Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

for

Molecularly-Defined Macrocycles Containing Azobenzene Main-Chain Oligomers: Modular Stepwise Synthesis, Chain-Length and Topology-Dependent Properties

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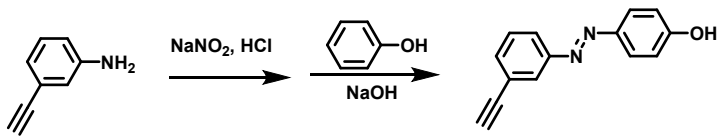
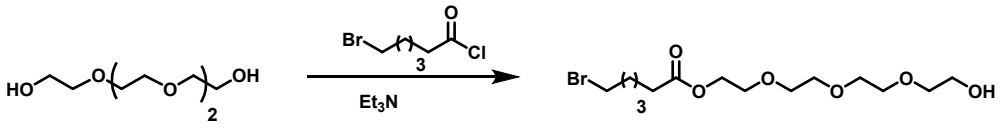
Synthetic procedures

Synthesis of HAAzo



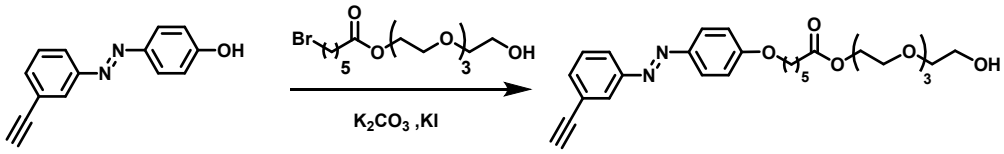
^{1}H NMR ($CDCl_3$), δ (TMS, ppm): 8.04-7.97 (s, 1H, ArH), 7.94-7.83 (m, 3H, ArH), 7.62-7.52 (d, 1H, ArH), 7.50-7.42 (m, 1H, ArH), 7.00-6.91 (d, 2H, ArH), 5.36-5.27 (s, 1H, ArOH), 3.17-3.10 (s, 1H, ArC≡CH).

Synthesis of Br-TEG-OH



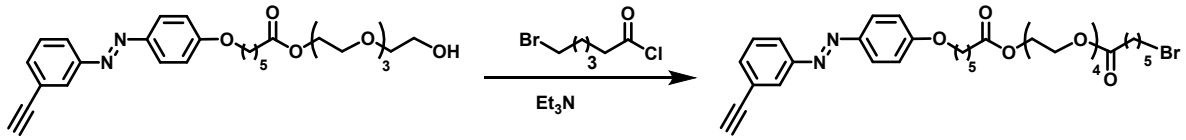
^{1}H NMR (300 MHz, $CDCl_3$) δ 4.27-4.20 (m, 2H, -COOC$\underline{H}_2$CH$_2$), 3.73 (dd, *J* = 8.8, 4.4 Hz, 4H, -CH$_2$C$\underline{H}_2$O-), 3.67 (s, 8H, -OC$\underline{H}_2$C$\underline{H}_2$O-), 3.64-3.59 (m, 2H, -C$\underline{H}_2$OH), 3.54 (t, *J* = 6.6 Hz, 1H, -BrC$\underline{H}_2$-), 3.41 (t, *J* = 6.7 Hz, 1H, -BrC$\underline{H}_2$-), 2.36 (t, *J* = 7.4 Hz, 3H, -C$\underline{H}_2$COO-, -O$\underline{H}$), 1.94-1.76 (m, 2H, -CH$_2$C$\underline{H}_2$-), 1.73-1.60 (m, 2H, -CH$_2$C$\underline{H}_2$-), 1.54-1.41 (m, 2H, -CH$_2$C$\underline{H}_2$-).

Synthesis of Azo-TEG-OH



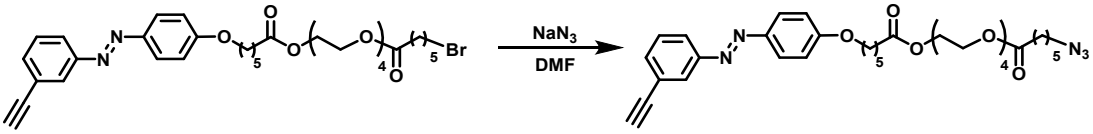
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.00 (s, 1H, phenyl), 7.89 (d, *J* = 13.9, 8.5 Hz, 3H, phenyl), 7.55 (d, *J* = 7.6 Hz, 1H, phenyl), 7.45 (t, *J* = 7.8 Hz, 1H, phenyl), 7.00 (d, *J* = 9.0 Hz, 2H, phenyl), 4.28-4.22 (m, 2H, -OCOC$\underline{H}$2-), 4.05 (t, *J* = 6.4 Hz, 2H, -OC$\underline{H}_2$CH$_2$-), 3.72 (dd, *J* = 5.1, 3.8 Hz, 4H, -OC$\underline{H}_2$C$\underline{H}_2$O-), 3.66 (s, 9H, -OC$\underline{H}_2$C$\underline{H}_2$O-), 3.63-3.57 (m, 2H, -C$\underline{H}_2$OH), 3.13 (s, 1H, -C≡CH), 2.40 (t, *J* = 7.4 Hz, 2H, -C$\underline{H}_2$COO-), 1.90-1.78 (m, 2H, -CH$_2$C$\underline{H}_2$-), 1.71 (dt, *J* = 12.7, 6.5 Hz, 2H, -CH$_2$C$\underline{H}_2$-), 1.62-1.46 (m, 2H), 1.43 (s, 2H, -CH$_2$C$\underline{H}_2$-).

Synthesis of (Azo-TEG)$_1$-Br



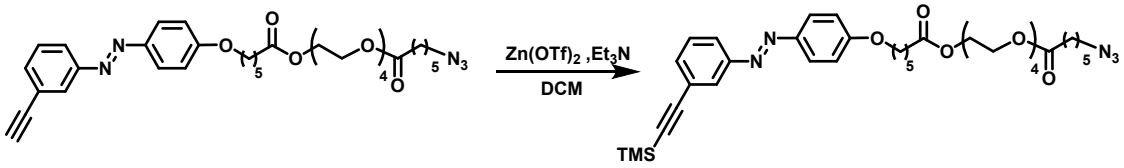
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.10-7.77 (m, 4H, phenyl), 7.49 (dt, *J* = 15.5, 7.7 Hz, 2H, phenyl), 7.00 (d, *J* = 9.0 Hz, 2H, phenyl), 4.24 (dd, *J* = 9.3, 4.3 Hz, 4H, -OCOC$\underline{H}_2$-), 4.05 (t, *J* = 6.4 Hz, 2H, -OC$\underline{H}_2$CH$_2$-), 3.73-3.67 (m, 4H, -OCOC$\underline{H}_2$-), 3.65 (s, 8H, -OC$\underline{H}_2$C$\underline{H}_2$O-), 3.63-3.57 (m, 2H, -C$\underline{H}_2$Br), 3.13 (s, 1H, -C≡CH), 2.37 (dt, *J* = 12.9, 7.4 Hz, 4H, -C$\underline{H}_2$COO-), 1.91-1.77 (m, 4H, -CH$_2$C$\underline{H}_2$-), 1.68 (ddd, *J* = 21.8, 15.0, 7.2 Hz, 4H, -CH$_2$C$\underline{H}_2$-), 1.60-1.42 (m, 4H, -CH$_2$C$\underline{H}_2$-).

Synthesis of alkynyl-Azo-TEG-N$_3$



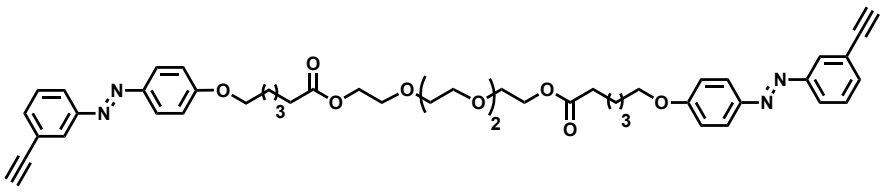
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.10-7.77 (m, 4H, pheny), 7.49 (dt, *J* = 15.5, 7.7 Hz, 2H, phenyl), 6.99 (d, *J* = 8.9 Hz, 2H, phenyl), 4.23 (dd, *J* = 9.3, 4.3 Hz, 4H, -OCOC$\underline{H}_2$-), 4.05 (t, *J* = 6.4 Hz, 2H, -OC$\underline{H}_2$CH$_2$-), 3.70 (dt, *J* = 8.3, 3.5 Hz, 4H, -OCOC$\underline{H}_2$-), 3.65 (d, *J* = 1.1 Hz, 8H, -OC$\underline{H}_2$C$\underline{H}_2$O-), 3.27 (t, *J* = 6.8 Hz, 2H, -C$\underline{H}_2$N$_3$), 3.13 (s, 1H, -C≡C$\underline{H}$), 2.53-2.28 (m, 4H, -C$\underline{H}_2$COO-), 1.92-1.31 (m, 12H, -CH$_2$C$\underline{H}_2$-).

Synthesis of TMS-Azo-TEG-N$_3$



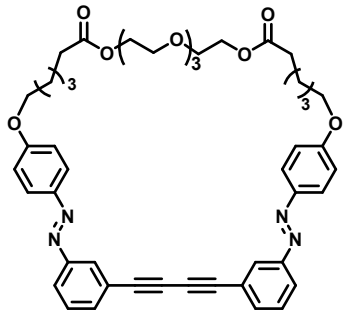
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.03-7.75 (m, 4H, pheny), 7.58-7.38 (m, 2H, phenyl), 6.99 (d, *J* = 8.1 Hz, 2H, phenyl), 4.23 (s, 4H, -OCOC$\underline{H}_2$-), 4.05 (s, 2H, -OC$\underline{H}_2$CH$_2$-), 3.69 (s, 4H , -OCOC$\underline{H}_2$-), 3.65 (s, 8H , -OC$\underline{H}_2$C$\underline{H}_2$O-), 3.27 (s, 2H, -C$\underline{H}_2$TMS), 2.46-2.29 (m, 4H, -C$\underline{H}_2$COO-), 1.92-1.31 (m, 12H, -CH$_2$C$\underline{H}_2$-), 0.27 (s, 9H, -Si$\underline{H}_3$).

Synthesis of *l*-(Azo_2-TEG_1) (n = 1)



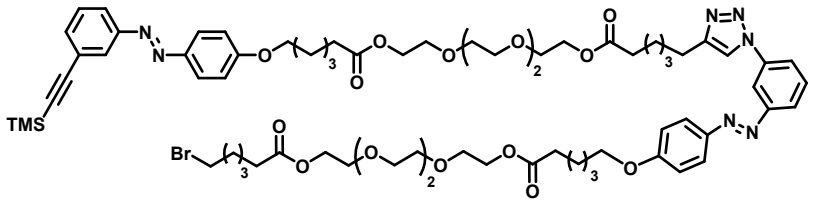
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.00 (s, 2H, phenyl), 7.95-7.82 (m, 6H, phenyl), 7.49 (dt, *J* = 15.5, 7.7 Hz, 4H, phenyl), 6.99 (d, *J* = 8.9 Hz, 4H , phenyl), 4.28-4.20 (m, 4H, -OCOC$\underline{H}_2$CH_2-), 4.04 (t, *J* = 6.4 Hz, 4H, -OC$\underline{H}_2$CH_2-), 3.73-3.61 (m, 12H, -CH_2C$\underline{H}_2$-), 3.13 (s, 2H, -C≡C$\underline{H}$), 2.39 (t, *J* = 7.4 Hz, 4H, -OCOC$\underline{H}_2$CH_2-), 1.90-1.45 (m, 12H, -CH_2C$\underline{H}_2$-).

Synthesis of *c*-(Azo_2-TEG_1) (n = 1)



^{1}H NMR (300 MHz, $CDCl_3$) δ 8.00 (s, 2H, phenyl), 7.95-7.82 (m, 6H, phenyl), 7.49 (dt, *J* = 15.5, 7.7 Hz, 4H, phenyl), 6.99 (d, *J* = 8.9 Hz, 4H, phenyl), 4.28-4.20 (m, 4H, -OCOC$\underline{H}_2$CH_2-), 4.04 (t, *J* = 6.4 Hz, 4H, -OC$\underline{H}_2$CH_2-), 3.73-3.61 (m, 12H, -CH_2C$\underline{H}_2$-), 2.39 (t, *J* = 7.4 Hz, 4H, -OCOC$\underline{H}_2$CH_2-), 1.90-1.45 (m, 12H, -CH_2C$\underline{H}_2$-).

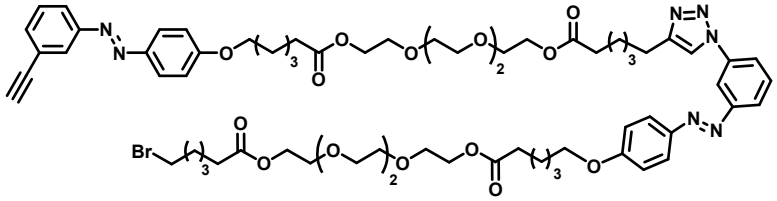
Synthesis of TMS-(Azo-$TEG)_2$-Br for general procedure for "CuAAC" reaction



^{1}H NMR (300 MHz, $CDCl_3$) δ 8.28 (s, 1H, triazole ring), 8.12-6.68 (m, 16H, pheny), 4.43 (t, *J* = 7.1 Hz,

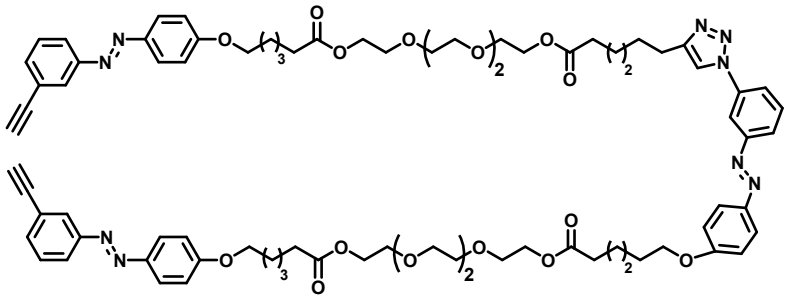
2H, trizaole-C$\underline{H}_2$CH$_2$-), 4.28-4.18 (m, 8H, -OCOC$\underline{H}_2$-), 4.04 (dd, *J* = 10.5, 6.2 Hz, 4H, -OC$\underline{H}_2$CH$_2$-), 3.70 (dd, *J* = 9.4, 4.7 Hz, 8H, -OCOC$\underline{H}_2$-), 3.65 (d, *J* = 1.4 Hz, 16H, -OC$\underline{H}_2$C$\underline{H}_2$O-), 3.40 (s, 2H, -C$\underline{H}_2$Br), 2.35 (s, 8H, -C$\underline{H}_2$COO-), 1.93-1.44 (m, 24H, -CH$_2$C$\underline{H}_2$-), 0.27 (s, 9H, -Si$\underline{H}_3$).

Synthesis of (Azo-TEG)$_2$-Br for alkyne deprotection



^{1}H NMR (300 MHz, $CDCl_3$) δ 8.28 (s, 1H, triazole ring), 8.12-6.68 (m, 16H, pheny), 4.43 (t, *J* = 7.1 Hz, 2H, trizaole-C$\underline{H}_2$CH$_2$-), 4.28-4.18 (m, 8H, -OCOC$\underline{H}_2$-), 4.04 (dd, *J* = 10.5, 6.2 Hz, 4H, -OC$\underline{H}_2$CH$_2$-), 3.70 (dd, *J* = 9.4, 4.7 Hz, 8H, -OCOC$\underline{H}_2$-), 3.65 (d, *J* = 1.4 Hz, 16H, -OC$\underline{H}_2$C$\underline{H}_2$O-), 3.40 (s, 2H, -C$\underline{H}_2$Br), 3.13 (s, 1H, -C≡CH), 2.35 (s, 8H, -C$\underline{H}_2$COO-), 1.93-1.44 (m, 24H, -CH$_2$C$\underline{H}_2$-).

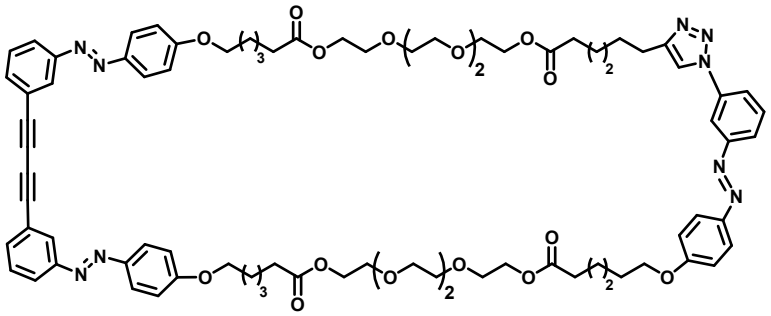
Synthesis of *l*-(Azo$_3$-TEG$_2$) (n = 2)



The *l*-(Azo$_3$-TEG$_2$) was prepared using the similar procedures as *l*-(Azo$_2$-TEG$_1$). A solution of (Azo-TEG)$_2$-Br (1.339 g, 1 mmol), HAAzo (0.888 g, 4 mmol), potassium carbonate (0.552 g, 1 mmol), a catalytic amount of potassium iodide, and 50 mL of DMF was prepared in a 100mL round bottom flask under vigorous stirring. The solution was stirred at 80 °C for 4h. After cooling to room temperature, deionized water (4×200 mL) was added and the mixture was extracted with ethyl acetate (200 mL). The organic layer obtained was dried with anhydrous $MgSO_4$ overnight, filtered, and evaporated in a reduced pressure. The final crude product was purified by column chromatography (silica gel, ethyl acetate) to

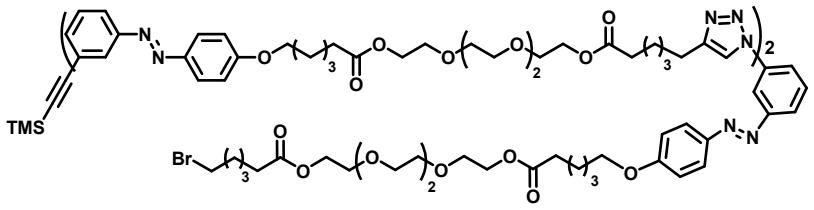
yield the *l*-(Azo_3-TEG_2) as yellow liquid (1.33 g, 90.9%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.27 (s, 1H, triazole ring), 8.07-6.81 (m, 24H, pheny), 4.42 (t, *J* = 7.1 Hz, 2H, trizaole-C$\underline{H}_2$CH_2-), 4.29-4.15 (m, 8H, -OCOC$\underline{H}_2$-), 4.03 (t, *J* = 6.3 Hz, 6H, -OC$\underline{H}_2$CH_2-), 3.75-3.66 (m, 8H, -OCOC$\underline{H}_2$-), 3.66-3.53 (m, 16H, -OC$\underline{H}_2$C$\underline{H}_2$O-), 3.13 (s, 2H, -C≡C$\underline{H}$), 2.58-2.21 (m, 8H, -C$\underline{H}_2$COO-), 2.12-1.19 (m, 24H, -CH_2C$\underline{H}_2$-).

Synthesis of *c*-(Azo_3-TEG_2) (n = 2)



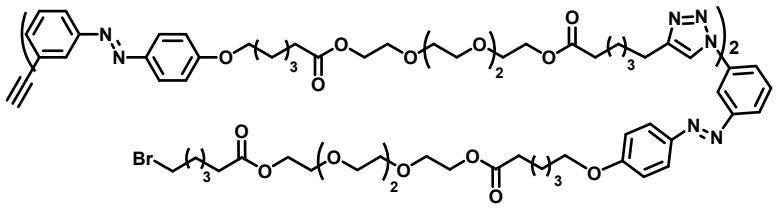
To a 1000 mL three-necked round-bottomed flask was added acetone (800 mL), triethylamine 50 mL, CuI (0.955 g, 50 mmol), and TMEDA (1.5 mL, 10 mmol), and the solution was stirred for 1 h. The *l*-(Azo_3-TEG_2) (0.148 g, 0.1 mmol) in 20 mL of acetone was added to CuI/TMEDA mixture at room temperature *via* syring pump at rate of 0.4 mL/h. After the addition of polymer solution was completed, the reaction was allowed to proceed for another period of 24 h. The reaction solution was concentrated in a reduced pressure, deionized water (3×500 mL) was added and the mixture was extracted with ethyl acetate (400 mL) to remove the copper catalyst residues. The organic layer obtained was dried with anhydrous $MgSO_4$ overnight, filtered, and evaporated in a reduced pressure. The final crude product was purified by column chromatography (silica gel, ethyl acetate) to yield *c*-(Azo_3-TEG_2) as yellow liquid (0.082 g, 80%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.27 (s, 1H, triazole ring), 8.07-6.81 (m, 24H, pheny), 4.42 (t, *J* = 7.1 Hz, 2H, trizaole-C$\underline{H}_2$CH_2-), 4.29-4.15 (m, 8H, -OCOC$\underline{H}_2$-), 4.03 (t, *J* = 6.3 Hz, 6H, -OC$\underline{H}_2$CH_2-), 3.75-3.66 (m, 8H, -OCOC$\underline{H}$2-), 3.66-3.53 (m, 16H, -OC$\underline{H}_2$C$\underline{H}_2$O-), 2.58-2.21 (m, 8H, -C$\underline{H}_2$COO-), 2.12-1.19 (m, 24H, -CH_2C$\underline{H}_2$-).

Synthesis of TMS-(Azo-TEG)$_3$-Br



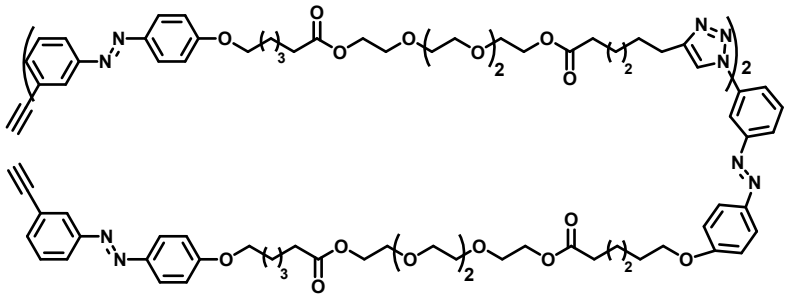
The TMS-(Azo-TEG)$_3$-Br was prepared from (Azo-TEG)$_2$-Br (3.3g, 2.46 mmol) and TMS-Azo-TEG-N_3 (2.13 g, 2.95 mmol) according to the general procedure for click coupling reaction. The product was purified by column chromatography (silica gel, THF/petroleum ether = 1/1) to yield TMS-(Azo-TEG)$_3$-Br as yellow liquid (4.77 g, 94%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.28 (s, 2H, triazole ring), 8.09-6.76 (m, 32H, pheny), 4.41 (dd, *J* = 15.5, 8.5 Hz, 4H, trizaole-C$\underline{H}_2$CH$_2$-), 4.23 (s, 14H, -OCOC$\underline{H}_2$-), 4.04 (d, *J* = 4.2 Hz, 6H, -OC$\underline{H}_2$CH$_2$-), 3.75-3.67 (m, 12H, -OCOC$\underline{H}_2$-), 3.64 (d, *J* = 3.8 Hz, 32H, -OC$\underline{H}_2$C$\underline{H}_2$O-), 3.40 (t, *J* = 6.7 Hz, 2H, -C$\underline{H}_2$Br), 2.37 (dt, *J* = 14.8, 7.3 Hz, 12H, -C$\underline{H}_2$COO-), 1.93-1.44 (m, 36H, -CH$_2$C$\underline{H}_2$-), 0.27 (s, 9H, -Si$\underline{H}_3$).

Synthesis of (Azo-TEG)$_3$ -Br



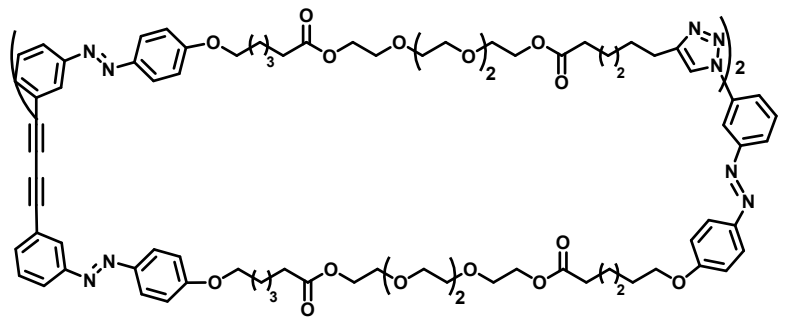
The (Azo-TEG)$_3$-Br was prepared from the TMS-(Azo-TEG)$_3$-Br (4.77 g, 2.3 mmol) according to the general procedure for alkyne deprotection, yielding 4.44 g of a viscous yellow oil (97%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.28 (s, 2H, triazole ring), 8.09-6.76 (m, 32H, pheny), 4.41 (dd, *J* = 15.5, 8.5 Hz, 4H, trizaole-C$\underline{H}_2$CH$_2$-), 4.23 (s, 14H, -OCOC$\underline{H}_2$-), 4.04 (d, *J* = 4.2 Hz, 6H, -OC$\underline{H}_2$CH$_2$-), 3.75-3.67 (m, 12H, -OCOC$\underline{H}_2$-), 3.64 (d, *J* = 3.8 Hz, 32H, -OC$\underline{H}_2$C$\underline{H}_2$O-), 3.40 (t, *J* = 6.7 Hz, 2H, -C$\underline{H}_2$Br), 3.13 (s, 1H, -C≡CH), 2.37 (dt, *J* = 14.8, 7.3 Hz, 12H, -CH$_2$COO-), 1.93-1.44 (m, 36H, -CH$_2$C$\underline{H}_2$-).

Synthesis of *l*-(Azo_4-TEG_3) (n = 3)



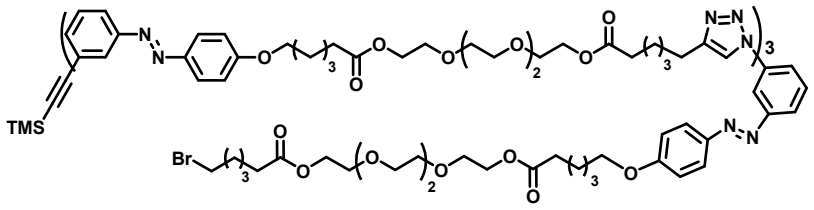
The *l*-(Azo_4-TEG_3) was prepared from (Azo-TEG)$_3$-Br (1.99 g, 1 mmol) using the similar procedures as *l*-(Azo_2-TEG_1). The yield *l*-(Azo_4-TEG_3) as yellow liquid (2.06 g, 97%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.28 (t, *J* = 1.6 Hz, 2H, triazole ring), 8.09-6.62 (m, 32H, pheny), 4.41 (t, *J* = 7.0 Hz, 4H, trizaole-C$\underline{H}_2$CH$_2$-), 4.23 (dt, *J* = 6.1, 3.4 Hz, 12H, -OCOC$\underline{H}_2$-), 4.03 (t, *J* = 6.3 Hz, 8H, -OC$\underline{H}_2$CH$_2$-), 3.73-3.66 (m, 12H, -OCOC$\underline{H}_2$-), 3.64 (dd, *J* = 5.1, 1.9 Hz, 24H, -OC$\underline{H}_2$C$\underline{H}_2$O-), 3.13 (s, 2H, -C≡CH), 2.52-2.27 (m, 12H, -C$\underline{H}_2$COO-), 2.07-1.26 (m, 24H, -CH$_2$C$\underline{H}_2$-).

Synthesis of *c*-(Azo_4-TEG_3) (n = 3)



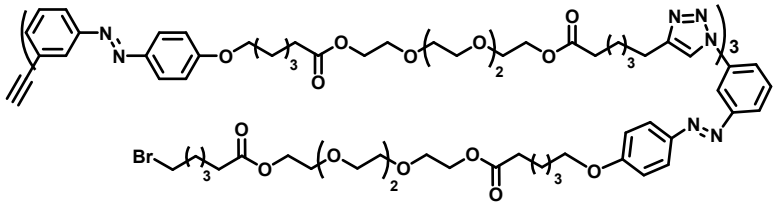
The *c*-(Azo_4-TEG_3) was prepared from *l*-(Azo_4-TEG_3) (158 mg, 0.07 mmol) according to the cyclization procedure above, using a 300 eq CuI. The yield *l*-(Azo_4-TEG_3) was purified by preparative GPC as yellow liquid (137 mg, 80%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.25 (s, 2H, triazole ring), 8.10-6.63 (m, 32H, pheny), 4.52-4.29 (m, 4H, trizaole-C$\underline{H}_2$CH$_2$-), 4.31-4.12 (m, 12H, -OCOC$\underline{H}_2$-), 4.02 (dd, *J* = 7.5, 5.0 Hz, 8H, -OC$\underline{H}_2$CH$_2$-), 3.69 (dt, *J* = 9.0, 3.4 Hz, 12H, -OCOC$\underline{H}_2$-), 3.65-3.54 (m, 24H, -OC$\underline{H}_2$C$\underline{H}_2$O-), 2.58-2.22 (m, 12H, -C$\underline{H}_2$COO-), 2.06-1.08 (m, 24H, -CH$_2$C$\underline{H}_2$-).

Synthesis of TMS-(Azo-TEG)$_4$-Br



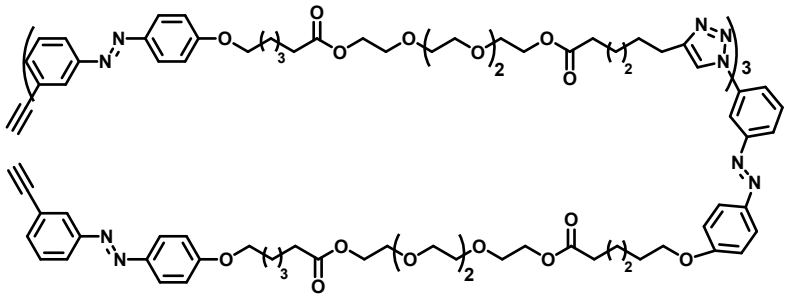
The TMS-(Azo-TEG)$_4$-Br was prepared from (Azo-TEG)$_3$-Br (2.4 g, 1.2 mmol) and TMS-Azo-TEG-N_3 (1.04 g, 1.44 mmol) according to the "CuAAC" reaction above. The product was purified by column chromatography (silica gel, THF/petroleum ether = 2/1) to yield TMS-(Azo-TEG)$_4$-Br as yellow liquid (2.93 g, 90%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.28 (s, 3H, triazole ring), 8.03-6.43 (m, 32H, pheny), 4.42 (t, *J* = 7.0 Hz, 6H, trizaole-C$\underline{H}_2$CH$_2$-), 4.23 (td, *J* = 7.9, 3.9 Hz, 16H, -OCOC$\underline{H}_2$-), 4.11-3.95 (m, 8H, -OC$\underline{H}_2$CH$_2$-), 3.72-3.65 (m, 16H, -OCOC$\underline{H}$2-), 3.64 (dd, *J* = 5.2, 1.8 Hz, 32H, -OC$\underline{H}_2$C$\underline{H}_2$O-), 3.57-3.32 (m, 2H, -C$\underline{H}_2$Br), 2.48-2.28 (m, 16H, -C$\underline{H}_2$COO-), 2.12-1.30 (m, 48H, -CH$_2$C$\underline{H}_2$-), 0.27 (s, 9H, -Si$\underline{H}_3$).

Synthesis of (Azo-TEG)$_4$-Br



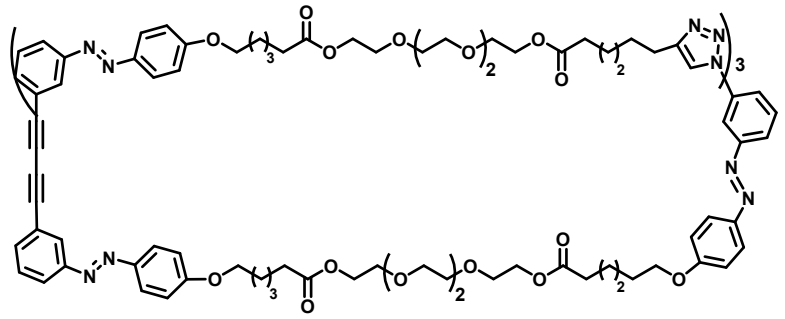
The (Azo-TEG)$_4$-Br was prepared from TMS-(Azo-TEG)$_4$-Br (2.93 g, 1 mmol) according to the alkyne deprotection above, yielding 2.56 g of a yellow liquid (97%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.28 (d, *J* = 1.4 Hz, 3H, triazole ring), 8.10-6.71 (m, 32H, pheny), 4.52-4.32 (m, 6H, trizaole-C$\underline{H}_2$CH$_2$-), 4.23 (td, *J* = 8.1, 4.0 Hz, 16H, -OCOC$\underline{H}_2$-), 4.04 (dd, *J* = 10.4, 6.2 Hz, 8H, -OC$\underline{H}_2$CH$_2$-), 3.69 (dd, *J* = 9.7, 4.6 Hz, 16H, -OCOC$\underline{H}_2$-), 3.64 (dd, *J* = 5.1, 1.9 Hz, 32H, -OC$\underline{H}_2$C$\underline{H}_2$O-), 3.60-3.35 (m, 2H, -C$\underline{H}_2$Br), 3.12 (d, *J* = 10.8 Hz, 2H, -C≡CH), 2.37 (dt, *J* = 14.9, 5.8 Hz, 16H, -C$\underline{H}_2$COO-), 2.05-1.24 (m, 48H, -CH$_2$C$\underline{H}_2$-).

Synthesis of *l*-(Azo_5-TEG_4) (n = 4)



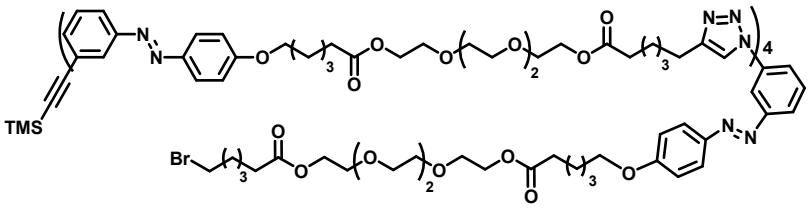
The *l*-(Azo_5-TEG_4) was prepared from (Azo-TEG)$_4$-Br (1.32 g, 0.5 mmol) using the similar proceduresas *l*-(Azo_2-TEG_1). The product was purified by column chromatography (silica gel, THF/petroleum ether = 2/1) to yield *l*-(Azo_5-TEG_4) as yellow liquid (1.28 g, 90%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.27 (t, *J* = 1.6 Hz, 3H, triazole ring), 8.06-6.69 (m, 40H, pheny), 4.50-4.32 (m, 6H, trizaole-C$\underline{H}_2$CH$_2$-), 4.28-4.14 (m, 16H, -OCOC$\underline{H}_2$-), 4.03 (t, *J* = 6.3 Hz, 10H, -OC$\underline{H}_2$CH$_2$-), 3.69 (td, *J* = 5.0, 2.6 Hz, 16H, -OCOC$\underline{H}_2$-), 3.64 (dd, *J* = 5.0, 2.0 Hz, 32H, -OC$\underline{H}_2$C$\underline{H}_2$O-), 3.11 (d, *J* = 10.6 Hz, 2H, -C≡CH), 2.54-2.22 (m, 16H, -C$\underline{H}_2$COO-), 2.06-1.23 (m, 48H, -CH$_2$C$\underline{H}_2$-).

Synthesis of *c*-(Azo_5-TEG_4) (n = 4)



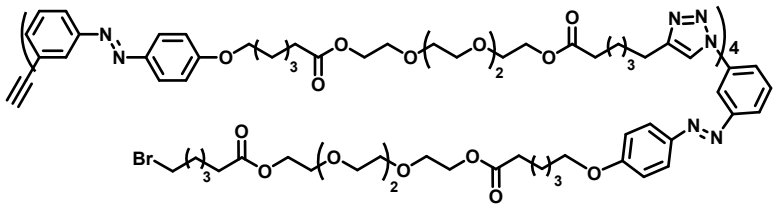
The *c*-(Azo_5-TEG_4) was prepared from *l*-(Azo_5-TEG_4) (139 mg, 0.05 mmol) according to the general procedure for cyclization, using a 300 eq CuI. The yield *c*-(Azo_5-TEG_4) was purified by preparative GPC as yellow liquid (121 mg, 75%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.26 (s, 3H, triazole ring), 8.09-6.82 (m, 40H, pheny), 4.39 (dd, *J* = 14.7, 7.6 Hz, 6H, trizaole-C$\underline{H}_2$CH$_2$-), 4.22 (td, *J* = 7.9, 4.2 Hz, 16H, -OCOC$\underline{H}_2$-), 4.10-3.94 (m, 10H, -OC$\underline{H}_2$CH$_2$-), 3.68 (dd, *J* = 9.4, 4.3 Hz, 16H, -OCOC$\underline{H}_2$-), 3.65-3.45 (m, 32H, -OC$\underline{H}_2$C$\underline{H}_2$O-), 2.36 (ddd, *J* = 17.4, 8.4, 5.4 Hz, 16H, -C$\underline{H}_2$COO-), 2.05-1.20 (m, 48H, -CH$_2$C$\underline{H}_2$-).

Synthesis of TMS-(Azo-TEG)$_5$-Br



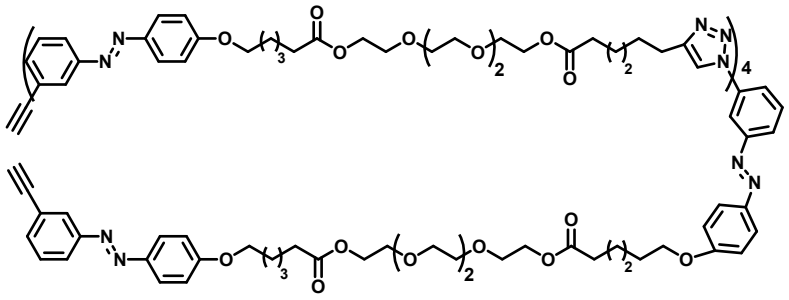
The TMS-(Azo-TEG)$_5$-Br was prepared from (Azo-TEG)$_4$-Br (1.95 g, 0.738 mmol) and TMS-Azo-TEG-N_3 (0.64 g, 0.885 mmol) according to the CuAAC procedure above. The product was purified by column chromatography (silica gel, THF/petroleum ether = 3/1) to yield TMS-(Azo-TEG)$_5$-Br as yellow liquid (2.23 g, 90%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.28 (s, 4H, triazole ring), 8.13-6.79 (m, 40H, pheny), 4.42 (t, *J* = 6.8 Hz, 8H, trizaole-C$\underline{H}_2$CH$_2$-), 4.31-4.15 (m, 20H, -OCOC$\underline{H}_2$-), 4.13-3.93 (m, 10H, -OC$\underline{H}_2$CH$_2$-), 3.69 (dd, *J* = 9.7, 4.8 Hz, 20H, -OCOC$\underline{H}_2$-), 3.64 (dd, *J* = 5.3, 1.8 Hz, 40H, -OC$\underline{H}_2$C$\underline{H}_2$O-), 3.46 (dt, *J* = 38.7, 6.7 Hz, 2H, -C$\underline{H}_2$Br), 2.44-2.24 (m, 20H, -C$\underline{H}_2$COO-), 2.04-1.19 (m, 60H, -CH$_2$C$\underline{H}_2$-), 0.29-0.20 (m, 9H, -Si$\underline{H}_3$).

Synthesis of (Azo-TEG)$_5$-Br



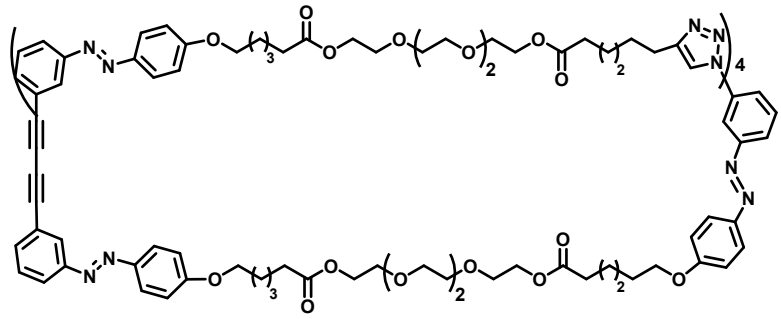
The (Azo-TEG)$_5$-Br was prepared from TMS-(Azo-TEG)$_5$-Br (2.23 g, 6.6 mmol) according to the alkyne deprotection above, yielding 2.06 g of a viscous yellow oil (94%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.27 (s, 4H, triazole ring), 8.03-6.87 (m, 40H, pheny), 4.49-4.34 (m, 8H, trizaole-C$\underline{H}_2$CH$_2$-), 4.31-4.16 (m, 20H, -OCOC$\underline{H}_2$-), 4.10-3.98 (m, 10H, -OC$\underline{H}_2$CH$_2$-), 3.69 (dd, *J* = 9.7, 4.7 Hz, 20H, -OCOC$\underline{H}_2$-), 3.64 (dd, *J* = 5.3, 1.8 Hz, 40H, -OC$\underline{H}_2$C$\underline{H}_2$O-), 3.40 (t, *J* = 6.7 Hz, 2H, -C$\underline{H}_2$Br), 3.11 (d, *J* = 10.5 Hz, 1H, -C≡CH), 2.47-2.26 (m, 20H, -C$\underline{H}_2$COO-), 2.06-1.31 (m, 60H, -CH$_2$C$\underline{H}_2$-).

Synthesis of *l*-(Azo_6-TEG_5) (n = 5)



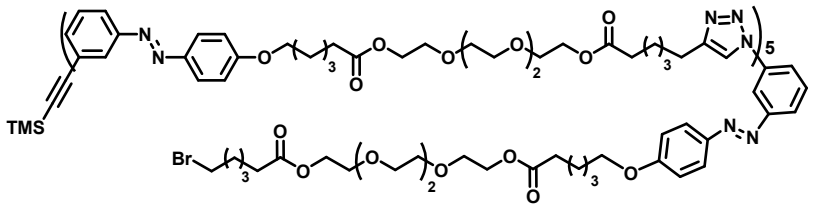
The *l*-(Azo_6-TEG_5) was prepared from (Azo-TEG)$_5$-Br (548 mg, 0.16 mmol) using the similar procedures of preparing the *l*-(Azo_2-TEG_1). The product was purified by column chromatography (silica gel, THF/petroleum ether = 3/1) to yield *l*-(Azo_6-TEG_5) as yellow liquid (453 mg, 86%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.28 (s, 4H, triazole ring), 8.07-6.60 (m, 48H, pheny), 4.41 (t, *J* = 7.0 Hz, 8H, trizaole-C$\underline{H}_2$CH$_2$-), 4.22 (dd, *J* = 8.7, 3.9 Hz, 20H, -OCOC$\underline{H}_2$-), 4.03 (t, *J* = 6.3 Hz, 12H, -OC$\underline{H}_2$CH$_2$-), 3.68 (dd, *J* = 8.6, 4.0 Hz, 20H, -OCOC$\underline{H}$2-), 3.64 (d, *J* = 3.7 Hz, 40H, -OC$\underline{H}_2$C$\underline{H}_2$O-), 3.14 (s, 2H, -C≡CH), 2.47-2.26 (m, 20H, -C$\underline{H}_2$COO-), 2.04-1.27 (m, 60H, -CH$_2$C$\underline{H}_2$-).

Synthesis of *c*-(Azo_6-TEG_5) (n = 5)



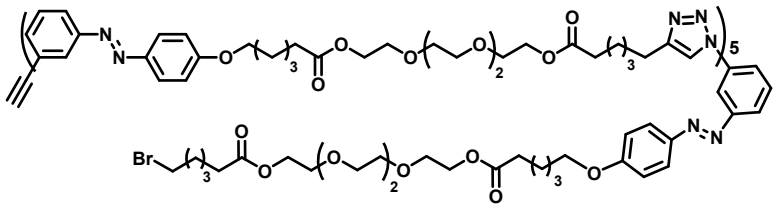
The *c*-(Azo_6-TEG_5) was prepared from *l*-(Azo_6-TEG_5) (112 mg, 0.03 mmol) according to similarcyclization procedure above, using a 400 eq CuI. The yield *c*-(Azo_6-TEG_5) was purified by preparative GPC as yellow liquid (100 mg, 75%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.28 (s, 4H, triazole ring), 8.07-6.60 (m, 48H, pheny), 4.41 (t, *J* = 7.0 Hz, 8H, trizaole-C$\underline{H}_2$CH$_2$-), 4.22 (dd, *J* = 8.7, 3.9 Hz, 20H, -OCOC$\underline{H}_2$-), 4.03 (t, *J* = 6.3 Hz, 12H, -OC$\underline{H}_2$CH$_2$-), 3.68 (dd, *J* = 8.6, 4.0 Hz, 20H, -OCOC$\underline{H}_2$-), 3.64 (d, *J* = 3.7 Hz, 40H, -OC$\underline{H}_2$C$\underline{H}_2$O-), 2.47-2.26 (m, 20H, -C$\underline{H}_2$COO-), 2.04-1.27 (m, 60H, -CH$_2$C$\underline{H}_2$-)

Synthesis of TMS-(Azo-TEG)$_6$-Br



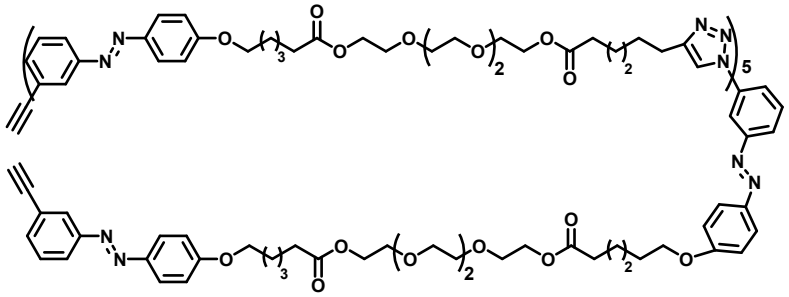
The TMS-(Azo-TEG)$_6$-Br was prepared from (Azo-TEG)$_5$-Br (2.4 g, 0.738 mmol) and TMS-Azo-TEG-N_3 (0.64 g, 0.885 mmol) according to the click coupling reaction above. The product was purified by column chromatography (silica gel, THF/petroleum ether = 3/1) to yield TMS-(Azo-TEG)$_6$-Br as yellow liquid (2.51 g, 85%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.28 (s, 5H,triazole ring), 8.13-6.79 (m, 56H, pheny), 4.50-4.31 (m, 10H, trizaole-C$\underline{H}_2$CH$_2$-), 4.30-4.17 (m, 24H, -OCOC$\underline{H}_2$-), 4.04 (dd, *J* = 8.2, 4.3 Hz, 12H, -OC$\underline{H}_2$CH$_2$-), 3.69 (dd, *J* = 9.6, 4.7 Hz, 24H, -OCOC$\underline{H}$2-), 3.64 (dd, *J* = 5.2, 1.8 Hz, 48H, -OC$\underline{H}_2$C$\underline{H}_2$O-), 3.46 (dt, *J* = 38.7, 6.7 Hz, 2H, -C$\underline{H}_2$Br), 2.38 (ddd, *J* = 16.6, 11.2, 5.8 Hz, 24H, -C$\underline{H}_2$COO-), 2.03-1.11 (m, 72H, -CH$_2$C$\underline{H}_2$-), 0.35-0.20 (m, 9H, -Si$\underline{H}_3$).

Synthesis of (Azo-TEG)$_6$ -Br



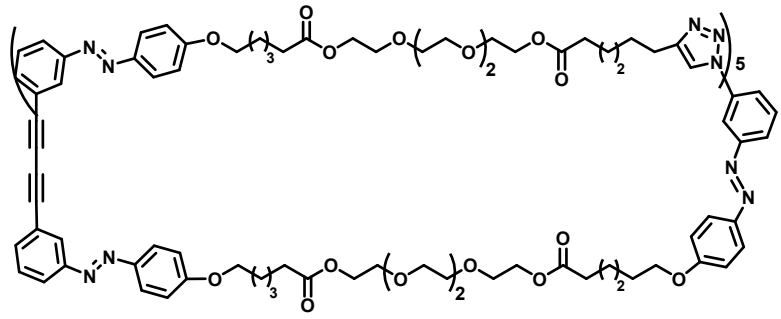
The (Azo-TEG)$_6$-Br was prepared from TMS-(Azo-TEG)$_6$-Br (2.51 g, 6.3 mmol) according to the general procedure for alkyne deprotection, yielding 2.35 g of a viscous yellow oil (95%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.28 (s, 5H, triazole ring), 8.13-6.79 (m, 56H, pheny), 4.50-4.31 (m, 10H, trizaole-C$\underline{H}_2$CH$_2$-), 4.30-4.17 (m, 24H, -OCOC$\underline{H}_2$-), 4.04 (dd, *J* = 8.2, 4.3 Hz, 12H, -OC$\underline{H}_2$CH$_2$-), 3.69 (dd, *J* = 9.6, 4.7 Hz, 24H, -OCOC$\underline{H}_2$-), 3.64 (dd, *J* = 5.2, 1.8 Hz, 48H, -OC$\underline{H}_2$C$\underline{H}_2$O-), 3.46 (dt, *J* = 38.7, 6.7 Hz, 2H, -C$\underline{H}_2$Br), 3.12 (d, *J* = 10.6 Hz, 2H, -C≡CH), 2.38 (ddd, *J* = 16.6, 11.2, 5.8 Hz, 24H, -C$\underline{H}_2$COO-), 2.03-1.11 (m, 72H, -CH$_2$C$\underline{H}_2$-).

Synthesis of *l*-(Azo_7-TEG_6) (n = 6)



The *l*-(Azo_7-TEG_6) was prepared from (Azo-TEG)$_6$-Br (408 mg, 0.1 mmol) using the similar procedures as *l*-(Azo_2-TEG_1). The product was purified by column chromatography (silica gel, THF/petroleum ether = 3/1) to yield *l*-(Azo_7-TEG_6) as yellow liquid (351 mg, 86%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.28 (t, *J* = 1.6 Hz, 5H, triazole ring), 8.04-6.87 (m, 56H, pheny), 4.47-4.34 (m, 10H, trizaole-C$\underline{H}_2$CH_2-), 4.23 (dt, *J* = 9.5, 3.2 Hz, 24H, -OCOC$\underline{H}_2$-), 4.03 (t, *J* = 6.4 Hz, 12H, -OC$\underline{H}_2$CH_2-), 3.72-3.66 (m, 24H, -OCOC$\underline{H}_2$-), 3.64 (dd, *J* = 5.1, 2.0 Hz, 48H, -OC$\underline{H}_2$C$\underline{H}_2$O-), 3.12 (d, *J* = 10.6 Hz, 2H, -C≡CH), 2.42-2.30 (m, 24H, -OCOC$\underline{H}_2$-), 2.06-1.22 (m, 72H, -CH_2C$\underline{H}_2$-).

Synthesis of *c*-(Azo_7-TEG_6) (n = 6)



The *c*-(Azo_7-TEG_6) was prepared from *l*-(Azo_7-TEG_6) (82 mg, 0.02 mmol) according to the similar procedure as cyclization above, using a 400 eq CuI. The yield *c*-(Azo_7-TEG_6) was purified by preparative GPC as yellow liquid (73 mg, 70%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.27 (s, 5H, triazole ring), 8.07-6.60 (m, 56H, pheny), 4.40 (dd, *J* = 8.8, 5.2 Hz, 10H, trizaole-C$\underline{H}_2$CH_2-), 4.21 (dd, *J* = 6.2, 3.2 Hz, 24H, -OCOC$\underline{H}_2$-), 4.02 (t, *J* = 6.3 Hz, 12H, -OC$\underline{H}_2$CH_2-), 3.79-3.65 (m, 24H, -OCOC$\underline{H}_2$-), 3.63 (dd, *J* = 4.5, 1.8

Hz, 48H, -OC$\underline{H_2}$C$\underline{H_2}$O-), 2.41-2.30 (m, 24H, -OCOC$\underline{H_2}$-), 2.04-1.27 (m, 72H, -CH$_2$C$\underline{H_2}$-).

The generated *c*-(Azo$_{n+1}$-TEG$_n$) (when n was larger than 3) was needed to purify by the preparative-GPC to move small amounts of linear precursor. The corresponding GPC traces before and after preparative-GPC can be seen from Figure S2.

Additional Figures:

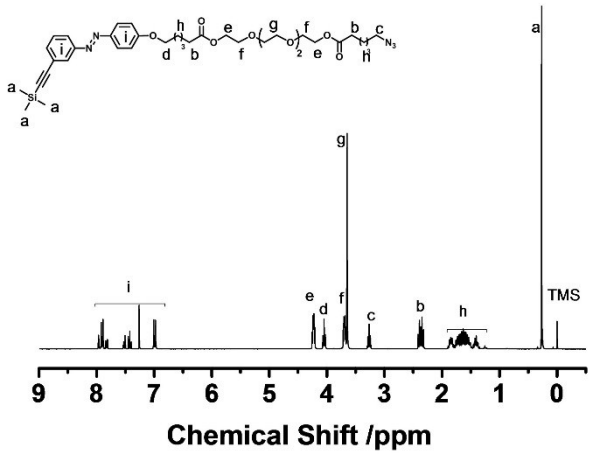


Figure S1. ^{1}H NMR spectrum of TMS-Azo-TEG-N$_3$ in CDCl$_3$.

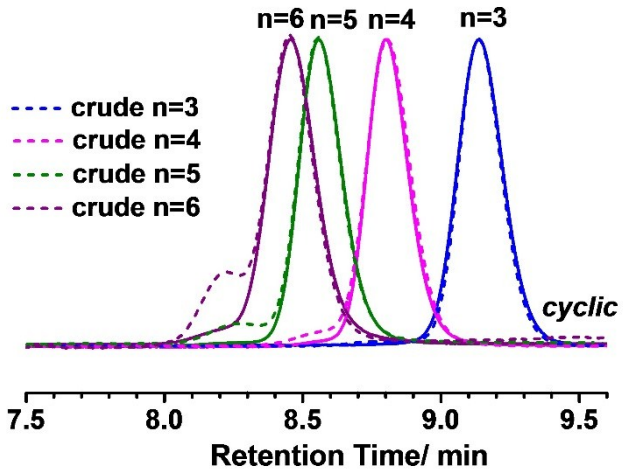


Figure S2. The GPC trace of *c*-(Azo$_{n+1}$-TEG$_n$) before and after pre-GPC using THF as the eluent (n = 3-6).

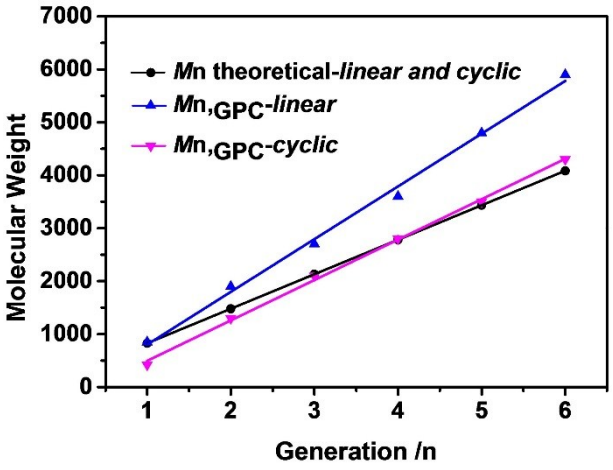


Figure S3. The dependence of the theoretical and experimental (determined by GPC) molecular weights of *l*-(Azo_{n+1}-TEG_n) and *c*-(Azo_{n+1}-TEG_n) on generation (n).

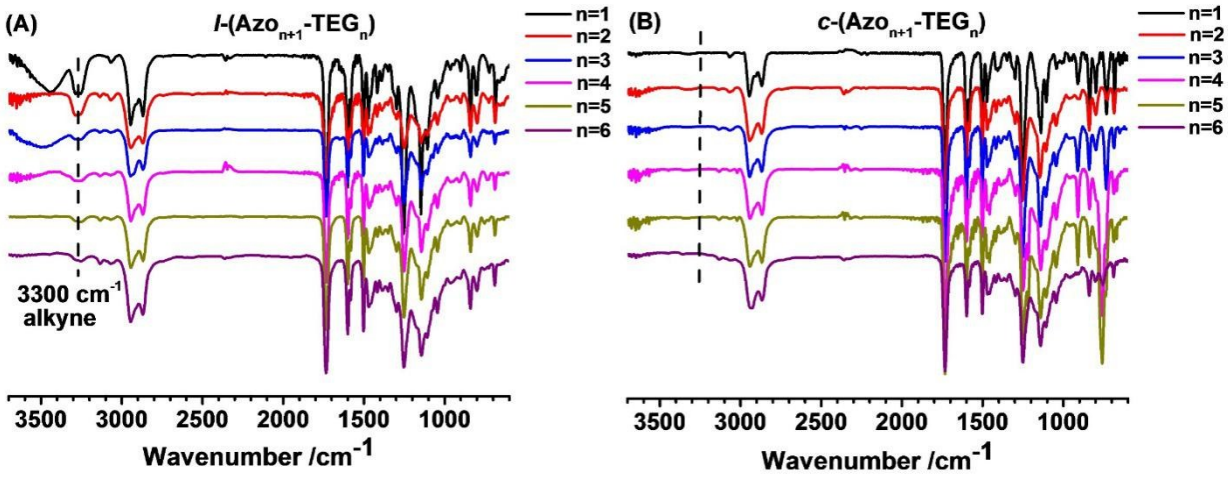


Figure S4. The FT-IR spectra of *l*-(Azo_{n+1}-TEG_n) (A) and *c*-(Azo_{n+1}-TEG_n) (B) (n = 1-6).

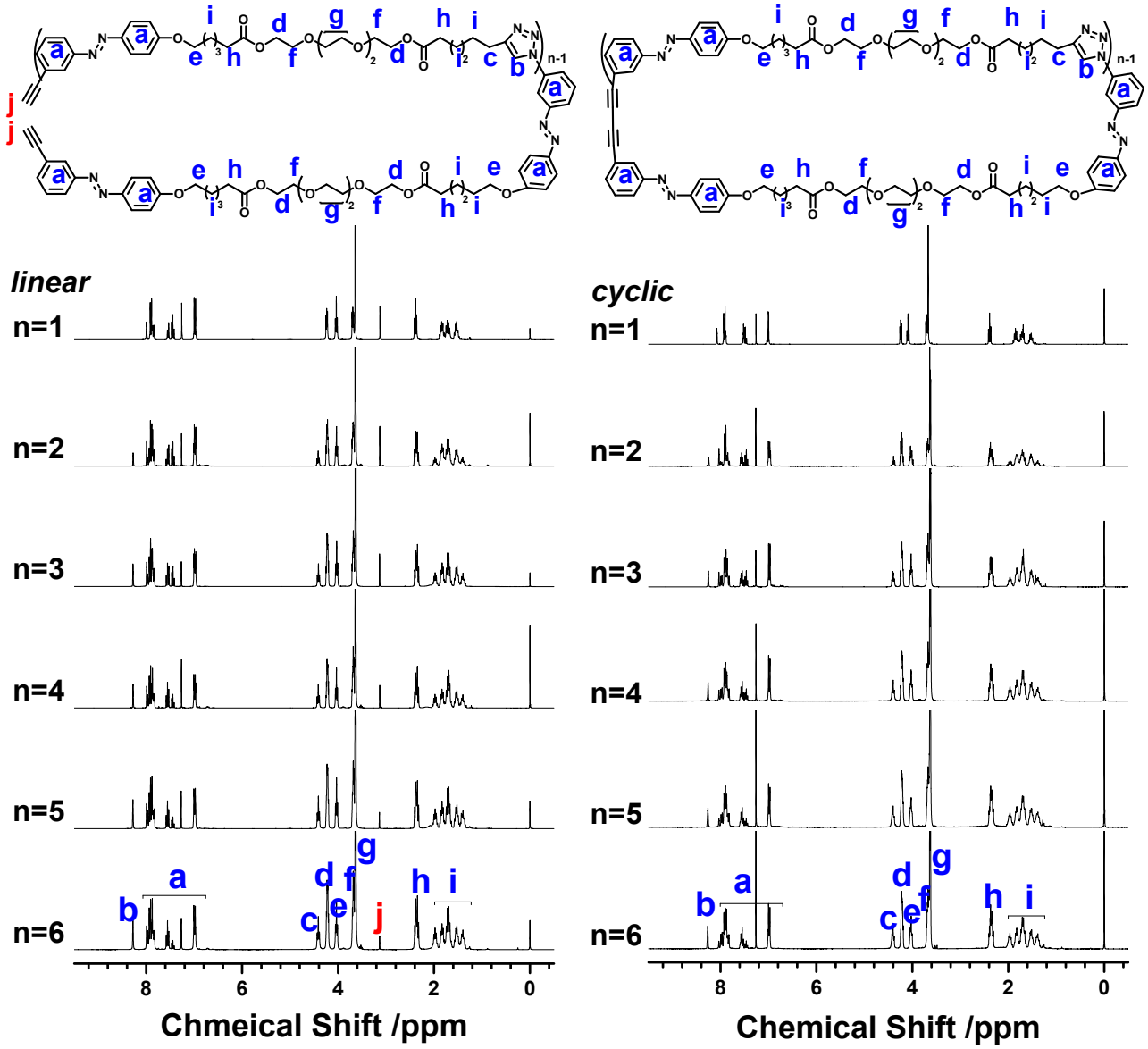


Figure S5. ^{1}H NMR spectra of the *l*-(Azo_{n+1}-TEG_n) and *c*-(Azo_{n+1}-TEG_n) in $CDCl_3$ (n=1-6).

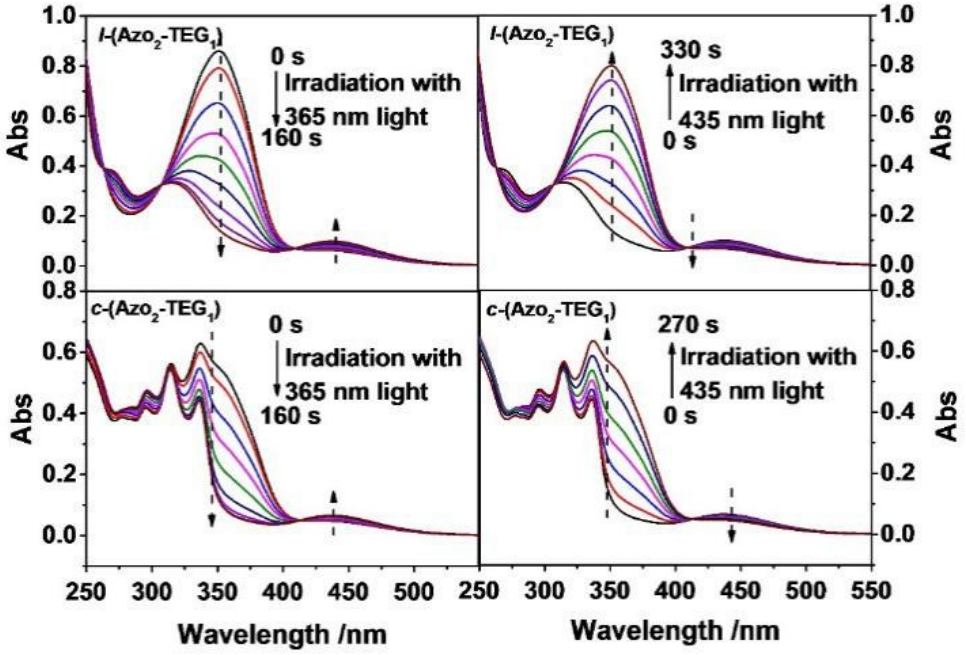


Figure S6. The UV-*vis* absorption spectra of *l*-(Azo_2-TEG_1) and *c*-(Azo_2-TEG_1) in DCM under irradiation with 365 nm UV light and 435 nm visible light at different time intervals until the photo-stationary were achieved, respectively. The concentration of solution is 1.5×10^{-3} mg/mL for both linear and cyclic polymers.

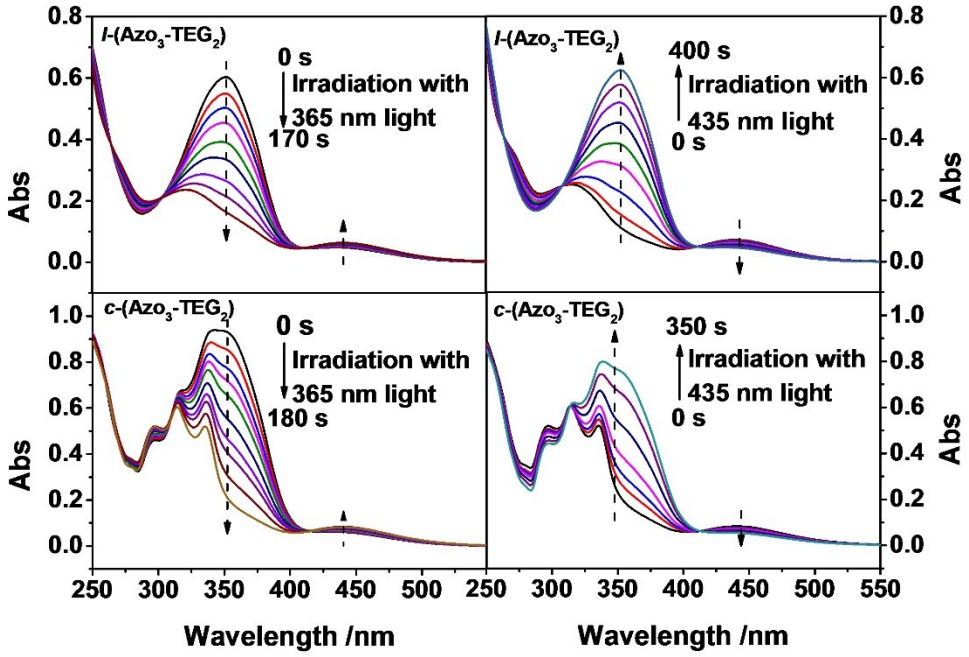


Figure S7. The UV-*vis* absorption spectra of *l*-(Azo_3-TEG_2) and *c*-(Azo_3-TEG_2) in DCM under irradiation with 365 nm UV light and 435 nm visible light at different time intervals until the photo-stationary were achieved, respectively. The concentration of solution is 1.78×10^{-3} mg/mL for both linear and cyclic polymers.

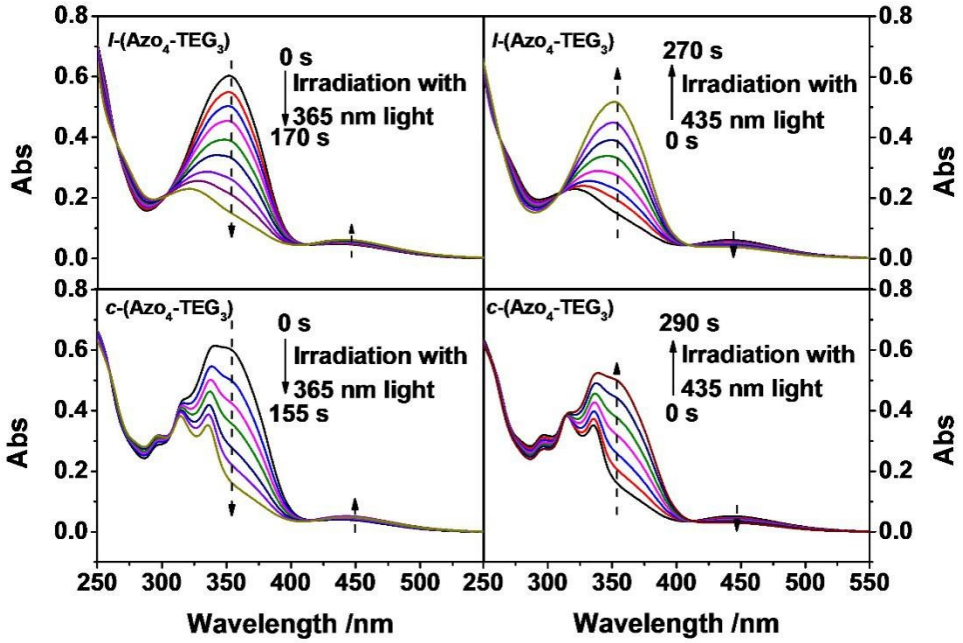


Figure S8. The UV-*vis* absorption spectra of *l*-(Azo_4-TEG_3) and *c*-(Azo_4-TEG_3) in DCM under irradiation with 365 nm UV lightand 435 nm visible light at different time intervals until the photo-stationary were achieved, respectively. The concentration of solution is 1.92×10^{-3} mg/mL for both linear and cyclic polymers.

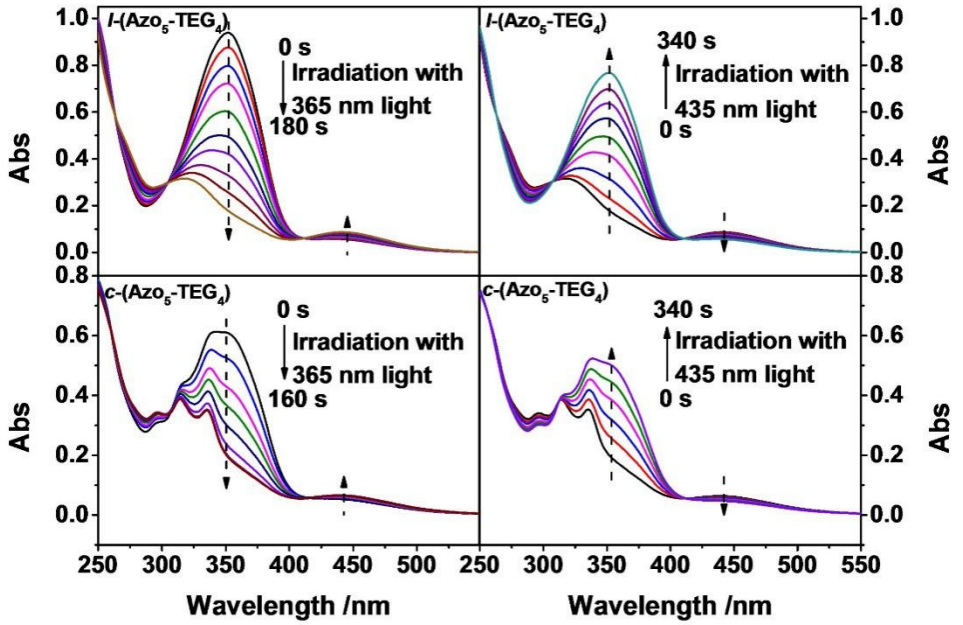


Figure S9. The UV-*vis* absorption spectra of *l*-(Azo_5-TEG_4) and *c*-(Azo_5-TEG_4) in DCM under irradiation with 365 nm UV light and 435 nm visible light at different time intervals until the photo-stationary were achieved, respectively. The concentration of solution is 2.01×10^{-3} mg/mL for both linear and cyclic polymers.

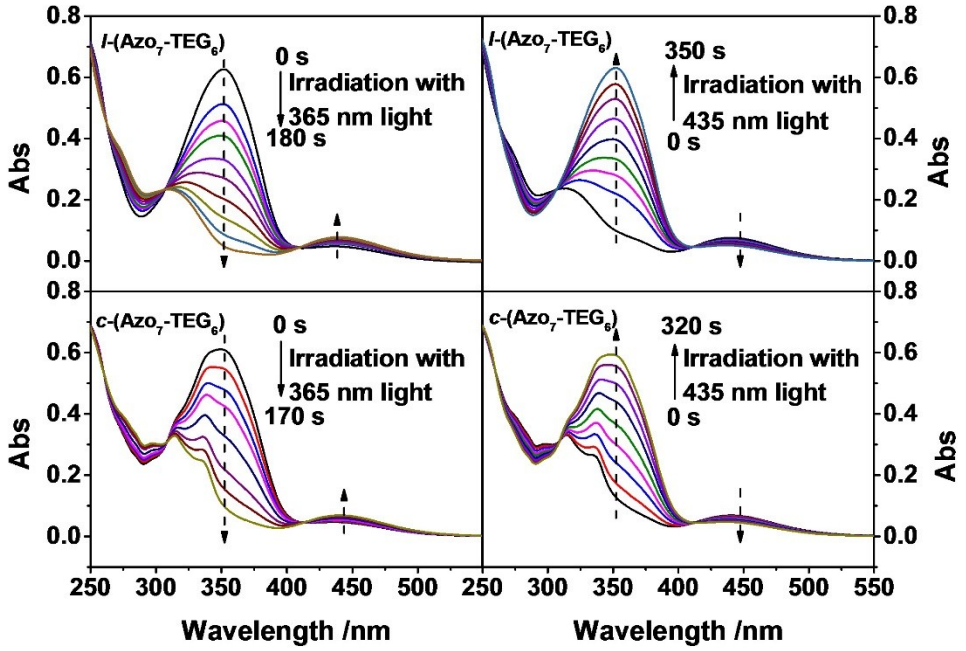


Figure S10. The UV-*vis* absorption spectra of *l*-(Azo_7-TEG_6) and *c*-(Azo_7-TEG_6) in DCM under irradiation with 365 nm UV light and 435 nm visible light at different time intervals until the photo-stationary were achieved, respectively. The concentration of solution is 2.46×10^{-3} mg/mL for both linear and cyclic polymers.

According to DFT and TDDFT calculations,[1] the HOMOs and LUMOs of *c*-(Azo_{n+1}-TEG_n) (n = 1-5) all predominately delocalize on the azobenzene (azo) and alkynyl (yne) group moieties.

As shown in Figure S11(A), the lowest energy band for the *c*-(Azo_2-TEG_1) is found around 472 nm mainly originated from HOMO-4→LUMO transitions, which can be assigned to $\pi^*_{azo}\rightarrow\pi^*_{azo}$ and $\pi^*_{azo}\rightarrow\pi^*_{yne}$ due to their orbital characters of corresponding starting and arriving states coming from the azobenzene moieties connected to 1, 3-diyne. For the *c*-(Azo_3-TEG_2) (Figures S11(B)) around 476 nm mainly originates from HOMO-7→LUMO transitions, which can also be assigned to $\pi^*_{azo}\rightarrow\pi^*_{azo}$ and $\pi^*_{azo}\rightarrow\pi^*_{yne}$ due to their orbital characters. However, for larger ring, the lowest energy band experimentally found for *c*-(Azo_4-TEG_3) (Figures S11(C)), *c*-(Azo_5-TEG_4) (Figures S11(D)), and *c*-(Azo_6-TEG_5) (Figures S11(E)) around 478 nm transitions are mainly assigned to $\pi^*_{azo}\rightarrow\pi^*_{azo}$, coming from the third azobenzene group moiety, which is totally different with those small ring complexes (*c*-(Azo_2-TEG_1) and *c*-(Azo_3-TEG_2)).

According to the calculations, in the UV-*vis* spectra, the absorption at 350 nm for complex *c*-(Azo_2-TEG_1) may come from the HOMO-2→LUMO+1 transition (π→π*). The characteristic azobenzene and alkynyl of HOMO-2 and LUMO+1 indicate that the HOMO-2→LUMO+1 absorption transition possesses an intramolecular charge transfer (ICT) character. Similarly, the absorptions at about 370 nm of *c*-(Azo_{n+1}-TEG_n) (n = 2-5) come from $\pi_{azo\ (or\ yne)}\rightarrow\pi^*_{azo\ (or\ yne)}$ character, probably with some mixing of a charge transfer character from the azobenzene and alkynyl ring.

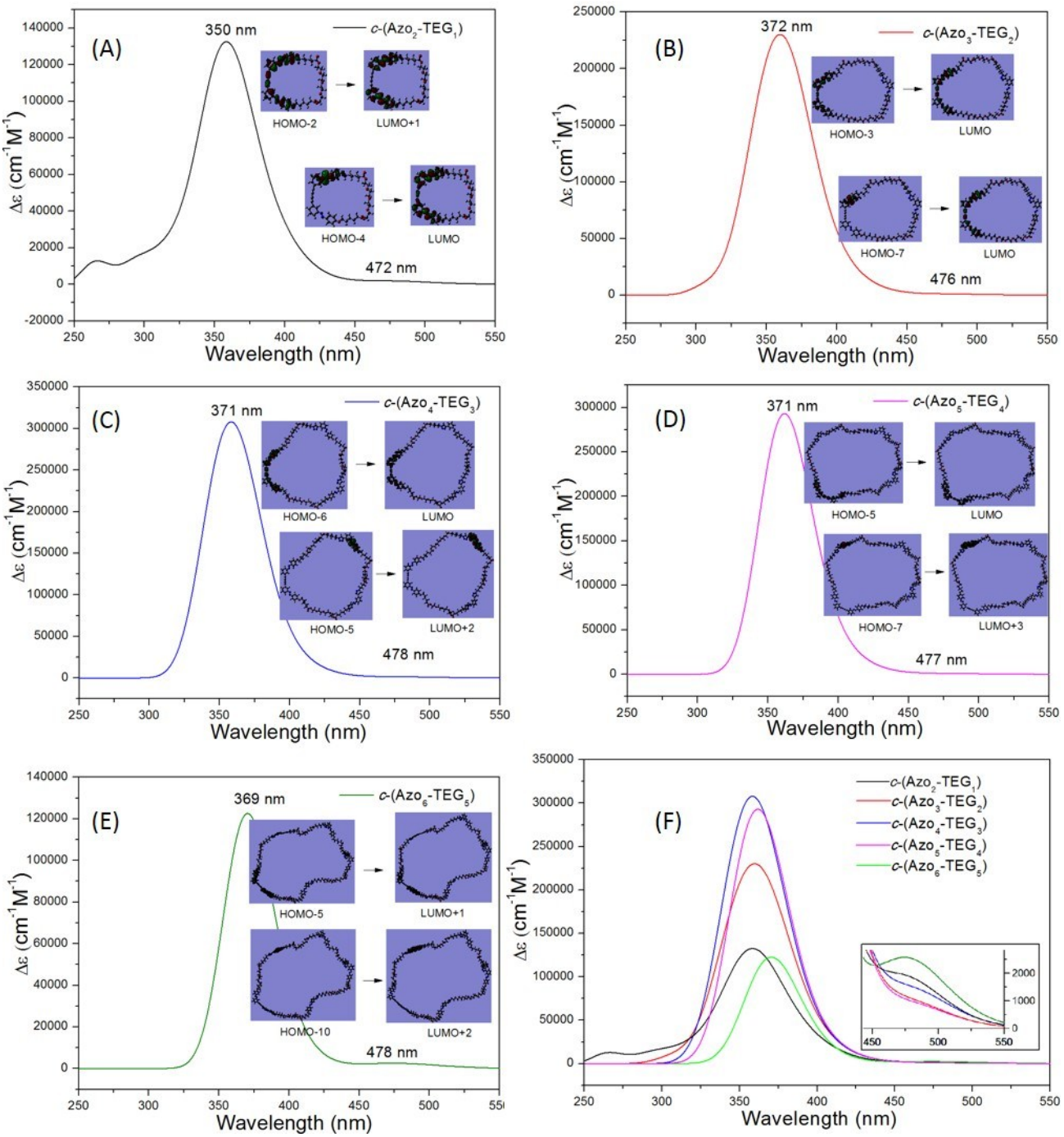


Figure S11. Calculated UV-*vis* spectra of the *c*-(Azo_{n+1}-TEG_n) (n = 1-5) at the level of B3LYP/6-31G*.

The first-order rate constant k_e of *trans*-to-*cis* photoisomerization was determined by the Formula S1:

$$Ln[(A_\infty - A_t)/(A_\infty - A_0)] = -k_e t \qquad \text{Formula S1}$$

Where A_∞, A_t, and A_0 are absorbance at about 350 nm corresponded to the π-π* transition of trans isomers of azobenzene at infinite time, time t and time zero with irradiation of 365 nm UV light (0.5 mW cm^{-2}) at room temperature, respectively.

The first-order rate constant k_H of *cis*-to-*trans* recovery was determined by the Formula S2:

$$Ln[(A_\infty - A_t)/(A_\infty - A_0)] = -k_H t \qquad \text{Formula S2}$$

Where A_∞, A_t, and A_0 are absorbance at about 350 nm corresponded to the π-π* transition of trans isomers of azobenzene at infinite time, time t and time zero with irradiation of 435 nm visible light (0.53 mW cm^{-2}) at room temperature, respectively.

The first-order kinetic curves of photo-isomerization are plotted in Figure S13

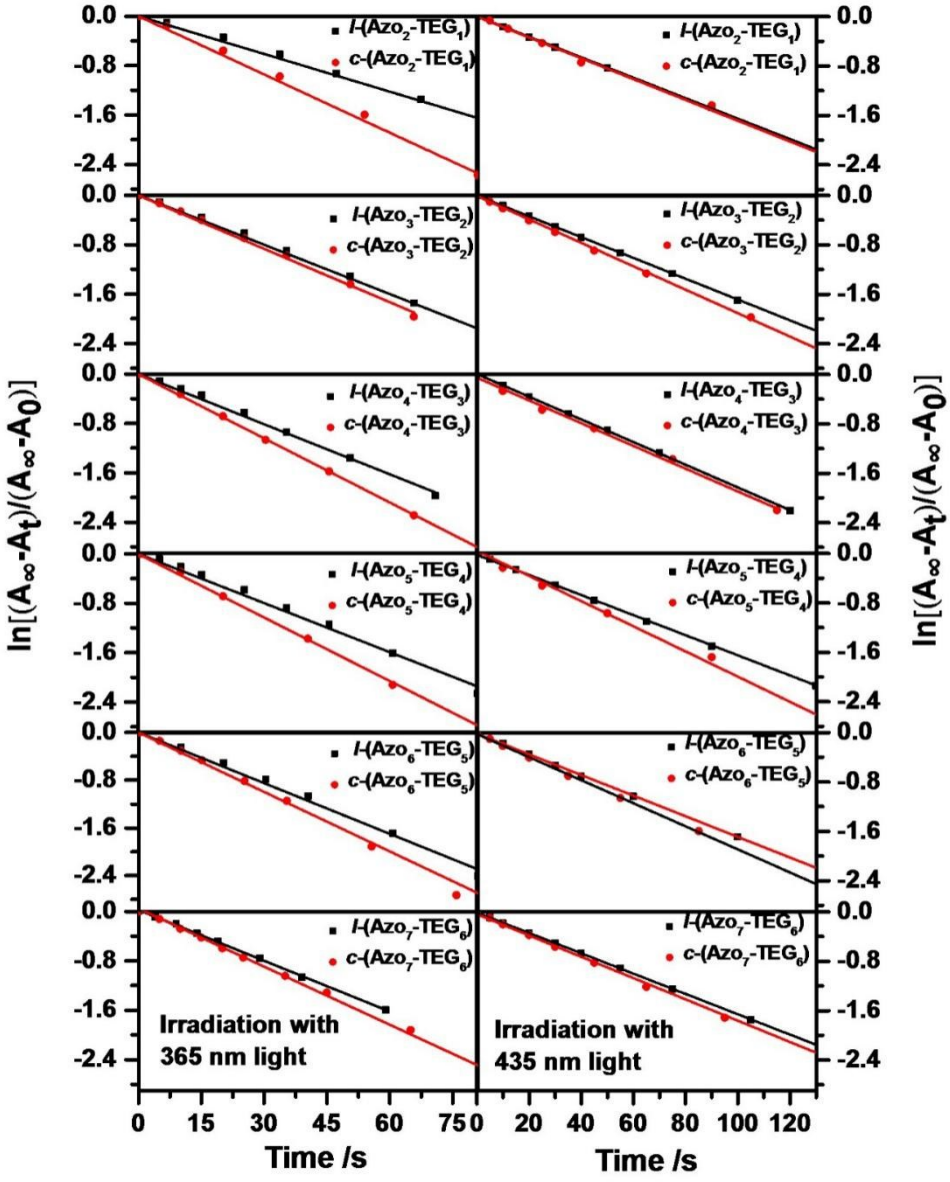


Figure S12. First-order kinetics for the photoisomerization of *trans*-to-*cis* and *cis*-to-*trans* recovery of *l*-(Azo_{n+1}-TEG_n) and *c*-(Azo_{n+1}-TEG_n) (n = 1-6) in DCM corresponding to Figure 3 and Figure S6-S10.

As we know, *trans* to *cis* isomerization of azobenzene moieties leads to new sets of resonances, and thus the resonances of the aromatic protons of the *cis*-azo isomers shift to higher field in ^{1}H NMR.[2] The characteristic signals of *cis*-azo isomers were confirmed from ^{1}H NMR spectra of *l*-(Azo_{n+1}-TEG_n) and *c*-(Azo_{n+1}-TEG_n) by contrasting their ^{1}H NMR spectra after UV light radiation (PSS_{uv} states). Therefore, the percentage of *cis*-azo isomers in the *l*-(Azo_{n+1}-TEG_n) ($F_{l\text{-}cis}$) and *c*-(Azo_{n+1}-TEG_n) ($F_{c\text{-}cis}$) could be calculated quantitatively according to Formula S3 and Formula S4.

$$F_{l\text{-}cis} = (1- I_{l\text{-}trans}/I_{l\text{-azo}}) \times 100\% \qquad \text{Formula S3}$$

$$F_{c\text{-}cis} = (1-I_{c\text{-}trans}/I_{c\text{-azo}}) \times 100\% \qquad \text{Formula S4}$$

Where $I_{l\text{-azo}}$ and $I_{c\text{-azo}}$ are the integrals of characteristic signals of *trans*-azo and cis- azo of *l*-(Azo_{n+1}-TEG_n) and *c*-(Azo_{n+1}-TEG_n) in the aromatic region, and $I_{l\text{-}tran}$ and $I_{c\text{-}tran}$ are the integrals of characteristic signals of *trans*-azo of *l*-(Azo_{n+1}-TEG_n) and *c*-(Azo_{n+1}-TEG_n) respectively.

For *l*-(Azo_2-TEG_1), $I_{l\text{-azo}}$ is the integrals of characteristic signals of *trans*-azo and *cis*-azo around from 8.03 ppm to 6.65 ppm, and $I_{l\text{-}tran}$ is the integrals of characteristic signals at 7.99 ppm, 7.95-7.81 ppm, 7.59-7.50 ppm, 7.44 ppm and 7.05-6.91 ppm respectively (Figure S13).

For *c*-(Azo_2-TEG_1), $I_{c\text{-azo}}$ is the integrals of characteristic signals of *trans*-azo and *cis*-azo around from 8.19 ppm to 6.55 ppm, and $I_{c\text{-}trans}$ is the integrals of characteristic signals of *trans*-azo of *c*-(Azo_2-TEG_1) at 8.07 ppm, 7.96-7.87 ppm, 7.56-7.50 ppm 7.47 ppm and 7.05-6.97 ppm respectively **(**Figure S13).

The calculation of $F_{l\text{-}cis}$ and $F_{c\text{-}cis}$ of *l*-(Azo_{n+1}-TEG_n) and *c*-(Azo_{n+1}-TEG_n) (n = 2-6) is similar to the described method above. For *l*-(Azo_{n+1}-TEG_n), $I_{l\text{-azo}}$ is the integrals of characteristic signals of *trans*-azo and *cis*-azo in the aromatic region around from 8.05 ppm to 6.57 ppm, and $I_{l\text{-}tran}$ is the integrals of characteristic signals of *trans*-azo at 7.99 ppm, 7.96-7.80 ppm, 7.60-7.51 ppm, 7.44 ppm and 7.03-6.94 ppm respectively. For *l*-(Azo_{n+1}-TEG_n), $I_{c\text{-azo}}$ is the integrals of characteristic signals of *trans*-azo and cis- azo in the aromatic region around from 8.09 ppm to 6.57 ppm, and $I_{c\text{-}trans}$ is the integrals of characteristic signals at 8.08-7.95 ppm, 7.94-7.78 ppm, 7.62-7.51 ppm, 7.45 ppm and 7.06-6.88 ppm respectively.

Using *l*-(Azo_3-TEG_2) and *c*-(Azo_3-TEG_2) as typical samples, ^{1}H NMR spectra are as follow (Figure S14). Unlike the *l*-(Azo_2-TEG_1) and *c*-(Azo_2-TEG_1) above, the aromatic protons of *l*-(Azo_3-TEG_2) and *c*-(Azo_3-TEG_2) appeared weak signals at higher field (6.5-6.9 ppm), which meant that a small amount of azobenzene moieties were assigned to *cis*-configuration.

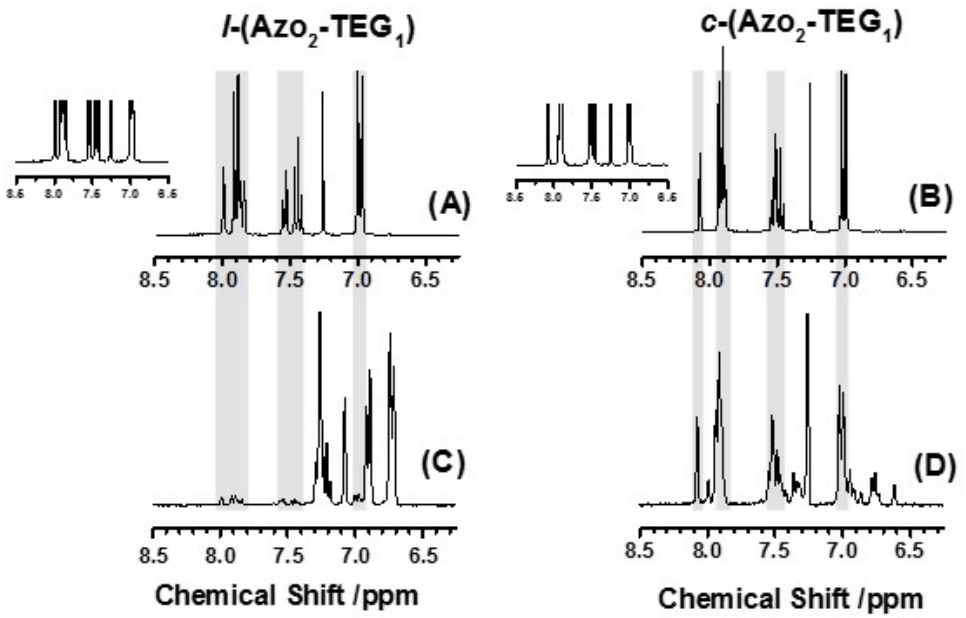


Figure S13. ^{1}H NMR spectra in the aromatic region of *l*-(Azo_2-TEG_1) and *c*-(Azo_2-TEG_1) in $CDCl_3$ at initial states (A), (B) and at the PSS_{uv} states (C), (D).

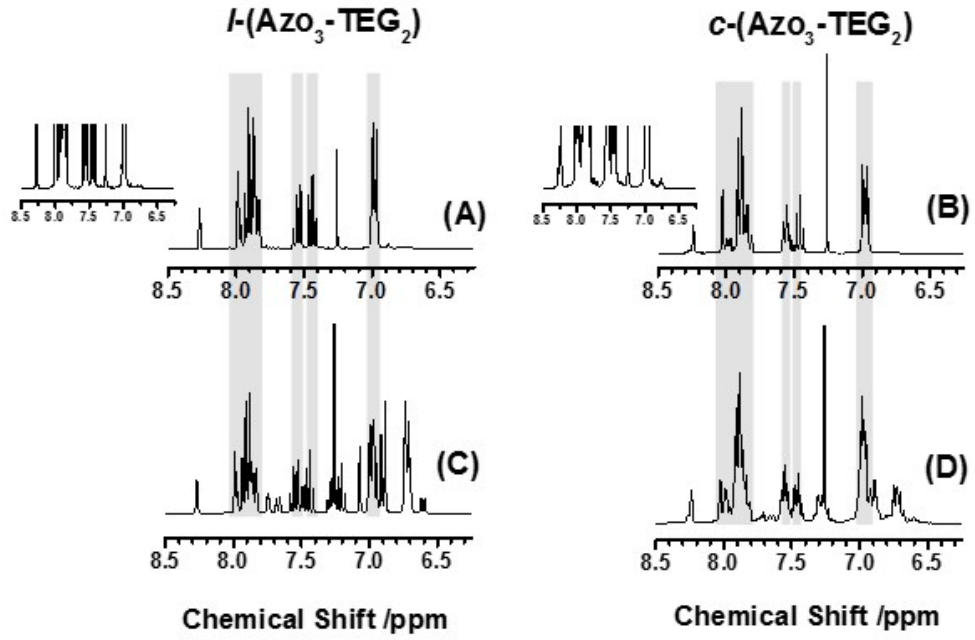


Figure S14. ^{1}H NMR spectra in the aromatic region of *l*-(Azo_3-TEG_2) and *c*-(Azo_3-TEG_2) in $CDCl_3$ at initial states (A), (B) and at the PSS_{uv} states (C), (D).

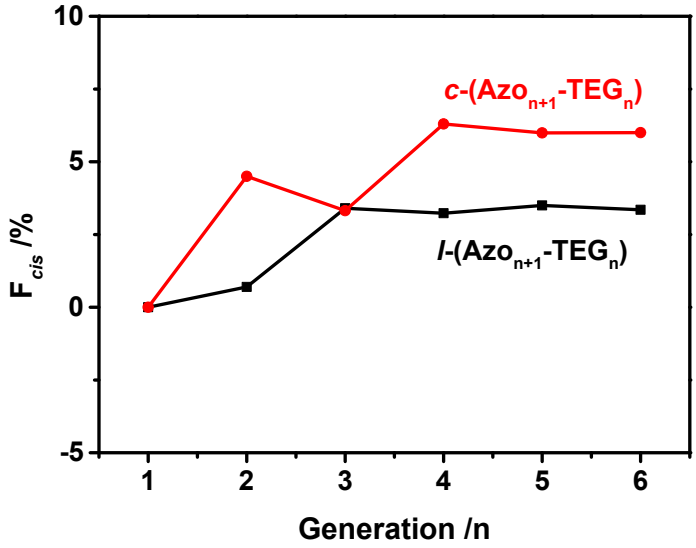


Figure S15. The evolution of *cis* isomers percentage estimated by NMR spectra with the generation (n) of *l*-(Azo_{n+1}-TEG_n) and *c*-(Azo_{n+1}-TEG_n) (n=1-6) in the initial states.

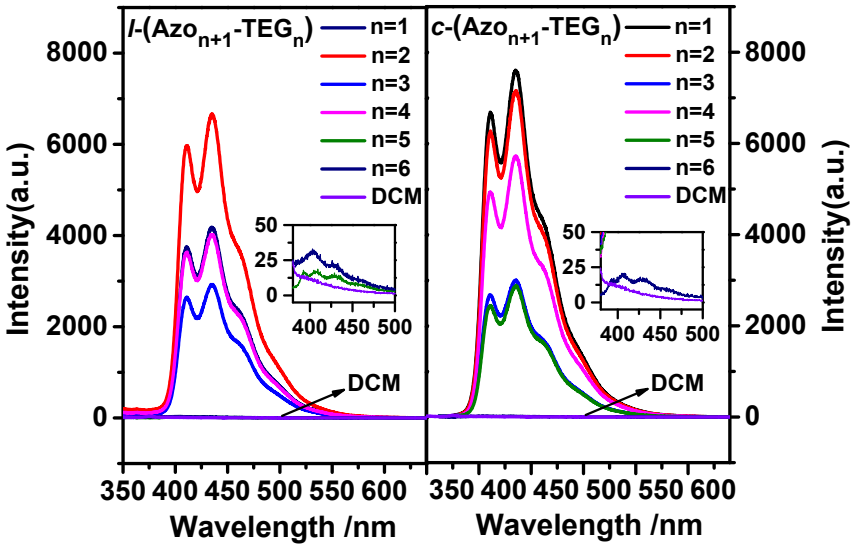


Figure S16. Fluorescence emission spectra (excitation wavelength at 350 nm) of *l*-(Azo_{n+1}-TEG_n) and *c*-(Azo_{n+1}-TEG_n) (n = 1-6) in DCM at room temperature. The concentration of solution is 3.6×10^{-8} mol/mL of azobenzene units for both linear and cyclic oligomers.

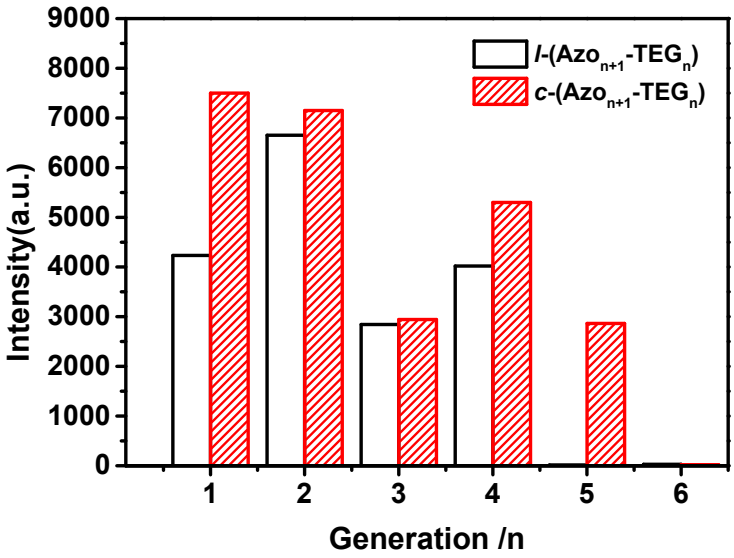


Figure S17. The evolution of fluorescence emission (excitation wavelength at 350 nm) of *l*-(Azo$_{n+1}$-TEG$_n$) and *c*-(Azo$_{n+1}$-TEG$_n$) (n=1-6) with generation (n) in DCM at room temperature.

Additional Tables

Table S1. Data corresponding to mass peaks in MALDI-TOF mass spectra (Figure 4) and molecular weights ($M_{n,\,GPC}$) determined by GPC of *l*-(Azo_{n+1}-TEG_n) and *c*-(Azo_{n+1}-TEG_n) (n = 1-6).

Sample	Theor. [Da]	Obsed. [*m/z*]	$M_{n,GPC}$ [Da]
l-(Azo_2-TEG_1)	830.39	835.11	850
c-(Azo_2-TEG_1)	828.37	850.52	420
l-(Azo_3-TEG_2)	1481.72	1504.26	1900
c-(Azo_3-TEG_2)	1479.70	1502.51	1300
l-(Azo_4-TEG_3)	2133.04	2156.51	2700
c-(Azo_4-TEG_3)	2131.03	2154.26	2100
l-(Azo_5-TEG_4)	2784.37	2807.95	3600
c-(Azo_5-TEG_4)	2782.35	2805.56	2800
l-(Azo_6-TEG_5)	3435.70	3458.98	4800
c-(Azo_6-TEG_5)	3433.68	3457.31	3500
l-(Azo_7-TEG_6)	4087.03	4110.02	5900
c-(Azo_7-TEG_6)	4085.01	4108.01	4300

Theor. calculated molecular mass (Da);

Theor. (*l*-(Azo_{n+1}-TEG_n)) (Da) = 830.39+ M_{mon} (651.33) × (n-1)

Theor. (*c*-(Azo_{n+1}-TEG_n)) (Da) = 828.37+ M_{mon} (651.33) × (n-1)

Obsed. (*l*-(Azo_{n+1}-TEG_n) and *c*-(Azo_{n+1}-TEG_n)): molecular mass obtained from MALDI-TOF mass spectra (*m/z*);

Calcd. (*l*-(Azo_{n+1}-TEG_n)) (Da) = 830.39+ M_{mon} (651.33) × (n-1)+ M_{Na} (22.99);

Calcd. (c-(Azo_{n+1}-TEG_n)) (Da) = 828.37+ M_{mon} (651.33) × (n-1)+ M_{Na} (22.99);

M_{Na} : the molecular mass of Na;

$M_{mon:}$ the molecular mass of monomer;

n : the number of repeat units of monomer;

Table S2. Data of photoresponsive behavior of the *l*-(Azo_{n+1}-TEG_n) and *c*-(Azo_{n+1}-TEG_n) (n = 1-6)

Sample	λmax (trans) (nm)	λmax (cis) (nm)	k_e s^{-1}	k'_e / k_e	k_H s^{-1}	k'_H / k_H
l-(Azo_2-TEG_1)	351.4	439.0	2.6	1.61	1.67	1.01
c-(Azo_2-TEG_1)	338.5	439.0	4.2		1.68	
l-(Azo_3-TEG_2)	352.5	439.0	2.6	1.07	1.67	1.12
c-(Azo_3-TEG_2)	343.0	439.0	3.0		1.87	
l-(Azo_4-TEG_3)	351.5	439.0	2.7	1.21	1.82	1.05
c-(Azo_4-TEG_3)	341.3	439.0	3.3		1.91	
l-(Azo_5-TEG_4)	352.0	439.0	2.4	1.41	1.63	1.20
c-(Azo_5-TEG_4)	342.2	439.0	3.4		1.96	
l-(Azo_6-TEG_5)	352.3	439.0	2.8	1.23	1.68	1.14
c-(Azo_6-TEG_5)	350.6	439.0	3.5		1.88	
l-(Azo_7-TEG_6)	352.5	439.0	2.6	1.15	1.65	1.07
c-(Azo_7-TEG_6)	351.3	439.0	3.1		1.77	

The quantum yield was calculated using the following equation:

$$\Phi S=\Phi_r[F_s A_r/F_r A_s](n_r/n_s)^2$$

where Φ_s is the fluorescence quantum yield of the sample, F is the area of the emission peak, n is the refractive index of solution, and A is the absorbance of the solution at the exciting wavelength. The subscripts r and s denote reference and sample, respectively.[3]

Table S3. The quantum yields (Φ_s) of the *l*-(Azo_{n+1}-TEG_n) and *c*-(Azo_{n+1}-TEG_n) (n = 1-6).

Sample	Φ_s (10^{-2})	Sample	Φ_s (10^{-2})
l-(Azo_2-TEG_1)	0.984	*c*-(Azo_2-TEG_1)	2.055
l-(Azo_3-TEG_2)	1.695	*c*-(Azo_3-TEG_2)	2.007
l-(Azo_4-TEG_3)	0.805	*c*-(Azo_4-TEG_3)	0.837
l-(Azo_5-TEG_4)	0.848	*c*-(Azo_5-TEG_4)	1.498
l-(Azo_6-TEG_5)	0.004	*c*-(Azo_6-TEG_5)	0.917
l-(Azo_7-TEG_6)	0.009	*c*-(Azo_7-TEG_6)	0.005

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