH 3.0 by careful addition of concentrated H_2SO_4. The product was obtained as a white precipitate and was isolated by filtration (11.42 g, 93%). ^{1}H NMR (DMSO-d_6): δ 8.091 (d, 1H, phenyl H, J = 2.0), 7.631 (dd, 1H, phenyl H, J_1 = 2.0 J_2 = 8.4), 6.731 (d, 1H, phenyl H, J = 8.4), 5.97 (br, 2H, NH_2) ^{13}C NMR (DMSO-d_6): δ 166.14, 152.63, 140.54, 130.71, 119.40, 112.89, 81.10 ppm. MS *m/z* = 263 (m + H^+).



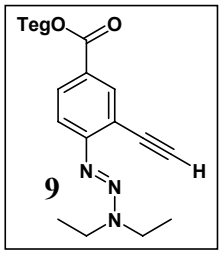
***N,N*-Diethyl-*N'*(3-Iodo-4-benzoic acid) triazene (6)** A solution of 5.81g of **5** (22.1 mmol, 1.0 eq) in 380 mL of acetonitrile, 80 mL of water, and 11 mL concentrated HCl in a 1000 mL round bottom flask with stirbar was covered with aluminum foil to protect contents from light, and cooled in a –5°C ice/acetone bath. A solution of 3.35 g $NaNO_2$ (48.6 mmol, 2.2 eq) in 50mL of ice/water was slowly added through an addition funnel. After the addition was complete the mixture was cannulated into a 2000 mL round bottom flask with stirbar containing a solution of 4.85 g diethylamine (6.93 mL, 66.3 mmol, 3.0 eq) and 9.16 g K_2CO_3 (66.3 mmol, 3.0 eq) in 80 mL water in a -5°C ice/acetone bath. Reaction was stirred for 90 minutes, and then allowed to warm up to room temperature. Concentrated HCl was added to bring pH to 4.5, and mixture was then extracted with 3 300mL portions of ethyl ether. The extract was dried over $MgSO_4$ and evaporated to obtain crude product as an orange/red solid. After purification by flash chromatography (0->15% EtOAc/DCM) a light yellow solid was obtained (5.83g, 76%). δ 8.591 (d, 1H, phenyl H, J = 2), 8.003 (dd, 1H, phenyl H, J_1 = 2 J_2 = 8.4), 7.423 (d, 1H, phenyl H, J = 8.4), 3.829-3.882 (m, 4H, CH_2), 1.313-1.397 (m, 6H, CH_2) ppm. ^{13}C NMR($CDCl_3$): δ 171.05, 154.74, 141.58, 130.87, 126.66, 116.82, 95.92, 49.87, 42.93, 14.59, 11.02. MS *m/z* = 347 (m + H^+).



***N,N*-Diethyl-*N'* {3-Iodo-4-benzoic acid 2-[2-(2-methoxy-ethoxy)-ethoxy]-ethyl ester} triazene (7)** 7.03 g of **6** (20.3 mmol, 1.05 eq) was dissolved in 200 mL of dry DCM to which 3.79 g of dimethylaminopyridine (30.9 mmol, 1.6 eq) was added. Mixture was cooled to 0°C, and 5.92 g of 1-ethyl-3-(3-dimethylaminopropyl)-carbodiimide (EDC) (30.9 mmol, 1.6 eq) in 100 mL dry DCM was added. After 20 minutes, 3.17 g triethylene glycol monomethyl ether (19.3 mmol, 1.0 eq) was added in 50 mL DCM. The reaction was stirred overnight, during which time the ice was allowed to melt. The mixture was evaporated and the residue partitioned between 60 mL water and 2 800 mL portions of EtOAc. The organic layer was washed with brine, dried over $MgSO_4$, and evaporated to give crude product. Purification by flash chromatography in 30->50% EtOAc/Hexanes gave a light yellow oil (8.70 g, 91%). ^{1}H NMR($CDCl_3$): δ 8.490 (d, 1H, phenyl H, J = 1.6), 7.921 (dd, 1H, phenyl H, J_1 = 1.6 J_2 = 8.4), 7.361 (d, 1H, phenyl H, J = 8.4), 4.430 (m, 2H, CO_2CH_2), 3.80 (m, 6H, CH_2), 3.65 (m, 6H, CH_2), 3.52 (m, 2H, CH_2), 3.341 (s, 3H, OCH_3), 1.309 (m, 6H, CH_3) ppm. ^{13}C NMR($CDCl_3$): δ 165.33, 153.92, 140.71, 130.24, 127.47, 116.61, 95.79, 71.95, 70.72, 70.64, 70.62, 69.23, 64.15, 59.07, 49.66, 42.70 ppm. MS *m/z* = 493 (m + H^+).



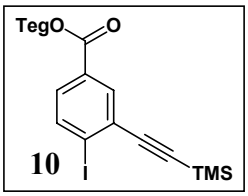
***N,N*-Diethyl-*N'* {3- trimethylsilanylethynyl 4-benzoic acid 2-[2-(2-methoxy-ethoxy)-ethoxy]-ethyl ester} triazene (8)** The general Sonogashira coupling procedure described above was used to prepare this compound. 8.70 g of **7** (17.6 mmol, 1.0 eq), 440 mg of $Pd(P\phi_3)_2Cl_2$ (0.63 mmol, 0.04 eq), and 34 mg CuI (0.176 mmol, 0.01 eq) were combined in a 330 mL schlenk flask with 180 mL TEA. TMS acetylene (3.73 mL/2.60 g, 26.5 mmol, 1.5 eq) was added to the solution. Reaction was stirred overnight at room temperature. After completion, the reaction solution was filtered through Celite with ether to wash, evaporated, and purified with flash chromatography in 20%->40% EtOAc/hexanes to give a light yellow oil (8.11 g, 99%). ^{1}H NMR ($CDCl_3$): δ 8.162 (d, 1H, phenyl H, J = 2.0), 7.902 (dd, 1H, phenyl H, J_1 = 2.0 J_2 = 8.8), 7.441 (d, 1H, phenyl H, J = 8.8), 4.459 (m, 2H, CO_2CH_2), 3.84 (m, 6H, CH_2), 3.69 (m, 6H, CH_2), 3.53 (m, 2H, CH_2), 3.365 (s, 3H, OCH_3), 1.31 (m, 6H, CH_3), 0.248 (s, 9H, $Si(CH_3)_3$) ppm. ^{13}C NMR($CDCl_3$): δ 166.15, 156.24, 135.31, 130.58, 125.94, 118.03, 116.53, 102.64, 98.83, 72.07, 70.83, 70.79, 70.75, 69.41, 64.15, 59.19, 49.69, 42.40, 14.62, 11.09, 0.16 ppm MS *m/z* = 464 (m + H^+).



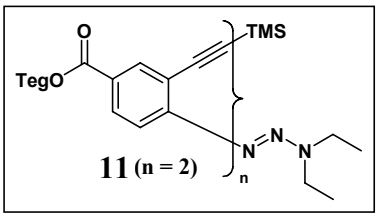
***N,N*-Diethyl-*N'* {3- ethynyl 4- benzoic acid 2-[2-(2-methoxy-ethoxy)-ethoxy]-ethyl ester} triazene (9)**

The general TMS deprotection procedure, listed above, was used to prepare this compound. 640 mg of **8** (1.40 mmol, 1.0 eq) was dissolved in 5.4 mL THF, and the solution was cooled to 0°C. 1.67 mL of 1M TBAF/THF with 5% water content was added to the mixture. After 5 minutes stirring, 5.4 mL hexane was added and the reaction stirred another 10 minutes. Purification was performed by

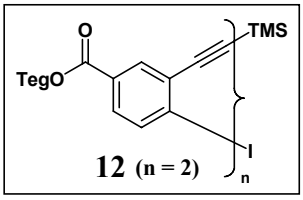
filtration of the reaction mixture through silica gel-packed pipettes, elution of absorbed produce with 1:1 EtOAc/Hexanes, and evaporation to give a light yellow oil (445 mg, 81%).



4-Iodo-3-trimethylsilanylethynyl-benzoic acid 2-[2-(2-methoxy-ethoxy)-ethoxy]-ethyl ester (10) This compound was prepared by microwave synthesis in 8 Biotage 2-5 mL vials. Each vial was filled with 250 mg of **8** (0.54 mmol, 1.0 eq), 6.8 mg of I_2 (27 μmol, 0.05 eq), and 10 g of MeI (4.4 mL, 71 mmol, ≈130 eq), a stirbar was added, and a septum crimped on. Microwave heat was applied to each tube, at a temperature of 150°C for a time of one hour. After all reactions had completed, the tubes were opened, combined, filtered through a filter paper and washed with ethyl ether, and evaporated under a N_2 stream. The residue was dissolved in 100 mL EtOAc, washed with 20 mL of 5% aqueous Na_2SO_3, dried over $MgSO_4$, and evaporated to yield crude product as a brown oil. Purification by flash chromatography in 20->40% EtOAc/Hexanes gave a yellow oil (2.12 g, 86%). ^{1}H NMR($CDCl_3$): δ 8.093 (d, 1H, phenyl H, J = 2.0), 7.926 (d, 1H, phenyl H, J = 8.4), 7.622 (dd, 1H, phenyl J_1 = 2.0 J_2 = 8.4), 4.471 (m, 2H, CO_2CH_2), 3.83 (m, 2H, CH_2), 3.67 (m, 6H, CH_2), 3.52 (m, 2H, CH_2), 3.367 (s, 3H, OCH_3), 0.260 (s, 9H, $Si(CH_3)_3$) ppm. ^{13}C NMR($CDCl_3$): δ 165.63, 139.12, 133.57, 130.32, 130.15, 130.12, 107.58, 105.69, 100.20, 72.06, 70.81, 70.78, 70.76, 69.23, 64.60, 59.21, -0.13 ppm MS *m/z* = 490 ($m + H^+$).



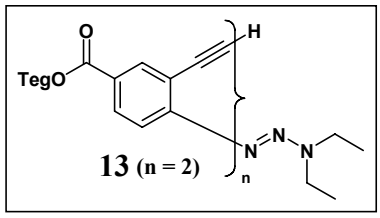
TMS-Es$_2$-Triazene (11) 1.05 g of **8** (2.26 mmol, 1.0 eq) was converted to **9** with the procedure described above. The product was not fully characterized, but was taken directly through Sonogashira coupling using the general procedure described above. The **9**, 1.53 g of **10** (3.69 mmol, 1.6 eq), 78 mg of $Pd(P\phi_3)_2Cl_2$ (111 μmol, 0.05 eq), and 7 mg CuI (37 μmol, 0.016 eq) were added to a schlenk flask with 60 mL of TEA and 60 mL of THF. The reaction was heated at 55°C overnight, worked up as described in the general procedure, and purified by flash chromatography in 0->10% acetone/$CHCl_3$ to obtain a yellow oil (1.38 g, 81%). ^{1}H NMR($CDCl_3$): δ 8.249 (d, 1H, phenyl H, J = 1.6), 8.171 (d, 1H, phenyl H, J = 1.6), 7.967 (dd, 1H, phenyl H, J_1 = 1.6 J_2 = 8.8), 7.934 (dd, 1H, phenyl H, J_1 = 1.6 J_2 = 8.0), 7.516 (d, 1H, phenyl H, J = 8.0), 7.508 (d, 1H, phenyl H, J = 8.8), 4.48 (m, 4H, CO_2CH_2), 3.83 (m, 8H, CH_2), 3.67 (m, 12H, CH_2), 3.51 (m, 4H, CH_2), 3.369 (s, 3H, OCH_3), 3.351 (s, 3H, OCH_3), 1.30 (m, 6H, CH_3), 0.263 (s, 9H, $Si(CH_3)_3$) ppm. ^{13}C NMR($CDCl_3$): δ 165.98, 165.61, 155.99, 134.99, 133.53, 131.68, 131.13, 131.04, 129.17, 129.11, 126.16, 125.82, 117.73, 116.69, 102.65, 99.99, 94.76, 92.00, 76.86, 72.06, 70.84, 70.81, 70.79, 70.76, 69.34, 69.30, 64.51, 64.05, 59.19, 59.17, 49.80, 42.56, 14.63, 11.04, 0.05 ppm MS *m/z* = 754 ($m + H^+$).



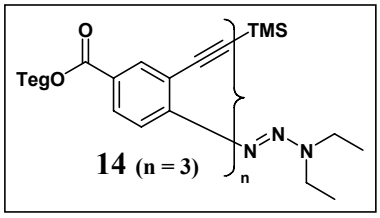
TMS-Es$_2$-Iodide (12) This compound was prepared by the general triazene activation procedure described above, with a longer reaction time and the addition of catalytic I_2. 274 mg of **11** (363 μmol, 1.0 eq), 2.4 mL MeI (5.5g, 0.15M in **11**) and 2.1 mg I_2 (18 μmol, 0.05 eq) were . Reaction was filtered through a Celite pad, washed with ethyl ether, and evaporated under a

N_2 stream. The residue was dissolved in 15 mL EtOAc, washed with 3 mL of 5% aqueous Na_2SO_3, dried over $MgSO_4$, and evaporated to yield crude product as a brown oil. Purification by flash chromatography in a 40%->80% EtOAc/Hexanes gradient gave a dark yellow oil (212 mg, 75%). ^{1}H NMR (CDCl3): δ 8.20 (m, 2H, phenyl H), 7.97 (m, 2H, phenyl H), 7.69 (m, 2H, phenyl H), 4.49 (m, 4H, CO_2CH_2), 3.84 (m, 4H, CH_2), 3.68 (m, 12H, CH_2), 3.54 (m, 4H, CH_2), 3.377 (s, 3H, OCH_3), 3.357 (s, 3H, OCH_3), 0.283 (s, 9H, $Si(CH_3)_3$) ppm. ^{13}C NMR ($CDCl_3$): δ 165.46, 139.30, 133.77, 133.74, 132.30, 130.59, 130.38, 130.05, 129.60, 129.21, 125.95, 107.16, 102.37, 100.47, 97.00, 91.88, 72.07, 72.06, 70.82, 70.80, 70.77, 69.27, 69.18, 64.63, 64.57, 59.21, 59.19, 0.10 ppm MS *m/z* = 781 (m + H^+).

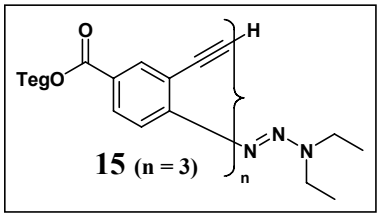
H-Es$_2$-Triazene (13) The general TMS deprotection procedure, listed above, was used to prepare this compound. 422 mg of **11** (560 μmol, 1.0 eq) was dissolved in 4.0 mL THF, cooled to 0°C, and reacted with 0.671 mL (1.6 eq) of 1M TBAF/THF + 5% H_2O. After 5 minutes, 4.0 mL of hexane was added to the reaction. After another 10 minutes of stirring, reaction mixture was injected onto a silica-packed pipette and eluted with 150 mL 2:1 EtOAc/Hexanes. Evaporation gave a yellow-orange oil (317 mg, 83%).



TMS-Es$_3$-Triazene (14) This compound was prepared by the general Sonogashira procedure described above. 317 mg of **13** (465 μmol, 1.2 eq), 190 mg of **10** (387 μmol, 1.0 eq), 8.1 mg of $Pd(P\phi_3)_2Cl_2$ (12 μmol, 0.03 eq), and 0.8 mg CuI (4 μmol, 0.01 eq) were added to a schlenk flask in 15 mL TEA and 30 mL THF. The reaction was heated at 55°C overnight, worked up as described in the general procedure, and purified by flash chromatography in 0->20% acetone/$CHCl_3$ to obtain an orange oil (350 mg, 87%). ^{1}H NMR ($CDCl_3$): δ 8.284 (d, 1H, phenyl H, J = 2.0), 8.265 (d, 1H, phenyl H, J = 2.0), 8.169 (d, 1H, phenyl H, J = 2.0), 8.01 (dd, 1H, phenyl H, J_1 = 2.0 J_2 = 8.4), 7.98 (dd, 1H, phenyl H, J_1 = 2.0 J_2 = 8.4), 7.90 (dd, 1H, phenyl H, J_1 = 2.0 J_2 = 8.4), 7.607 (d, 1H, phenyl H, J = 8.4), 7.575 (d, 1H, phenyl H, J = 8.4), 7.511 (d, 1H, phenyl H, J = 8.4), 4.49 (m, 6H, CO_2CH_2), 3.6-3.9 (m, 30H, CH_2), 3.53 (m, 4H, CH_2), 3.360 (s, 1H, OCH_3), 3.341 (s, 1H, OCH_3), 1.2-1.3 (m, 6H, CH_3), 0.285 (s, 9H, $Si(CH_3)_3$) ppm. ^{13}C NMR($CDCl_3$): δ values 165.82, 165.37, 165.31, 155.98, 135.03, 133.29, 132.37, 131.79, 131.00, 130.93, 130.07, 129.57, 129.49, 129.33, 129.16, 126.08, 125.80, 125.36, 117.40, 116.80, 102.29, 100.16, 95.21, 94.35, 92.24, 91.80, 71.94, 70.68, 70.64, 70.60, 69.22, 69.14, 69.12, 64.42, 64.33, 64.04, 59.06, 59.03, 49.54, 14.42, 10.91, 0.11 ppm MS *m/z* = 1044 (m + H^+).

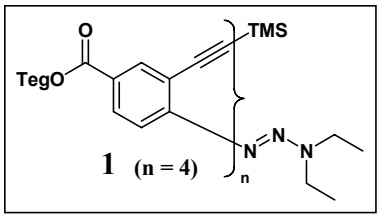


H-Es$_3$-Triazene (15) This compound was prepared by the general TMS deprotection procedure described above. 350 mg of **14** (335 μmol, 1.0 eq) was dissolved in 14 mL THF, cooled to 0°C, and reacted with 0.402 mL (1.2 eq) of 1M TBAF/THF + 5% H_2O. After 5 minutes, 14 mL hexane was added and the reaction was stirred for another 10 minutes.

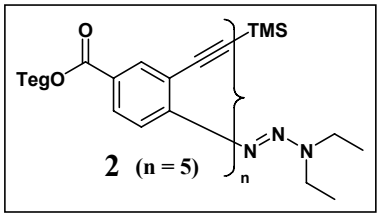


The reaction mixture was filtered through silica gel-packed pipettes and eluted with 2:1 EtOAc/Hexanes. Evaporation gave a yellow oil (305 mg, 94%).

TMS-Es$_4$-Triazene (1) This compound was prepared by the general Sonogashira procedure described above. 256 mg of **15** (263 μmol, 1.0 eq), 194 mg of **10** (395 μmol, 1.5 eq), 5.5 mg of $Pd(P\phi_3)_2Cl_2$ (8 μmol, 0.03 eq), and 0.5 mg of CuI (3 μmol, 0.01 eq) were added to a schlenk flask in 15 mL TEA and 30 mL THF. The reaction was heated at 55°C overnight, worked up as described in the general procedure, and purified by flash chromatography in 0->40% acetone/$CHCl_3$ to obtain a light yellow oil (284 mg, 77%). ^{1}H NMR($CDCl_3$): δ 8.299 (d, 1H, phenyl H, J = 2.0), 8.253 (d, 1H, phenyl H, J = 2.0), 8.196 (d, 1H, phenyl H, J = 2.0), 8.110 (d, 1H, phenyl H, J = 2.0), 8.011 (dd, 1H, phenyl H, J_1 = 2.0 J_2 = 8.4), 7.983 (dd, 1H, phenyl H, J_1 = 2.0 J_2 = 8.4), 7.926 (dd, 1H, phenyl H, J_1 = 2.0 J_2 = 8.4), 7.866 (dd, 1H, phenyl H, J_1 = 2.0 J_2 = 8.4), 7.668 (d, 1H, phenyl H, J = 8.4), 7.615 (d, 1H, phenyl H, J = 8.4), 7.593 (d, 1H, phenyl H, J = 8.4), 7.451 (d, 1H, phenyl H, J = 8.4), 4.43-4.56 (m, 8H, CO_2CH_2), 3.6-3.9 (m, 36H, CH_2), 3.48-3.58 (m, 8H, CH_2), 3.32-3.38 (m, 12H, OCH_3), 1.18-1.27 (m, 6H, CH_3), 0.280 (s, 9H, $Si(CH_3)_3$) ppm. ^{13}C NMR(CDCl3): δ 165.73, 165.30, 165.25, 165.20, 155.82, 135.02, 133.61, 133.25, 132.51, 132.17, 131.95, 130.94, 130.81, 129.90, 129.81, 129.74, 129.55, 129.36, 129.10, 125.93, 125.82, 125.53, 125.17, 117.32, 116.68, 102.29, 100.00, 95.37, 94.87, 93.75, 92.51, 92.14, 91.70, 71.92, 70.68, 70.64, 70.60, 69.22, 69.15, 69.11, 69.08, 64.38, 64.01, 59.05, 59.03, 49.50, 42.27, 14.42, 10.93, -0.11 ppm. MS *m/z* = 1335 ($m + H^+$).

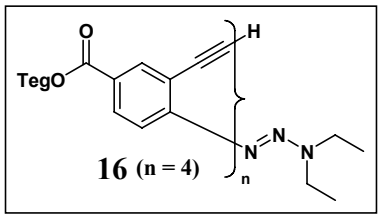


TMS-Es$_5$-Triazene (2) This compound was prepared by the general Sonogashira procedure described above. 234 mg of **15** (241 μmol, 1.0 eq) , 207 mg of **12** (265 μmol, 1.1 eq), 8.5 mg of $Pd(P\phi_3)_2Cl_2$ (12 μmol, 0.05 eq), and 0.5 mg of CuI (2.4 μmol, 0.01 eq) were added to a schlenk flask in 50 mL TEA and 100 mL THF. The reaction was heated at 55°C overnight, worked up as described in the general procedure, and purified by flash chromatography in 0->30% acetone/$CHCl_3$ to obtain an orange oil (269 mg, 69%). ^{1}H NMR (CD_3CN): δ 8.203 (d, 1H, phenyl H, J = 2.0), 8.019 (dd, 1H, phenyl H, J_1 = 2.0 J_2 = 8.4), 7.948 (d, 1H, phenyl H, J = 2.0), 7.843 (dd, 1H, phenyl H, J_1 = 2.0 J_2 = 8.4), 7.835 (d, 1H, phenyl H, J = 2.0), 7.832 (d, 1H, phenyl H, J = 2.0), 7.779 (d, 1H, phenyl H, J = 8.4),7.771 (d, 1H, phenyl H, J = 2.0), 7.766 (dd, 1H, phenyl H, J_1 = 2.0 J_2 = 8.4), 7.753 (dd, 1H, phenyl H, J_1 = 2.0 J_2 = 8.4), 7.645 (dd, 1H, phenyl H, J_1 = 2.0 J_2 = 8.4), 7.510 (d, 1H, phenyl H, J = 8.4),7.426 (d, 1H, phenyl H, J = 8.4),7.318 (d, 1H, phenyl H, J = 8.4),7.304 (d, 1H, phenyl H, J = 8.4), 4.35-4.48 (m, 10H, CO_2CH_2), 3.35-3.80 (m, 54H, CH_2), 3.20-3.28 (m, 15H, OCH_3), 1.10-1.30 (m, 6H, CH_3), 0.235 (s, 9H, $Si(CH_3)_3$) ppm. ^{13}C NMR(CD_3CN): δ 166.56, 166.26, 166.16, 166.08, 166.05, 157.03, 136.21, 134.41, 134.14, 133.95, 133.82, 133.76, 133.42, 131.89, 131.84, 131.70, 131.19, 131.18, 130.93, 130.92, 130.75, 130.64, 130.53, 130.52, 130.42, 130.16, 127.01, 126.87, 126.70, 126.45, 126.04, 118.46, 117.63, 103.47, 101.25, 96.39, 96.06, 95.29, 95.21, 93.81, 93.17, 93.15, 93.00, 73.00, 72.96, 71.73, 71.72,

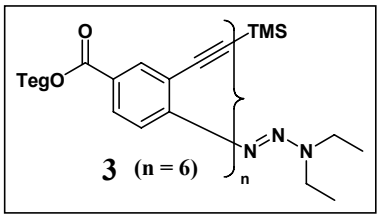


71.69, 71.66, 71.48, 71.46, 71.44, 71.40, 71.39, 70.02, 69.99, 69.97, 65.99, 65.91, 65.86, 65.82, 65.29, 59.31, 59.27, 50.78, 47.98, 43.54, 15.06, 11.72, 0.45 ppm.

H-Es$_4$-Triazene (16) This compound was prepared by the general TMS deprotection procedure described above. 146 mg of **1** (109 μmol, 1.0 eq) was dissolved in 6 mL THF, cooled to 0°C, and reacted with 0.120 mL (120 μmol, 1.1 eq) of 1M TBAF/THF + 5% H_2O. After 5 minutes, 6 mL hexane was added and the reaction was stirred for another 10 minutes. The reaction mixture was injected onto a dry 12g ISCO silica cartridge and eluted with a 0->20% acetone/$CHCl_3$ gradient to obtain a light yellow oil (101 mg, 73%).



TMS-Es$_6$-Triazene (3) This compound was prepared by the general Sonogashira procedure described above. 101 mg of **16** (75.7 μmol, 1.0 eq), 64.9 mg of **12** (83.2 μmol, 1.1 eq), 1.6 mg of $Pd(P\phi_3)_2Cl_2$ (2.3 μmol, 0.03 eq), and 0.2 mg of CuI (0.7 μmol, 0.01 eq) were added to a schlenk flask in 5.5 mL TEA and 11 mL THF. The reaction was heated at 55°C overnight, worked up as described in the general procedure, and purified by flash chromatography in 0->35% acetone/$CHCl_3$ to obtain an orange oil (117 mg, 81%). ^{1}H NMR (CD_3CN): δ 7.934 (d, 1H, phenyl H, J = 2.0), 7.926 (d, 1H, phenyl H, J = 2.0), 7.827 (dd, 1H, phenyl H, J_1 = 2.0 J_2 = 8.4), 7.759 (dd, 1H, phenyl H, J_1 = 2.0 J_2 = 8.4), 7.752 (d, 1H, phenyl H, J = 2.0), 7.717 (d, 1H, phenyl H, J = 2.0), 7.713 (dd, 1H, phenyl H, J_1 = 2.0 J_2 = 8.4), 7.703 (dd, 1H, phenyl H, J_1 = 2.0 J_2 = 8.4), 7.626 (d, 1H, phenyl H, J = 8.4), 7.598 (d, 1H, phenyl H, J = 2.0), 7.564 (d, 1H, phenyl H, J = 2.0), 7.551 (dd, 1H, phenyl H, J_1 = 2.0 J_2 = 8.4), 7.540 (dd, 1H, phenyl H, J_1 = 2.0 J_2 = 8.4), 7.430 (d, 1H, phenyl H, J = 8.4), 7.346 (d, 1H, phenyl H, J = 8.4), 7.245 (d, 1H, phenyl H, J = 8.4), 7.162 (d, 1H, phenyl H, J = 8.4), 7.117 (d, 1H, phenyl H, J = 8.4), 4.25-4.45 (m, 12H, CO_2CH_2), 3.35-3.80 (m, 64H, CH_2), 3.20-3.30 (m, 18H, OCH_3), 1.15-1.25 (m, 6H, CH_3), 0.283 (s, 9H, $Si(CH_3)_3$) ppm. ^{13}C NMR($CDCl_3$): δ 166.65, 166.16, 166.09, 166.03, 165.95, 165.91, 156.83, 136.04, 133.98, 133.86, 133.63, 133.61, 133.53, 133.50, 133.45, 133.29, 131.68, 131.65, 130.95, 130.82, 130.79, 130.75, 130.74, 130.66, 130.59, 130.35, 130.32, 130.28, 130.23, 130.18, 130.03, 126.83, 126.62, 126.60, 126.48, 126.25, 126.06, 118.49, 117.40, 103.57, 101.40, 96.15, 95.79, 95.52, 95.42, 95.18, 93.47, 93.35, 93.31, 93.10, 92.98, 72.97, 72.96, 72.91, 71.72, 71.70, 71.69, 71.66, 71.60, 71.47, 71.42, 71.40, 71.38, 71.35, 70.09, 70.08, 70.05, 70.02, 65.93, 65.92, 65.88, 65.77, 65.75, 65.29, 59.39, 59.37, 59.36, 59.35, 59.34, 59.32, 50.81, 47.75, 43.57, 15.05, 11.71, 0.57 ppm.



II. 1D NMR Traces Measurements. ^{1}H, ^{13}C NMR, COSY, HMBC, and ROESY spectra were obtained at 600 MHz with a Bruker 600 NMR spectrometer and analyzed with Bruker XWIN NMR, Top-Spin, and/or Mestre-C programs. All plots below have been labeled for each proton on each ring, 3a = proton a ring 3.

1D NMR traces for the solvent titration were calibrated on the TMS (tetramethylsilane) in the deuterated solvents. Further solvent correction to formulate the Δppm charts were performed based on an average Δppm of +0.05 observed for the monomer through trimer which should not shift due to π-π stacking with a change in solvent from $CDCl_3$ to CD_3CN. All ^1H NMR and COSY spectra for the solvent titrations for oligomers **1** and **2** were taken at 299K, and 1.25mM. The ^1H NMR and COSY spectra for the solvent titrations for oligomer **3** was taken at 305K and 1.25mM.

^1H NMR and COSY spectra for the temperature studies were performed at 1.25mM for the following temperatures in CD_3CN:

T_{Set} (K)	T_{actual} (°C)	**1**	**2**	**3**
253	-26.12	√	√	√
273	-2.64	√	√	√
288	15.22	√	√	√
298	25.89	√	√	√
305	33.80	X	X	√
308	37.19	√	√	√
323	54.14	√	√	√
343	76.74	√	√	√

Es_4 Solvent Titration

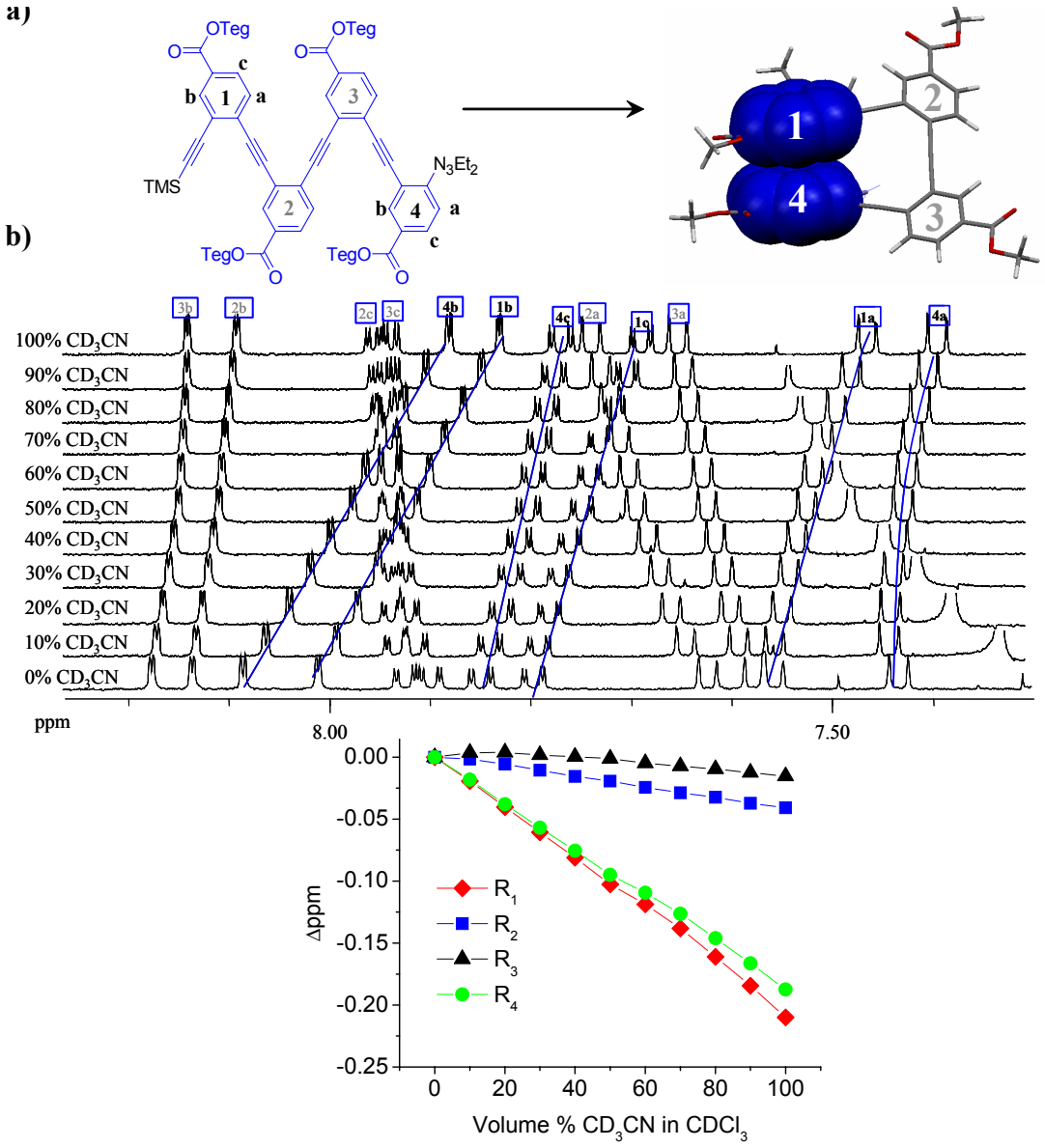


Figure S2: (a) Oligomer **1** extended and a molecular model of **1** folded with R_1 and R_4 stacked on top of one another. (b) Raw data for Solvent Titration performed from 0% CD_3CN (100% $CDCl_3$) to 100% CD_3CN. Each peak for each proton has been labeled: 1a = the a proton on R_1. Lines to follow the paths of protons 1a-1c and 4a-4c have been added for clarity. (c) Compressed data of the solvent titration for oligomer **1**, showing the Δppm values for each ring (R_n) of oligomer **1**. Each value was calculated by averaging the a, b, and c protons of each ring, and corrected for the addition of CD_3CN. The values have been normalized to a Δppm value of zero at 0% CD_3CN for clarity. **R_1 and R_4 both shift upfield (to negative values) dramatically while R_2 and R_3 clearly do not shift upfield with increasing CD_3CN concentration.**

Es_4 Temperature Study- CD_3CN

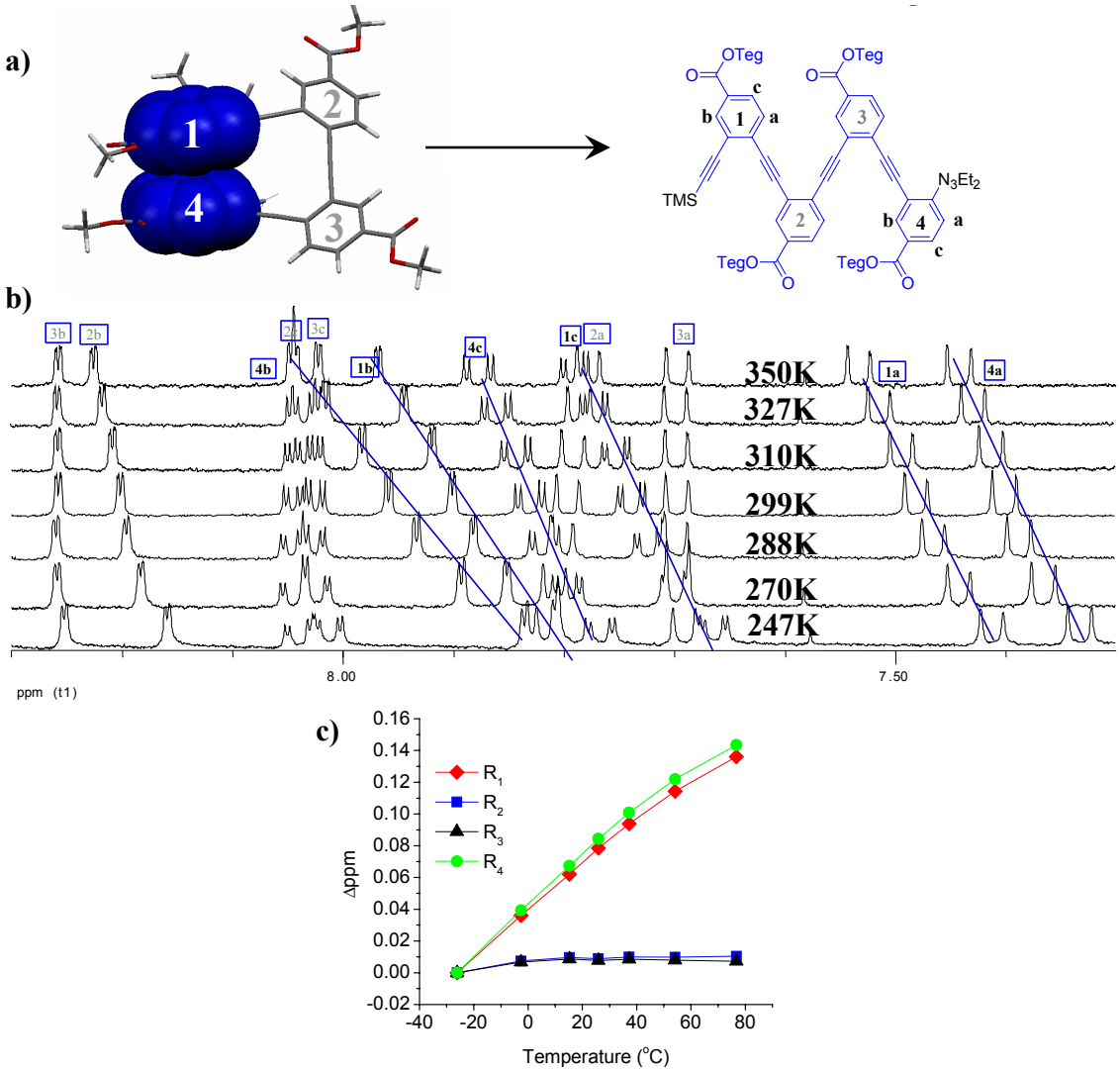


Figure S3: (a) Molecular model of **1** folded with R_1 and R_4 stacked on top of one another and oligomer **1** extended. (b) Raw data for the temperature study performed from 247K (-26°C) to 350K (77°C) in CD_3CN. Each peak for each proton has been labeled: 1a = the a proton on R_1. Lines to follow the paths of protons 1a-1c and 4a-4c have been added for clarity. (c) Compressed data of the temperature study for oligomer **1**, showing the Δppm values for each ring of oligomer **1** calculated by averaging the a, b, and c protons of each ring The values have been normalized to a Δppm value of zero at 247K for clarity. **R_1 and R_4 both shift downfield dramatically with increasing temperature while R_2 and R_3 clearly do not shift downfield.**

Es_4 ROESY Measurements

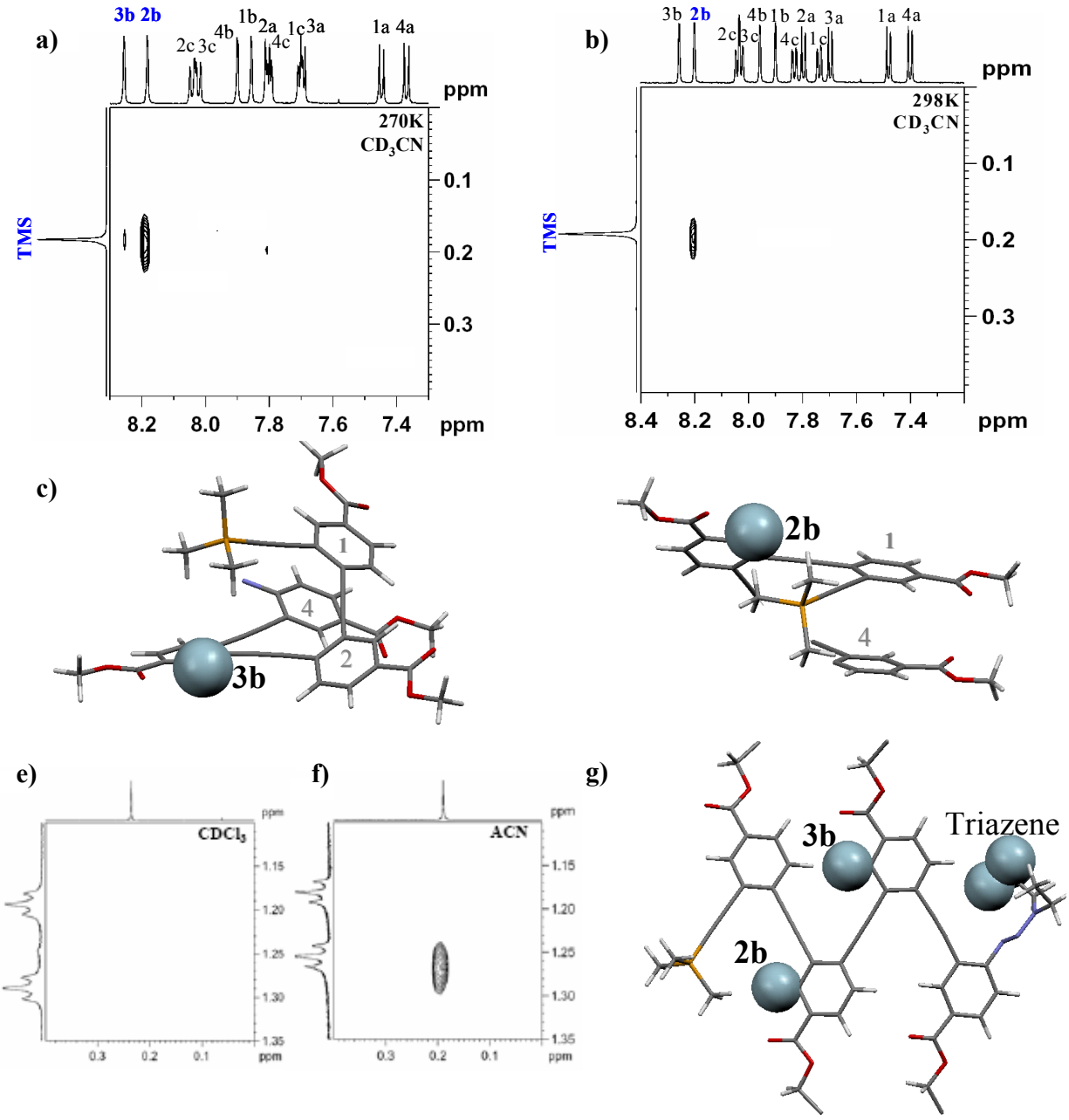


Figure S4: (a) and (b) ROESY spectra of tetramer **1** in CD_3CN at 270K (a) and 298K (b) showing the entire aryl region of the oligomer plotted versus the terminal trimethylsilyl (TMS) off of R_1. Given the 1D ^1H NMR data that indicated folding through the observation of π-π stacking for R_1 and R_4 this new ROESY data supports the existence of 2 conformers in solution. At 270K there are 2 cross peaks between the TMS and protons 2b and 3b as they are highlighted in the helical models shown in (c) and (d). Some elements of the models have been eliminated for clarity. These two cross peaks support the possibility of a dynamic folded system, as the only way for these two cross peaks to

exist is for the oligomer to vacillate between conformers that have the TMS both in the progression of the helix and flipped out side of it as shown in (c) and (d). Prior ROESY data lacking any interactions between the terminal TMS and the triazene on ring 4 in $CDCl_3$ (e) shows a very clear peak in CD_3CN (f), the folded solvent, at room temperature. The only way this interaction is possible is through the folding of oligomer **1**. Otherwise, as shown in (g), the TMS is out of the 5Å range of allowable interactions for ROESY behavior. Table S1 shows the calculations and model estimations for the observed cross peaks in (a) and (b) for oligomer **1**.

Table S1: ROESY distance calculations for oligomer **1**

Figure	Temp (K)	Reference Peak (A_1)	Observed Peak (A_2)	Intensity (A_1)	Intensity (A_2)	Reference Distance (r_1)	Calculated Distance (r_2)	Model Distance (r_1)
S5 (a)	270	2a to 2c	TMS to 2b	361631	54125	2.44	3.35	3.49
S5 (a)	270	2a to 2c	TMS to 3b	361631	6513	2.44	4.77	4.10
S5 not shown	270	2a to 2c	TMS to Triazene	361631	88448	2.44	2.99	2.72
S5 (b)	298	2a to 2c	TMS to 2b	562371	51925	2.44	3.63	3.49
S5 (f)	298	2a to 2c	TMS to Triazene	562371	903545	2.44	2.25	2.72

Es_5 Solvent Titration

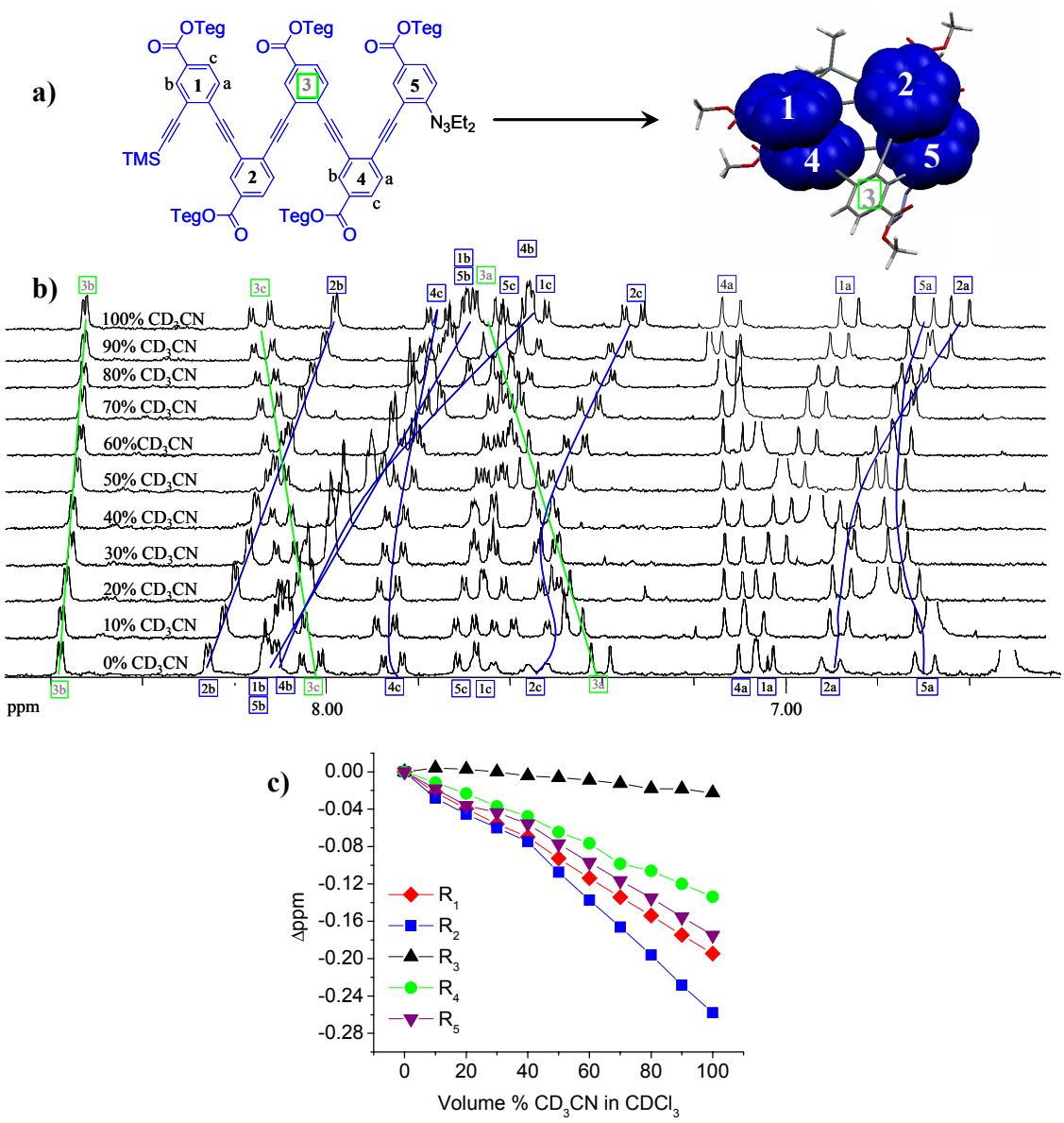


Figure S5: (a) Oligomer **2** extended and a molecular model of **2** folded with R_1 stacked over R_4 and R_2 stacked over R_5. (b) Raw data for Solvent Titration performed from 0% CD_3CN (100% $CDCl_3$) to 100% CD_3CN. Each peak for each proton has been labeled: 1a = the a proton on R_1. Lines to follow the paths of protons 1, 2, 4, and 5b, 2 and 3c, as well as 2 and 3a have been added. (c) Compressed data of the solvent titration for oligomer **2**, showing the Δppm values for each ring of oligomer **2** calculated by averaging the a, b, and c protons of each ring, and corrected for the addition of CD_3CN. The values have been normalized to a Δppm value of zero at 0% CD_3CN for clarity. **R_1 R_2, R_4, and**

R_5 all shift upfield dramatically while R_3 clearly does not shift upfield with increasing CD_3CN concentration.

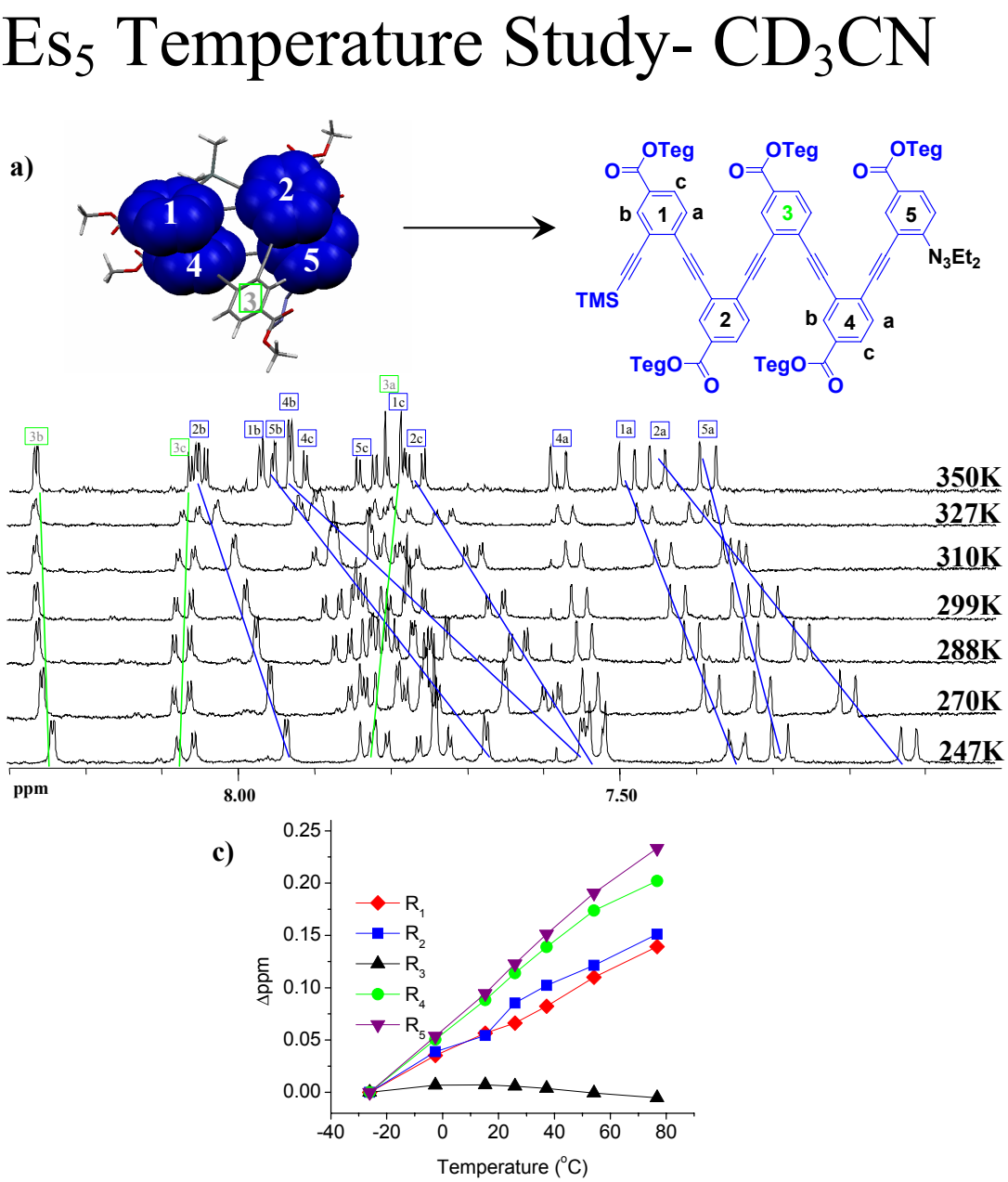


Figure S6: (a) Molecular model of **2** folded with folded with R_1 stacked over R_4 and R_2 stacked over R_5. Oligomer **2** extended. (b) Raw data for the temperature study performed from 247K (-26°C) to 350K (77°C) in CD_3CN. Each peak for each proton has been labeled: 1a = the a proton on R_1. Lines to follow the paths of protons 1, 2, 4, and 5b, 2 and 3c, as well as 2 and 3a have been added. (c) Compressed data of the temperature study for oligomer **2**, showing the Δppm values for each ring of oligomer **2** calculated by averaging the a, b, and c protons of each ring The values have been normalized to a Δppm value of zero at 247K for clarity. **R_3 clearly does not shift downfield with increasing temperature. $R_{1,2,4,5}$ all shift downfield dramatically with increasing temperature.**

Es_5 ROESY Measurements

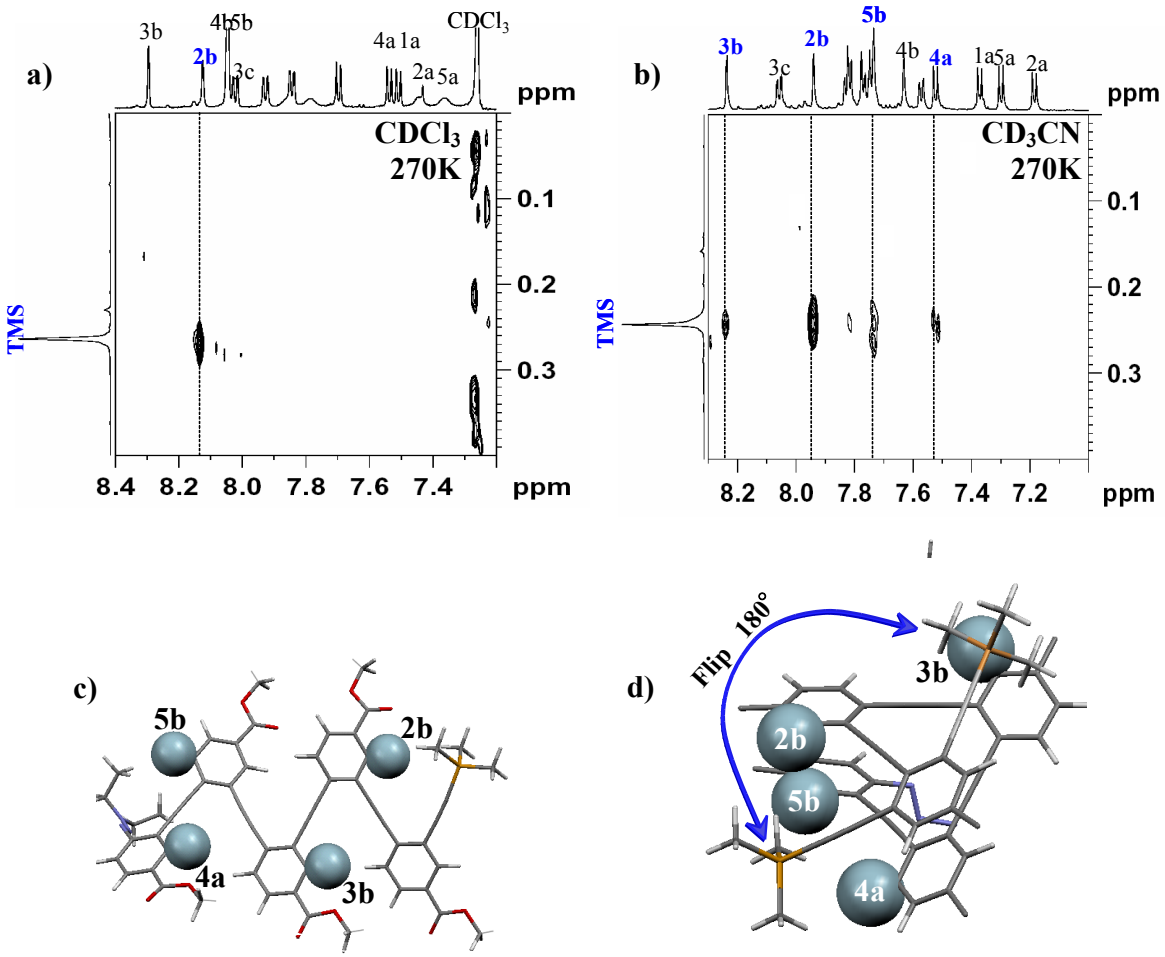


Figure S7: ROESY spectra of pentamer **2** in $CDCl_3$ (a) and CD_3CN (b) at 270K. Selected protons are labeled for the aryl region. Only one cross-peak is observed in the $CDCl_3$ between the TMS and the aryl region, peak 2b on R_2. This is reasonable because even in an extended conformation (c) with the ring relatively flat, the TMS and 2b can be ~ 3 Å away from one another. Keeping in mind that the system is dynamic, in an unfolded conformation this is the only reasonable explanation for this cross peak in $CDCl_3$. In CD_3CN however, a number of cross peaks are observed between the terminal TMS and the aryl region. All peaks are highlighted by model (d). It is clear that a peak between 3b and the TMS would occur if the TMS terminus was in the progression of the helix over R_3. The distance calculated for this structure is 4.47 Å which is in line with the model prediction of 3.43Å. Though the calculated value is larger than the model prediction it is reasonable if the structure is dynamic and the TMS is flipping back and forth with R_1 in solution. The other more interesting possible position for the TMS would be for it to assume a position nestled in the hydrophobic pocket created near the

stacked rings of this system, $R_{1,4}$ and $R_{2,5}$ shown in (e). This option would put the TMS in very close proximity to protons 2b, 5b, and 4a. This is precisely what is observed in (b). The dynamic nature of this structure as folded provides for peaks with each of these protons. Table S3 gives distances calculated from the cross peak interactions for each interaction and values for the distances as predicted by the models. Though the calculated distances for these interactions are large as compared with the model predictions for a compact and folded structure, it should again be noted that these structures are dynamic in solution. It should be noted that it would be impossible for the TMS to have cross peaks with either 4a or 5b if the structure were extended as shown in (c) as the model approximated distances between these atoms are 13.0Å and 12.9 Å respectively.

Table S2: ROESY distance calculations for oligomer **2**

Figure	Temp (K)/ Solvent	Reference Peak (A_1)	Observed Peak (A_2)	Intensity (A_1)	Intensity (A_2)	Reference Distance (r_1)	Calculated Distance (r_2)	Model Distance (r_1)
S8(a)	270 $CDCl_3$	3a to 3c	TMS to 2b	528313	91704	2.44	3.27	2.94
S8(b)	270 CD_3CN	3a to 3c	TMS to 2b	766360	124138	2.44	3.30	3.29
S8(b)	270 CD_3CN	3a to 3c	TMS to 3b	766360	20032	2.44	4.48	3.43
S8(b)	270 CD_3CN	3a to 3c	TMS to 4a	766360	13904	2.44	4.76	2.97
S8(b)	270 CD_3CN	3a to 3c	TMS to 5b	766360	10923	2.44	4.96	2.70

Es_6 Solvent Titration

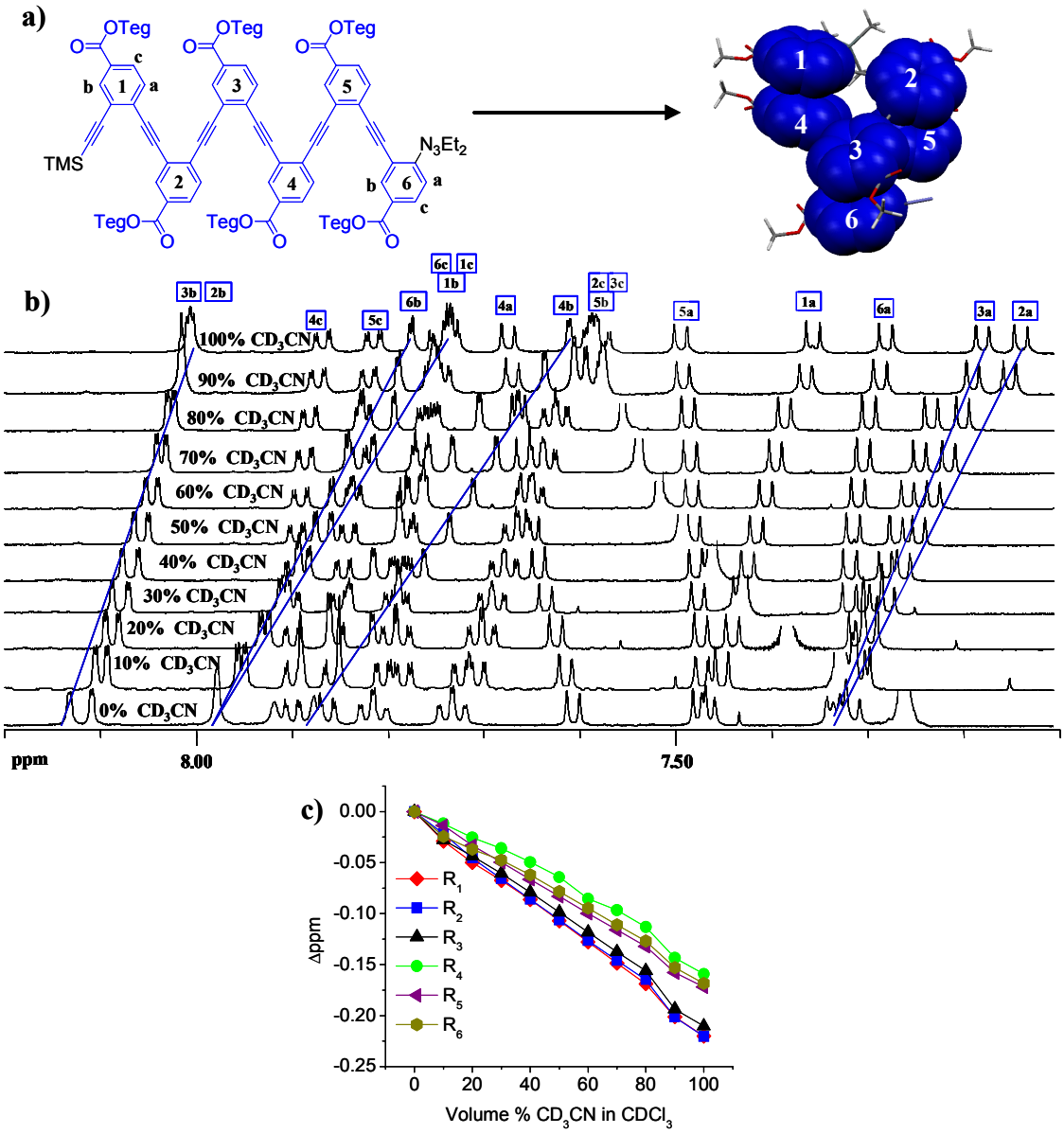


Figure S8: (a) Oligomer **3** extended and a molecular model of **3** folded with R_1 stacked over R_4, R_2 stacked over R_5, and R_3 stacked over R_6. (b) Raw data for Solvent Titration performed from 0% CD_3CN (100% $CDCl_3$) to 100% CD_3CN. Each peak for each proton has been labeled: 1a = the a proton on R_1. Lines to follow the paths of protons all b protons, and 2 and 3a have been added for clarity. (c) Compressed data of the solvent titration for oligomer **3**, showing the Δppm values for each ring of oligomer **3** calculated by averaging the a, b, and c protons of each ring, and correcting for the addition of CD_3CN (which would shift the protons downfield by 0.06 ppm per 10% of CD_3CN added). The values have been normalized to a Δppm value of zero at 0% CD_3CN for clarity. **All rings R_1 – R_6 shift upfield (to negative values) dramatically, indicative of π-π stacking.**

Es_6 Temperature Study- CD_3CN

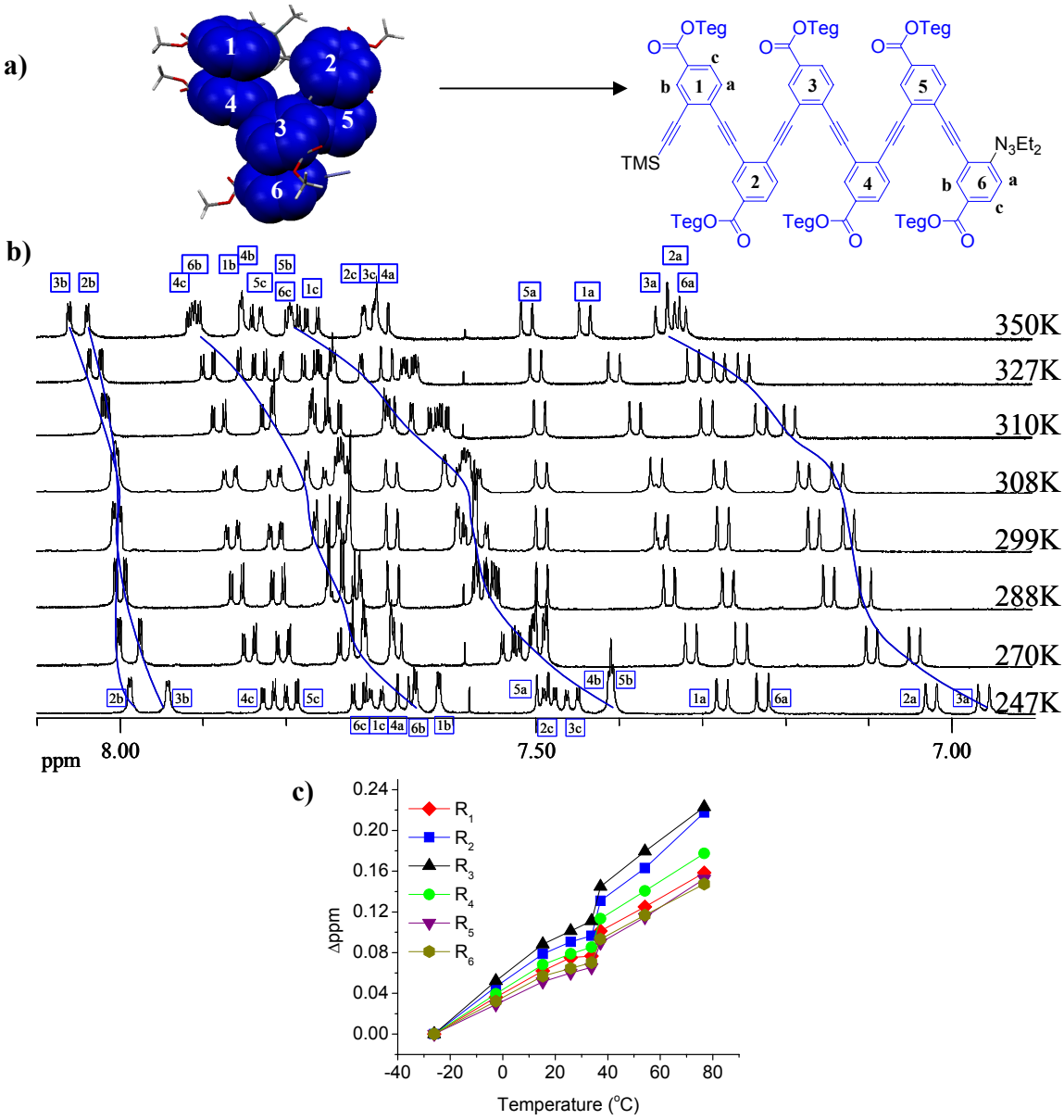


Figure S9: (a) Molecular model of **3** folded with folded with R_1 stacked over R_4, R_2 stacked over R_5, and R_3 stacked over R_6. Oligomer **3** extended. (b) Raw data for the temperature study performed from 247K (-26°C) to 350K (77°C) in CD_3CN. Each peak for each proton has been labeled: 1a = the a proton on R_1. Lines to follow the paths of protons 3b, 2b, 6b, 5b, and 3a have been added. (c) Compressed data of the temperature study for oligomer **3**, showing the Δppm values for each ring of oligomer **2** calculated by averaging the a, b, and c protons of each ring The values have been normalized to a Δppm value of zero at 247K for clarity. **All rings R_1-R_6 clearly shift downfield with increasing temperature.**

Es_6 ROESY Measurements

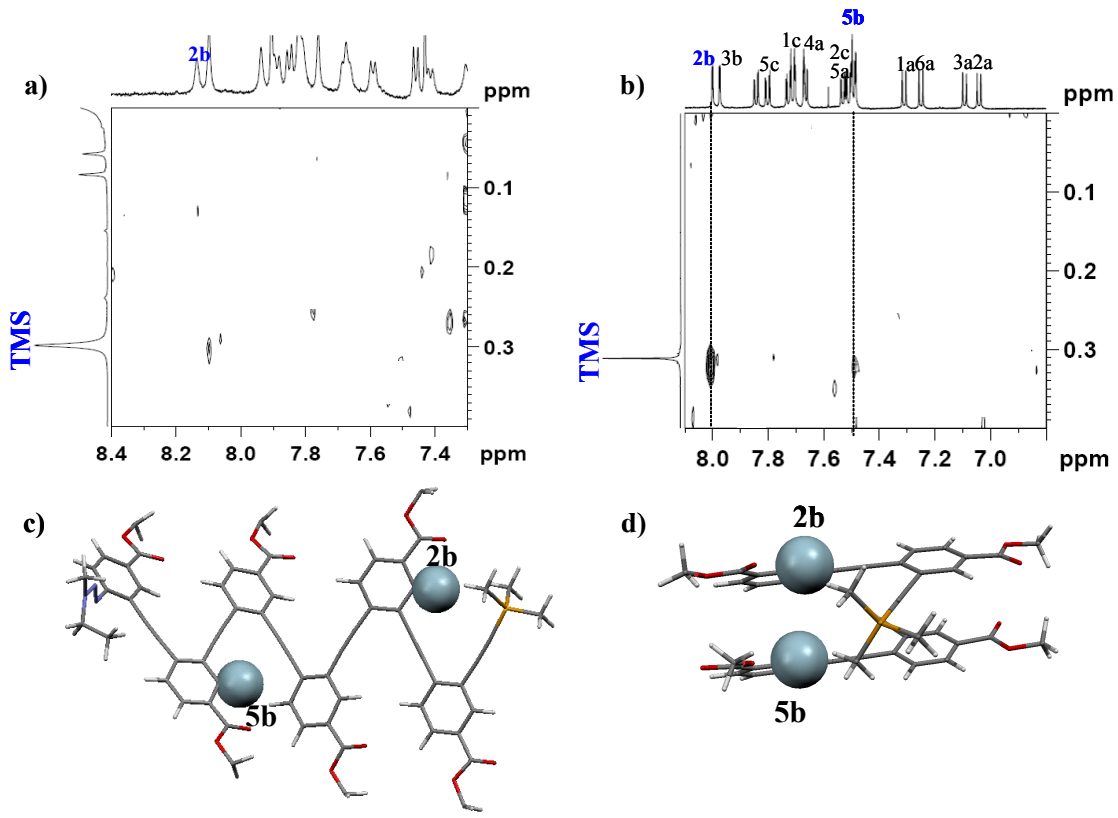


Figure S10: ROESY spectra of hexamer **3** in $CDCl_3$ (a) and CD_3CN (b) at 270K. (c) Model of **3** fully extended prominently showing protons 2b and 5b. (d) Helical conformation of **3** showing TMS nestled in hydrophobic region near R_1-R_4 and R_2-R_5. The only cross peak observed in $CDCl_3$ is reasonable because it could be exhibited even with an extended structure as shown in (c). In figure (b), two cross peaks are visible in CD_3CN with protons 2b and 5b. This is inline with all previous data: the π-π stacking shown in CD_3CN vs. $CDCl_3$ supports a folded structure. The ROESY data shown hear fully supports folding. Table S3 shows the calculated versus the measured model distances for the TMS versus protons 2b and 5b. It should be noted that for (c) the shortest distance between the TMS and proton 5b was 12.4 Å which would be well out of range for NOE interactions.

Table S3: ROESY distance calculations for oligomer **3**

Figure	Temp (K)/ Solvent	Reference Peak (A_1)	Observed Peak (A_2)	Intensity (A_1)	Intensity (A_2)	Reference Distance (r_1)	Calculated Distance (r_2)	Model Distance (r_1)
S11(a)	270 $CDCl_3$	6a to 6c	TMS to 2b	161090	91704	2.44	3.27	2.76
S11(b)	270 CD_3CN	2a to 2c	TMS to 2b	161090	23525	2.44	3.37	3.48
S11(b)	270 CD_3CN	2a to 2c	TMS to 5b	161090	18508	2.44	3.50	3.01