Supplementary Information (SI) for Polymer Chemistry.

Electronic Supplementary Information

Polymeric toroidal assemblies from ionic homopolymers with shackling photo-responsive behavior

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Experimental Part

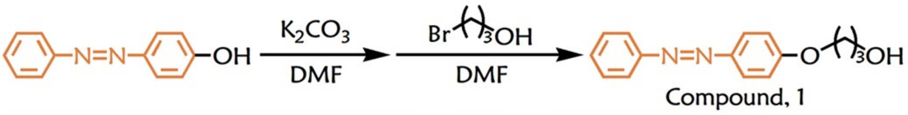
Materials

10-Undecenoic acid (99%, Alfa Aesar), 3-bromo-1-propanol (97+%, Alfa Aesar), isonicotinoyl chloride hydrochloride (98%, Alfa Aesar), 4-dimethylaminopyridine (DMAP) (98%, Energy Chemical), 1-[3-(dimethylamino)propyl]-3-ethyl carbodiimide hydrochloride (EDCI·HCl) (99%, Energy Chemical), benzylidene[1,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene] dichloro(tricyclo hexylphosphine) ruthenium (Grubbs second-generation catalyst) (Aldrich), and triethylamine (95%, Aldrich) were used as received without purification. 4-Hydroxyazobenzene (98%) was purchased from Shanghai DiBo Chemical Technology Co., LTD. 2,2,5-Trimethyl-1,3-dioxane-5-caboxylic acid (97%) was purchased from Beijing HWRK Chem Co., LTD. Solvents were distilled over drying agents under nitrogen prior to use. Hydroxy-azobenzene compounds were synthesized according to the procedure described in the literature.

Characterization

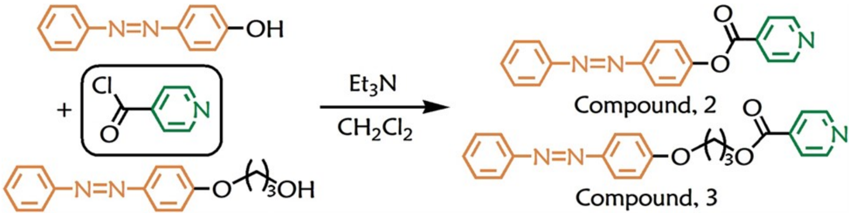
^{1}H (500 MHz) and ^{13}C (125 MHz) NMR spectra were recorded on a Bruker DPX spectrometer using tetramethylsilane as an internal standard and using $CDCl_3$ as the solvent at ambient temperature. Polymer samples were analyzed using a TOSOH EsoSEC HLC-8320GPC system, comprising an autosampler, two TSKgel SuperHZM-M (4.6 mm I.D. × 15 cm), TSKgel SuperH-RC, and TSKgel guardcolumn SuperHZ-L columns, UV-8320 detector and refractive index (RI) detector. GPC measurements were carried out at 40 °C using DMF (Fischer, HPLC grade) as the eluent with a flow rate of 1 mL/min. Relative molecular weights and molecular weight distributions were calculated using PStQuick MP-M standards. The GPC Workstation EcoSEC-WS comprises system control and data analysis software for use with EcoSEC. Hydrodynamic diameter and polydispersity index of the nanoaggregates were measured by dynamic light scattering (DLS) using a Malvern Zetasizer Nano-ZS light scattering apparatus (Malvern Instruments, UK) with a He–Ne laser (633 nm, 4 mW) at 25 °C at a scattering angle of 90°. The solution of homopolymers with the concentrations of 5 × 10^{-4} mol/L for particle size measurements was filtered using a Millex-GV (Millipore) membrane filter (0.45 μm pore size). TEM images were recorded on the JEOL2100F microscopes operating at an accelerating voltage of 200 kV. The sample solutions with different concentrations (a certain amount of homopolymer directly dissolved in THF) were dropped onto a carbon coated Cu grids and dried under ambient temperature for 24 h. SEM images were obtained by Nova NanoSEM 450 with an operation voltage of 50 V~30 kV and current of 0.6 pA~200 nA. The THF solution of the sample with different concentrations was dropped onto a clean silicon wafer and dried naturally. UV–Vis absorption spectra were measured on an Agilent Cary 60 spectrometer. UV light irradiation was carried out with a 5 W UV lamp with the wavelength at 365 nm (1000 mW cm^{-2}). Irradiation by visible light was performed using a 3 W Philips day light bulb (> 400 nm, 600 mW cm^{-2}). Elemental analysis (EA) was conducted with an Elementar Vario EL. Liquid chromatography−mass (LC−MS) spectrometry was performed with a liquid chromatograph−mass spectrometer (Agilent Technology 1200), using a C_{18} column, with 20 min of elution using a gradient solution of CH_3CN-H_2O (containing 0.05% trifluoroacetic acid), with a UV detector and an electrospray ionization source. The purity of all compounds was analyzed by the analytical LC−MS system described, and the purity is > 95%. The molecular mass was evaluated using the analytical LC−MS system.

*Synthesis of Azo-Compounds, **1***



4-Hydroxyazobenzene (7.92 g, 40 mmol), potassium carbonate (13.8 g, 100 mmol), and 80 mL of DMF were charged into a 250 mL Schlenk flask. The reaction mixture was heated at 80 °C for 6 h under nitrogen allowing for the potassium salt formed. A solution of 3-bromo-1-propanol (7.54 g, 48 mmol) in 40 mL of DMF was then added dropwise to the above mixture. After 24 h of stirring at 60 °C, the reaction mixture was poured into excess water and the crude product was precipitated out, and further purified by recrystallization by methanol to give a brown crystalline solid compound, **1** (8.04 g, 78.2% yield). ^{1}H NMR (CDCl$_3$), δ (ppm): 7.98–7.81 (m, 4H, *o*-Ar*H*N=NArH + *o*-ArHN=NAr*H*), 7.52–7.46 (t, 3H, *p*-Ar*H*N=NArH + *m*-Ar*H*N=NArH), 7.10–7.01 (d, 2H, *m*-ArHN=NAr*H*), 4.23–4.18 (d, 2H, OC*H*$_2$CH$_2$CH$_2$OH), 3.98–3.82 (d, 2H, OCH$_2$CH$_2$C*H*$_2$OH), 2.20–2.07 (d, 2H, OCH$_2$C*H*$_2$CH$_2$OH). Anal. Calcd for C: 70.32, H: 6.25, N: 10.93, O: 12.50; Found C: 70.30, H: 6.29, N: 10.93, O: 12.48.

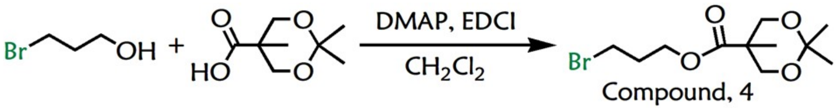
*Synthesis of Azo-Pyridine Compounds, **2** and **3***



4-Hydroxyazobenzene (2.97 g, 15 mmol) or compounds, **1** (15 mmol) was dissolved in 40 mL of CH$_2$Cl$_2$, then 4.2 mL (3.03 g, 30 mmol) of dry Et$_3$N was added under nitrogen. The reaction mixture was cooled to 0 °C before isonicotinoyl chloride hydrochloride (3.20 g, 18 mmol) in 30 mL of CH$_2$Cl$_2$ was added dropwise. The reaction mixture was then warmed to room temperature and stirred at 50 °C for further 24 h. After cooling to room temperature, the mixture was filtered, the filtrate was washed six times with water (6 × 60 mL), and the organic layer was dried over anhydrous MgSO$_4$. Solvent was then removed under reduced pressure and further purified by recrystallization by methanol to afford 4.12 g of compound, **2** as a red-brown powder in 90.6% yield, 4.78 g of compound, **3** as a red-brown crystalline solid in 88.3% yield. Compound, **2**, ^{1}H NMR (CDCl$_3$), δ (ppm): 8.93–8.87 (d, 2H, *o*-Ar*H*N), 8.08–7.95 (m, 4H, *m*-Ar*H*N + *o*-

*H*ArN=NAr), 7.95–7.81 (*m*, 2H, *o*-ArN=NAr*H*), 7.57–7.45 (t, 3H, *m*-*H*ArN=NAr+ *p*-*H*ArN=NAr), 7.44–7.37 (d, 2H, *p*-ArN=NAr*H*). EI/MS: Calcd. for $C_{18}H_{13}N_3O_2$: 303.10; found: 303.12. Anal. calcd for C: 71.28, H: 4.32, O: 10.55, N: 13.85; found C: 71.24, H: 4.32, O: 10.60, N: 13.84. Compound, **3**, ^{1}H NMR ($CDCl_3$), δ (ppm): 8.91–8.74 (d, 2H, *o*-Ar*H*N), 8.07–7.83 (m, 6H, *m*-Ar*H*N + *o*-*H*ArN=NAr*H*), 7.61–7.46 (t, 3H, *m*-*H*ArN=NAr+ *p*-*H*ArN=NAr), 7.10–6.99 (d, 2H, *p*-ArN=NAr*H*), 4.69–4.58 (d, 2H, $OCH_2CH_2CH_2OCO$), 4.33–4.21 (d, 2H, $OCH_2CH_2CH_2OCO$), 2.42–2.23 (d, 2H, $OCH_2CH_2CH_2OCO$). EI/MS: Calcd. for $C_{21}H_{19}N_3O_3$: 361.39; found: 361.26. Anal. calcd for C: 69.79, H: 5.30, O: 13.28, N: 11.63; found C: 69.74, H: 5.32, O: 13.30, N: 11.64.

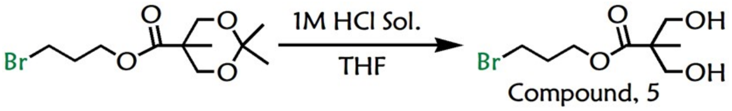
*Synthesis of Diene Monomer (**M1**)*



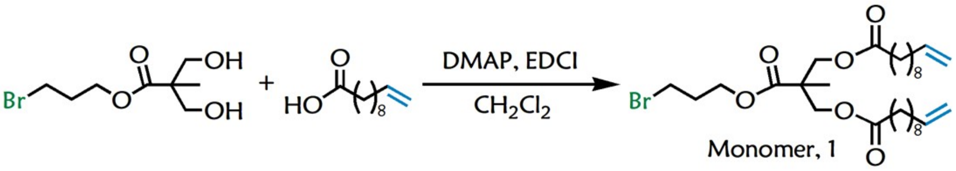
Compound, 4

3-Bromo-1-propanol (4.17 g, 30 mmol), 2,2,5-trimethyl-1,3-dioxane-5-caboxylic acid (6.26 g, 36 mmol), and DMAP (0.44 g, 3.60 mmol) were dissolved in CH_2Cl_2 (75 mL), and the mixture was stirred at 0 °C for 15 min. EDCI (6.90 g, 36 mmol) was then added to the former solution and stirred for 3 days under nitrogen flow after the solution was warmed to room temperature. The resulting mixture was washed three times with saturated brine, dilute HCl solution, and deionized water (5 × 60 mL) respectively, and the organic layer was dried over anhydrous $MgSO_4$. The solvent was then evaporated, and the colorless liquid compound, **4** was used directly for the next reaction without further purification (8.15 g, 92.1% yield). ^{1}H NMR ($CDCl_3$), δ (ppm): 4.51–3.95 (m, 6H, OCH_2CCH_2O + CH_2OCO), 3.56–3.38 (d, 2H, $BrCH_2CH_2$), 2.26–1.93 (m, 2H, $BrCH_2CH_2$), 1.55–1.23 (m, 9H, CH_3 + $OC(CH_3)_2O$). EI/MS: Calcd. for $C_{11}H_{19}O_4Br$: 295.16; found: 295.12. Anal. calcd for C: 44.76, H: 6.49, O: 21.68, Br: 27.07; found C:

44.77, H: 6.50, O: 21.64, Br: 27.09.

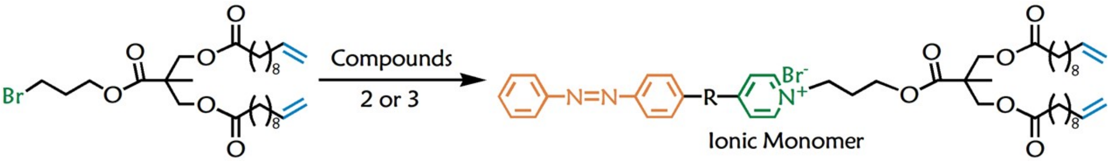


Then, as-prepared compound, **4** (7.38 g, 25 mmol) was dissolved in THF (60 mL) and HCl solution (60 mL, 1 M), and the mixture was slightly turbid. After stirring for 2 h, the system became clear. The reaction was monitored by column chromatography until the reactant reacted completely. The THF solvent was then evaporated under reduced pressure, and the aqueous layer was extracted with CH_2Cl_2 several times. The organic layer was dried over anhydrous $MgSO_4$, the solvent was evaporated to obtain the colorless liquid compound, **5** (6.07 g, 95.2% yield). ^{1}H NMR ($CDCl_3$), δ (ppm): 4.49–4.20 (m, 4H, $HOCH_2CCH_2OH$), 3.97–3.75 (d, 2H, CH_2OCO), 3.62–3.34 (d, 2H, $BrCH_2CH_2$), 2.27–1.96 (m, 2H, $BrCH_2CH_2$), 1.46–1.21 (m, 3H, CH_3). EI/MS: Calcd. for $C_8H_{15}O_4Br$: 255.10; found: 255.06. Anal. calcd for C: 37.66, H: 5.93, O: 25.09, Br: 31.32; found C: 37.68, H: 5.95, O: 25.06, Br: 31.31.



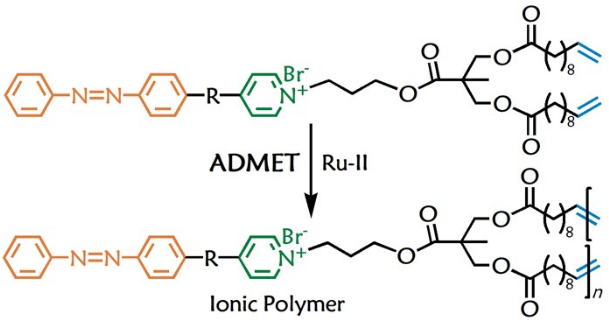
Finally, the as-obtained compound, **5** (5.1 g, 20 mmol), 10-undecenoic acid (9.2 g, 50 mmol), and DMAP (0.59 g, 4.8 mmol) were dissolved in CH_2Cl_2 (60 mL), and the mixture was stirred at 0 °C for 15 min. EDCI (9.23 g, 48 mmol) was then added to the former solution and further stirred for 5 days under nitrogen flow after the solution was warmed to room temperature. The resulting solution was washed three times with deionized water (3 × 50 mL), and the organic layer was dried over anhydrous $MgSO_4$. The solvent was then evaporated, and the crude product was purified by chromatographic purification (silica gel, CH_2Cl_2/hexane = 1: 8~1: 2) to give colorless viscous liquid diene monomer, **M1** (8.85 g, 75.4% yield). ^{1}H NMR ($CDCl_3$), *δ* (ppm): 5.87–5.62 (d, 2H, C*H*=CH_2), 5.05–4.83 (m, 4H, CH=CH_2), 4.32–4.01 (m, 6H, CH_2OCO + OCOCH_2CCH_2OCO), 3.53–3.41, 3.37–3.20 (d, 2H, BrC$H_2$$CH_2$), 2.36–1.81 (m, 10H, C$H_2$$CH_2$$(CH_2)_5CH_2$ + BrCH_2CH_2), 1.63–1.42 (d, 4H, CH_2C$H_2$$(CH_2)_5$$CH_2$), 1.35–0.98 (m, 23H, C$H_3$ + (CH_2)$_5$). EI/MS: Calcd. for $C_{30}H_{51}O_6Br$: 587.61; found: 587.86. Anal. calcd for C: 61.31, H: 8.75, O: 16.34, Br: 13.60; found C: 61.24, H: 8.82, O: 16.33, Br: 13.61.

*Synthesis of Ionic Azo-Diene Monomers (**IAzoC$_p$Ms**)*



A solution of **M1** (1.76 g, 3 mmol) and compound, **2** or **3** (3.6 mmol) in toluene (10 mL) was heated at reflux for 72 h. After the mixture cooled, the solid was precipitated, and poured out the toluene solution. The residue was washed with toluene and diethylether, respectively for 5 times and then dried in a vacuum oven. A dark-red viscous solid, **IAzoC$_p$Ms** (> 90% yield) was obtained. **IAzoC$_0$M**, ^{1}H NMR ($CDCl_3$), *δ* (ppm): 9.01–8.76 (d, 2H, *o*-Ar*H*N$^+$), 8.15–7.84 (m, 6H, *m*-Ar*H*N$^+$ + *o*-*H*ArN=NAr*H*), 7.63–7.36 (m, 5H, *m*-*H*ArN=NAr*H*+ *p*-*H*ArN=NAr), 5.90–5.72 (d, 2H, C*H*=CH_2), 5.08–4.87 (m, 4H, CH=CH_2), 4.37–4.13 (m, 8H, N$^+$C$H_2$$CH_2CH_2$ + OCOCH_2CCH_2OCO), 2.34–1.86 (m, 10H, C$H_2$$CH_2$$(CH_2)_5CH_2$ + N$^+$$CH_2CH_2$$CH_2$), 1.71–1.50 (d, 4H, CH_2C$H_2$$(CH_2)_5$$CH_2$), 1.46–1.02 (m, 23H, C$H_3$ + (CH_2)$_5$). EI/MS: Calcd. for $C_{48}H_{64}N_3O_8Br$: 890.92; found: 891.36. Anal. calcd for C: 64.71, H: 7.24, O: 14.36, N: 4.72, Br: 8.97; found C: 64.80, H: 7.27, O: 14.31, N: 4.66, Br: 8.96. **IAzoC$_3$M**, ^{1}H NMR ($CDCl_3$), *δ* (ppm): 8.94–8.68 (d, 2H, *o*-Ar*H*N$^+$), 8.09–7.82 (m, 6H, *m*-Ar*H*N$^+$ + *o*-*H*ArN=NAr*H*), 7.60–7.37 (m, 3H, *m*-*H*ArN=NAr+ *p*-*H*ArN=NArH), 7.11–6.89 (m, 2H, *m*-HArN=NAr*H*), 5.92–5.73 (d, 2H, C*H*=CH$_2$), 5.10–4.88 (m, 4H, CH=C*H*$_2$), 4.65–4.51 (m, 4H, N$^+$CH$_2$CH$_2$C*H*$_2$ + OCH$_2$CH$_2$C*H*$_2$OCO), 4.38–4.13 (m, 8H, N$^+$C*H*$_2$CH$_2$CH$_2$ + OCOC*H*$_2$CC*H*$_2$OCO + OC*H*$_2$CH$_2$CH$_2$OCO), 2.41–1.92 (m, 12H, OCH$_2$C*H*$_2$CH$_2$OCO + C*H*$_2$CH$_2$(CH$_2$)$_5$C*H*$_2$ + N$^+$CH$_2$C*H*$_2$CH$_2$), 1.87–1.51 (d, 4H, CH$_2$C*H*$_2$(CH$_2$)$_5$CH$_2$), 1.45–1.06 (m, 23H, C*H*$_3$ + (C*H*$_2$)$_5$). EI/MS: Calcd. for $C_{51}H_{70}N_3O_9Br$: 949.03; found: 949.42. Anal. calcd for C: 64.55, H: 7.43, O: 15.17, N: 4.43, Br: 8.42; found C: 64.61, H: 7.46, O: 15.13, N: 4.41, Br: 8.39.

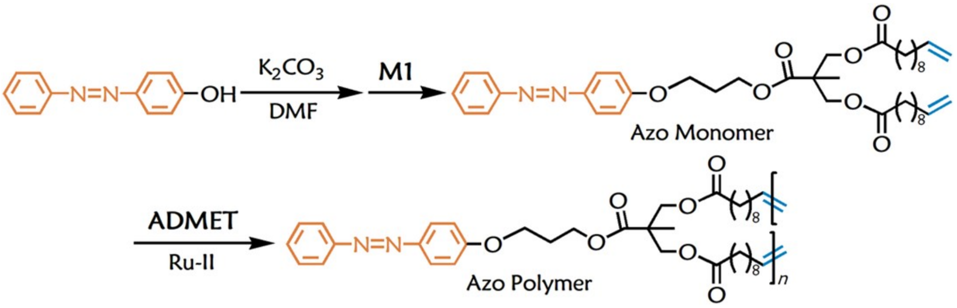
General ADMET Polymerization Procedure for Ionic Azo-Homopolymers Synthesis (IAzoC$_p$HPs)



In a nitrogen-filled Schlenk tube, a solution of Grubbs second-generation catalyst, **C1** (0.5 mol% to monomer) in 0.1 mL of degassed toluene with three freeze-vacuum-thaw cycles was added to a solution of the corresponding ionic azo-diene monomers, **IAzoC*p*Ms** (1.0 mmol) in 0.9 mL of IL, [bmim]PF$_6$ degassed with the same procedure. After the reaction mixture was stirred at 70 °C for 6~24 h, the polymerization was quenched by adding ethyl vinyl ether with stirring for 30 min. The solution was precipitated into an excess of cold methanol, and the precipitate was isolated by filtration and dried under vacuum to give the corresponding ionic ADMET azo-homopolymers, **IAzoC*p*HPs**. **IAzoC$_0$HP**, ^{1}H NMR (CDCl$_3$), δ (ppm): 8.97–8.74 (d, *o*-Ar*H*N$^+$), 8.16–7.72 (m, *m*-Ar*H*N$^+$ + *o*-*H*ArN=NAr*H*), 7.59–7.26 (m, *m*-*H*ArN=NAr*H*+ *p*-*H*ArN=NAr), 5.41–5.17 (d, C*H*=C*H*), 4.38–4.01 (m, N$^+$C*H*$_2$CH$_2$C*H*$_2$ +

$\mathrm{OCOC}H_2\mathrm{CC}H_2\mathrm{OCO}$), 2.42–1.80 (m, $\mathrm{C}H_2\mathrm{CH_2(CH_2)_5C}H_2$ + $\mathrm{N^+CH_2C}H_2\mathrm{CH_2}$), 1.71–1.02 (d, $\mathrm{C}H_3$ + $(\mathrm{C}H_2)_6$). **IAzoC$_3$HP**, ^{1}H NMR ($\mathrm{CDCl_3}$), δ (ppm): 8.91–8.67 (d, *o*-Ar*H*N$^+$), 8.07–7.85 (m, *m*-Ar*H*N$^+$ + *o*-*H*ArN=NAr*H*), 7.64–7.35 (m, *m*-*H*ArN=NAr+ *p*-*H*ArN=NArH), 7.03–6.91 (m, *m*-HArN=NAr*H*), 5.34–5.15 (d, C*H*=C*H*), 4.69–4.43 (m, $\mathrm{N^+CH_2CH_2C}H_2$ + $\mathrm{OCH_2CH_2C}H_2\mathrm{OCO}$), 4.34–4.07 (m, $\mathrm{N^+C}H_2\mathrm{CH_2CH_2}$ + $\mathrm{OCOC}H_2\mathrm{CC}H_2\mathrm{OCO}$ + $\mathrm{OC}H_2\mathrm{CH_2CH_2OCO}$), 2.40–1.96 (m, $\mathrm{OCH_2C}H_2\mathrm{CH_2OCO}$ + $\mathrm{C}H_2\mathrm{CH_2(CH_2)_5C}H_2$ + $\mathrm{N^+CH_2C}H_2\mathrm{CH_2}$), 1.71–1.42 (d, $\mathrm{CH_2C}H_2\mathrm{(CH_2)_5CH_2}$), 1.38–1.07 (m, $\mathrm{C}H_3$ + $(\mathrm{C}H_2)_5$).

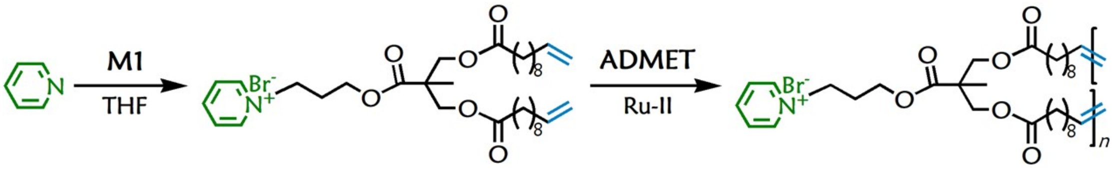
Azo-Diene Monomer Synthesis and ADMET Polymerization



4-Hydroxyazobenzene (0.99 g, 5 mmol), potassium carbonate (2.07 g, 15 mmol), and 20 mL of DMF were charged into a 100 mL Schlenk flask. The reaction mixture was heated at 80 °C for 6 h under nitrogen allowing for the potassium salt formed. A solution of **M1** (2.94 g, 5 mmol) in 10 mL of DMF was then added dropwise to the above mixture. After 24 h of stirring at 60 °C, the reaction mixture was poured into excess water and the crude product was precipitated out, and further purified by recrystallization by methanol to give a reddish-brown crystalline solid (2.71 g, 76.8% yield). ^{1}H NMR ($\mathrm{CDCl_3}$), δ (ppm): 7.86–7.79 (m, 4H, *o*-*H*ArN=NAr*H*), 7.45–7.36 (m, 3H, *p*-*H*ArN=NArH + *m*-*H*ArN=NArH), 6.94–6.92 (d, 2H, *m*-HArN=NAr*H*), 5.76–5.67 (d, 2H, $\mathrm{C}H\mathrm{=CH_2}$), 4.94–4.83 (m, 4H, $\mathrm{CH=C}H_2$), 4.29–4.26 (d, 2H, $\mathrm{OC}H_2\mathrm{CH_2CH_2}$), 4.21–4.13 (m, 4H, $\mathrm{C}H_2\mathrm{CC}H_2$), 4.05–4.02 (d, 2H, $\mathrm{OCH_2CH_2C}H_2$), 2.20–2.08 (d, 6H, CH_2 + OCH$_2$CH_2CH$_2$), 1.97–1.91, 1.52–1.15 (m, 31H, (CH_2)$_7$ + CH_3).

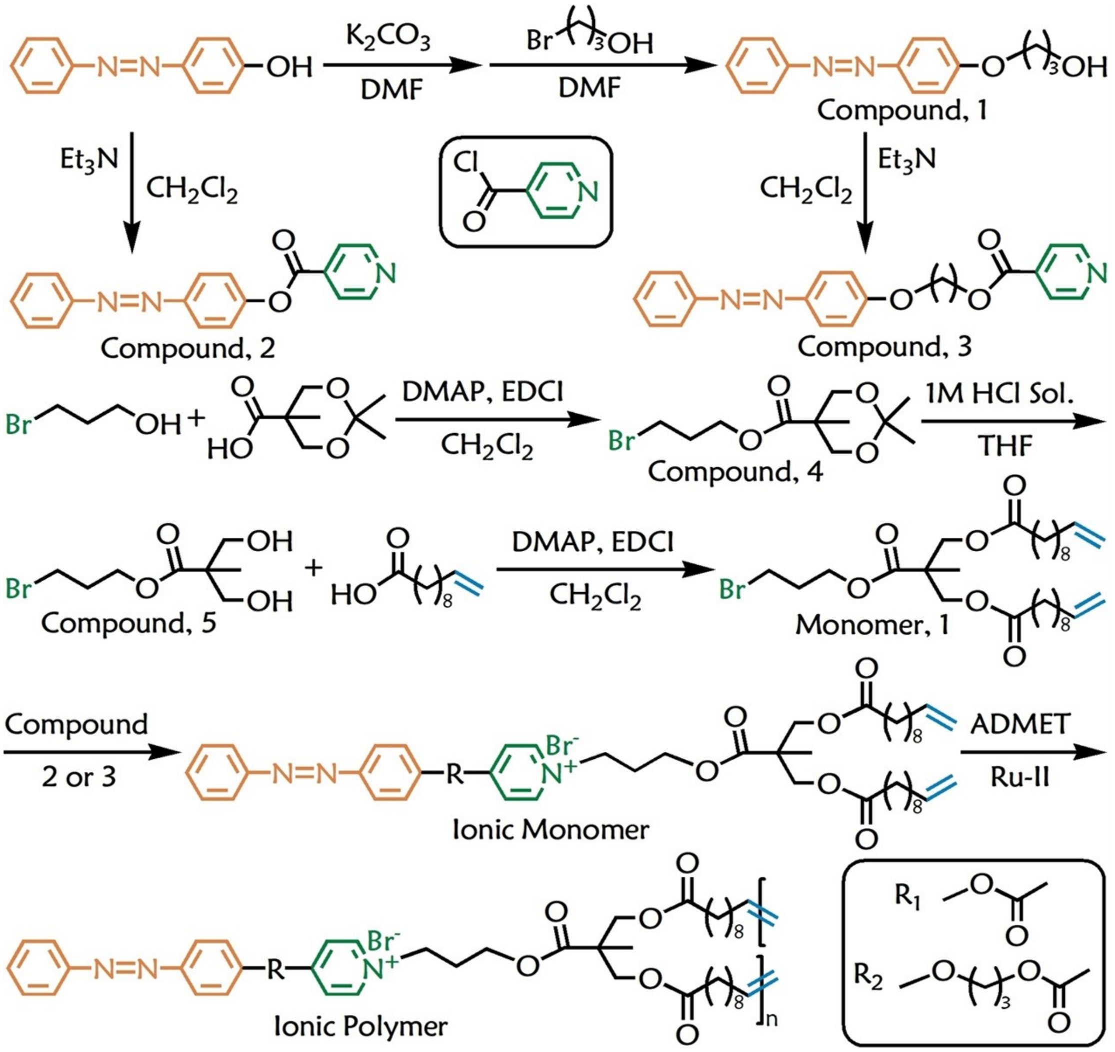
Subsequently, in a nitrogen-filled Schlenk tube, a solution of Grubbs second-generation catalyst (1.0 mol% to monomer) in 0.1 mL of degassed toluene with three freeze-vacuum-thaw cycles was added to a solution of above as-prepared monomer (0.5 mmol) in 0.4 mL of toluene degassed with the same procedure. After the reaction mixture was stirred at 70 °C for 24 h, the polymerization was quenched by adding ethyl vinyl ether with stirring for 30 min. The solution was precipitated into an excess of cold methanol, and the precipitate was isolated by filtration and dried under vacuum to give the ADMET azo-homopolymer, **AzoHP**. ^{1}H NMR (CDCl$_3$), δ (ppm): 7.90–7.79 (m, *o-H*ArN=NAr*H*), 7.44–7.34 (m, *p-H*ArN=NArH + *m-H*ArN=NArH), 6.94–6.90 (d, *m*-HArN=NAr*H*), 5.37–5.21 (d, C*H*=C*H*), 4.34–4.26 (d, OCH_2CH$_2$CH$_2$), 4.19–4.13 (m, CH_2CCH_2), 4.08–3.97 (d, OCH$_2$CH$_2$CH_2), 2.19–2.06 (d, CH_2 + OCH$_2$CH_2CH$_2$), 1.95–1.78, 1.49–1.16 (m, (CH_2)$_7$ + CH_3). GPC: M_n = 20.3 kDa, M_w/M_n = 1.41 for 24 h.

Pyridinium Bromide-Diene Monomer Synthesis and ADMET Polymerization



To a solution of the as-prepared **M1** (1.76 g, 3 mmol) in dry THF (5 mL) was added pyridine (0.4 g, 5 mmol) and the mixture was refluxed for 48 h. After cooling, the THF and the excess pyridine were removed by rotary evaporation and further heating under high vacuum for 24 hours at 60 °C to give ionic diene monomer, **Py-BrM** (1.83 g, 91.5%). ^{1}H NMR (CDCl$_3$), δ (ppm): 8.69–8.61 (d, 2H, *o*-Ar*H*N$^+$), 8.17–8.12 (m, 1H, *p*-Ar*H*N$^+$), 7.78–7.70 (d, 2H, *m*-Ar*H*N$^+$), 5.86–5.75 (m, 2H, C*H*=CH$_2$), 5.02–4.90 (m, 4H, CH=CH_2), 4.22–3.62 (m, 8H, N$^+$CH_2CH$_2$CH_2 + OCOCH_2CCH_2OCO), 2.30–2.26 (m, 2H, $N^+CH_2CH_2CH_2$), 2.07–1.94 (m, 8H, $OCOCH_2(CH_2)_6CH_2$), 1.76–1.25 (m, 27H, $(CH_2)_6 + CH_3$).

Subsequently, in a nitrogen-filled Schlenk tube, a solution of Grubbs second-generation catalyst (1.0 mol% to monomer) in 0.1 mL of degassed toluene with three freeze-vacuum-thaw cycles was added to a solution of as-obtained monomer (0.5 mmol) in 0.4 mL of IL, [bmim]PF_6 degassed with the same procedure. After the reaction mixture was stirred at 70 °C for 24 h, the polymerization was quenched by adding ethyl vinyl ether with stirring for 30 min. The solution was precipitated into an excess of cold methanol, and the precipitate was isolated by filtration and dried under vacuum to give the ADMET pyridinium-homopolymer, **Py-BrHP**. ^1H NMR ($CDCl_3$), δ (ppm): 8.69–8.58 (m, *o*-Ar*H*N^+), 8.22–8.12 (d, *p*-Ar*H*N^+), 7.71–7.60 (d, *m*-Ar*H*N^+), 5.42–5.32 (d, C*H*=C*H*), 4.23–4.05 (m, $N^+CH_2CH_2CH_2$ + $OCOCH_2CCH_2OCO$), 2.37–2.29 (m, $N^+CH_2CH_2CH_2$), 1.98–1.27 (m, $(CH_2)_8 + CH_3$). GPC: M_n = 21.2 kDa, M_w/M_n = 1.59 for 24 h.



Scheme S1. Illustration for Constructing Side-Chain Ionic Azo-Homopolymers via ADMET Polymerization.

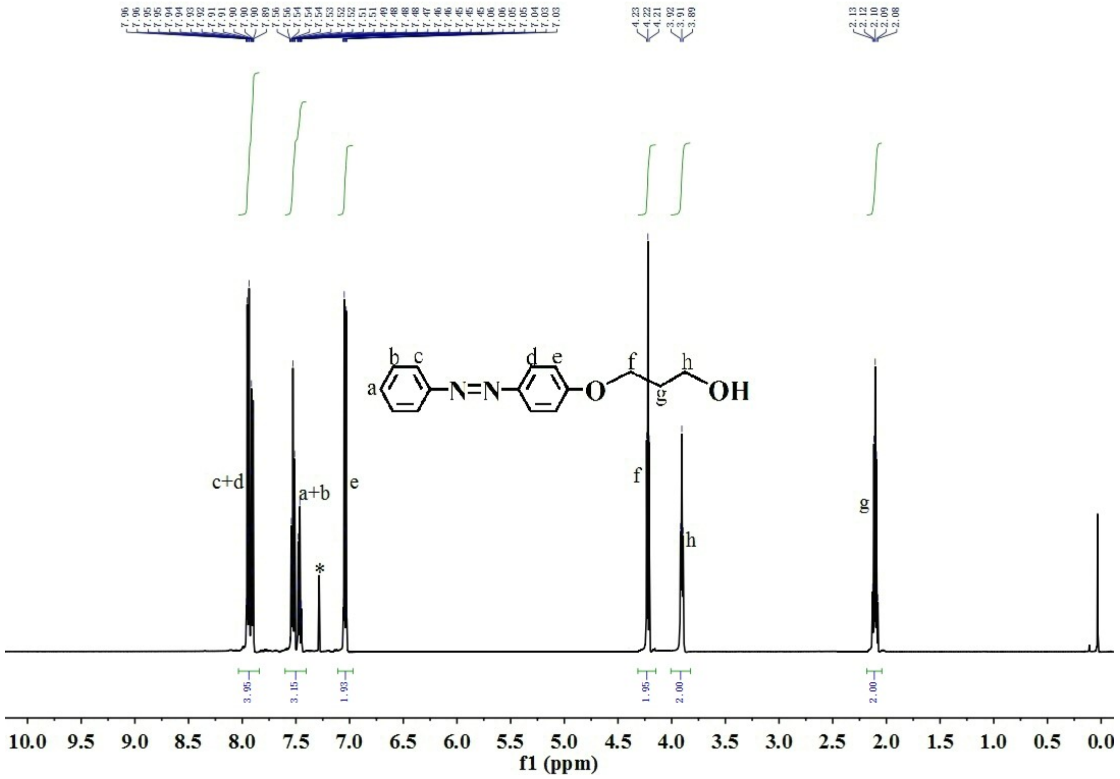


Figure S1. ^{1}H NMR spectrum of azo-compound, **1**.

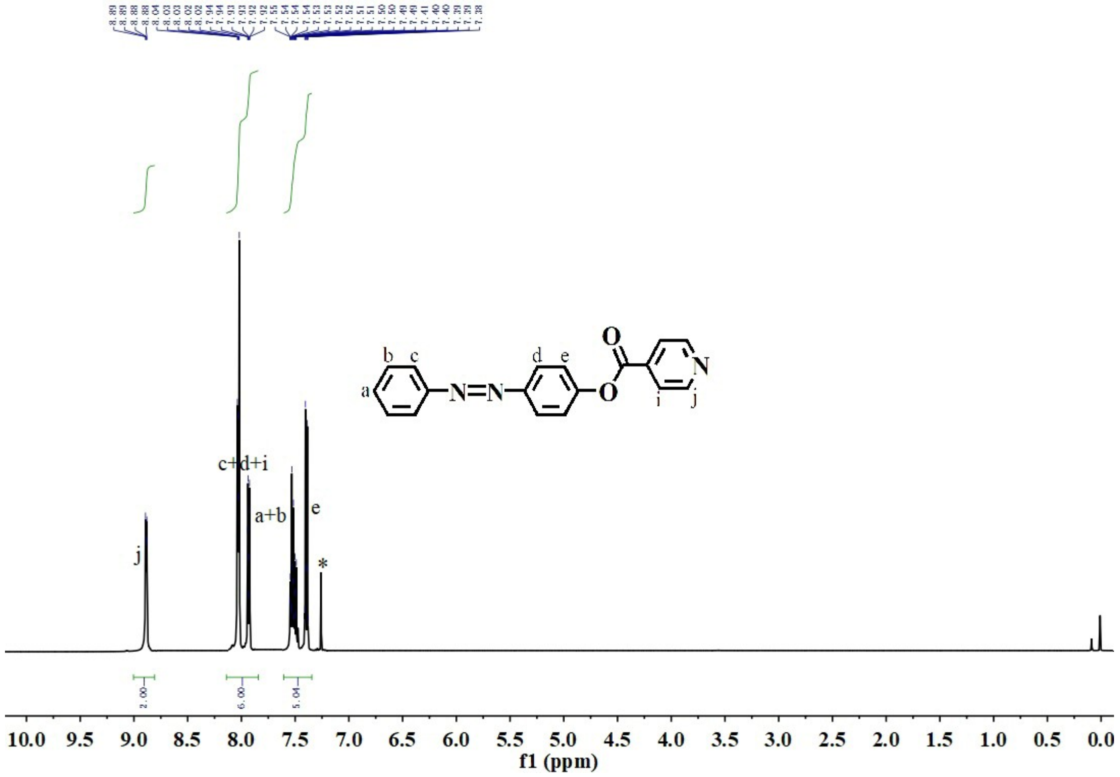


Figure S2. ^{1}H NMR spectrum of azo-pyridine compound, **2**.

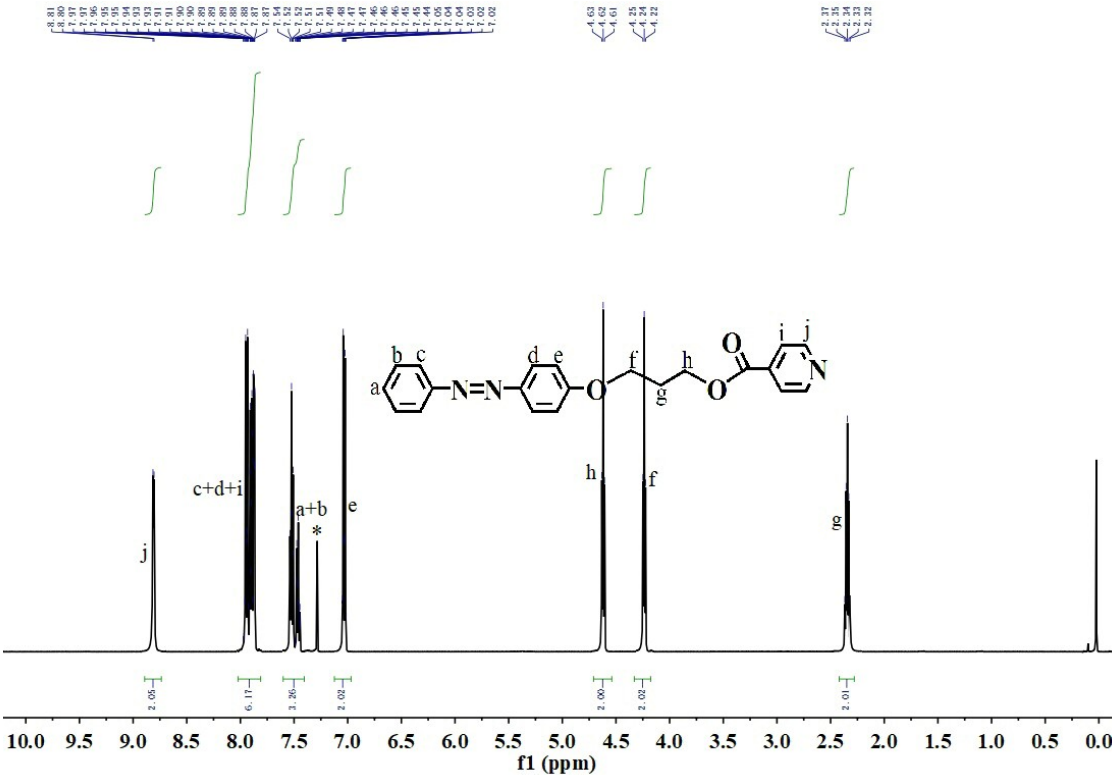


Figure S3. ^{1}H NMR spectrum of azo-pyridine compound, **3**.

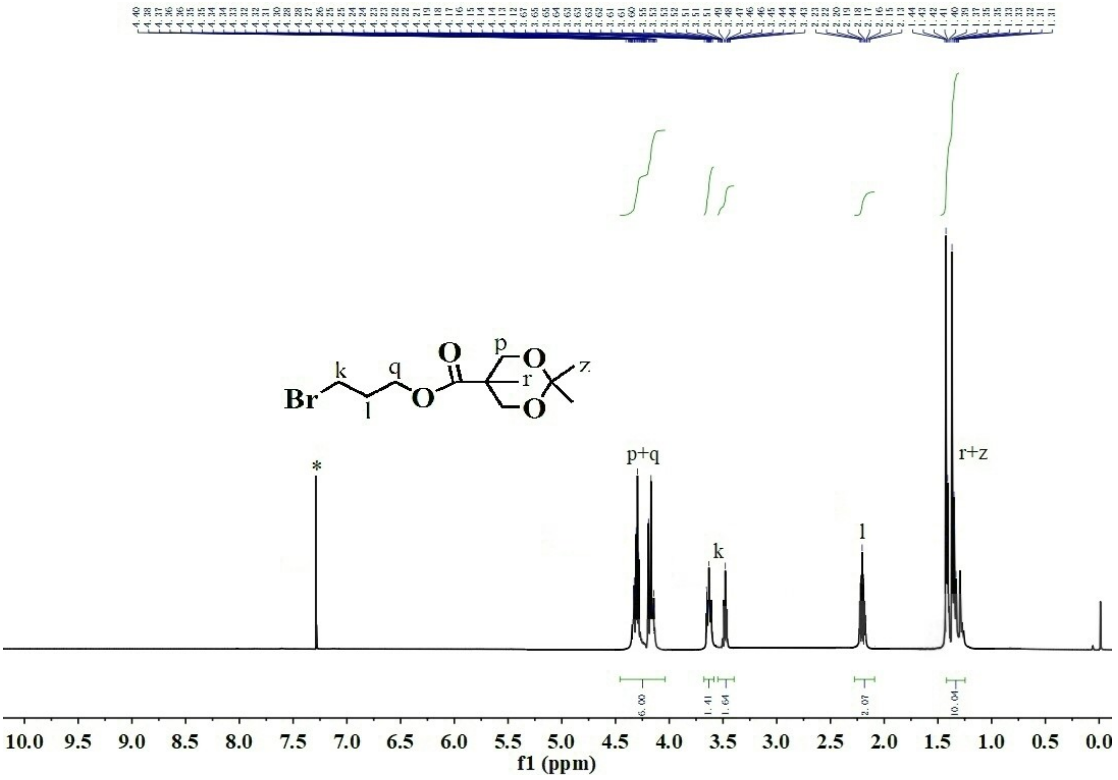


Figure S4. ^{1}H NMR spectrum of compound, **4**.

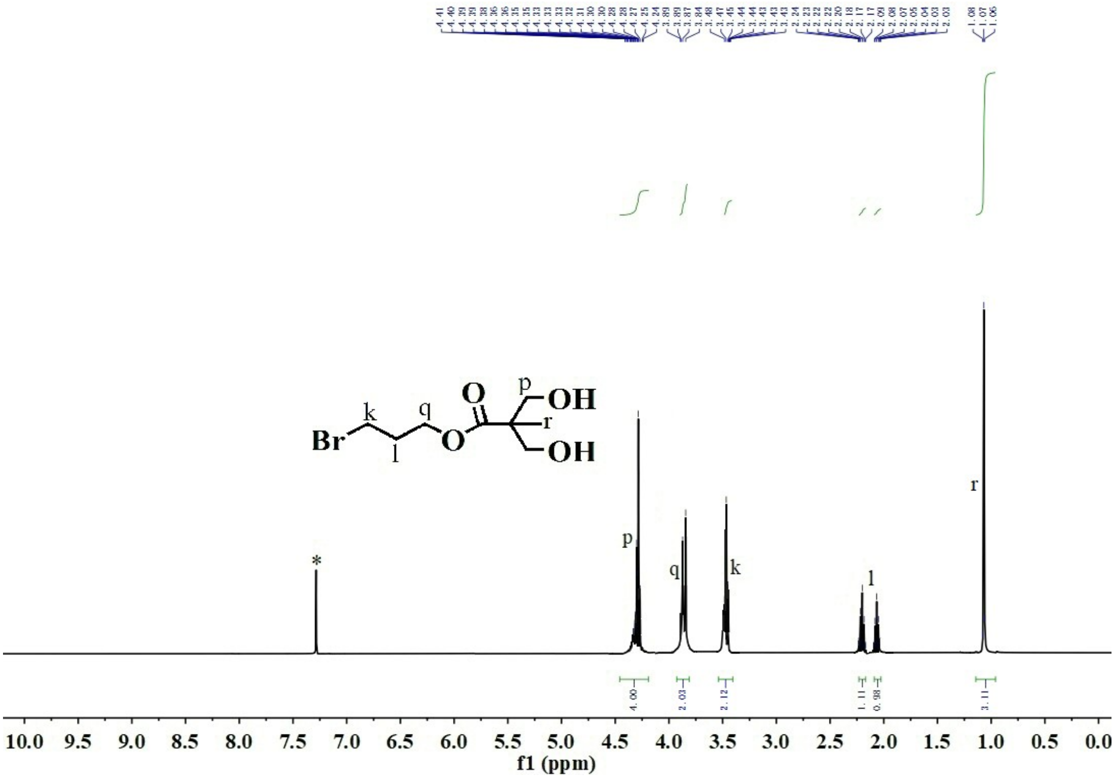


Figure S5. ^{1}H NMR spectrum of compound, **5**.

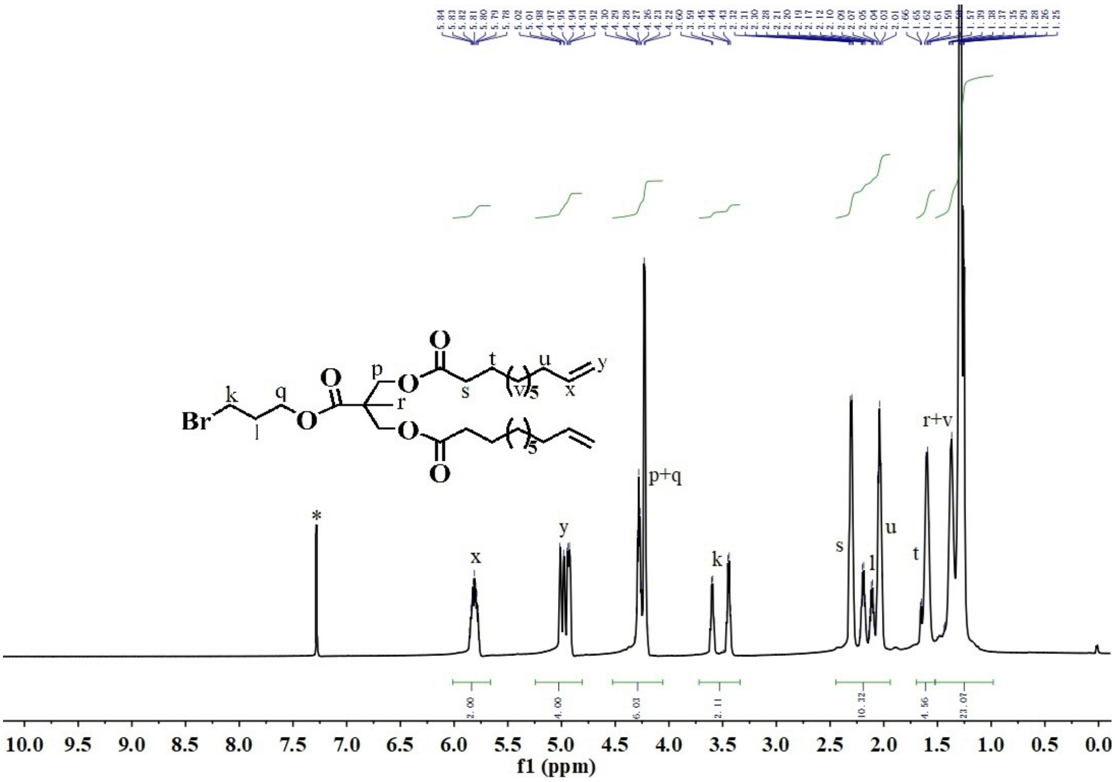


Figure S6. ^{1}H NMR spectrum of diene monomer, **M1**.

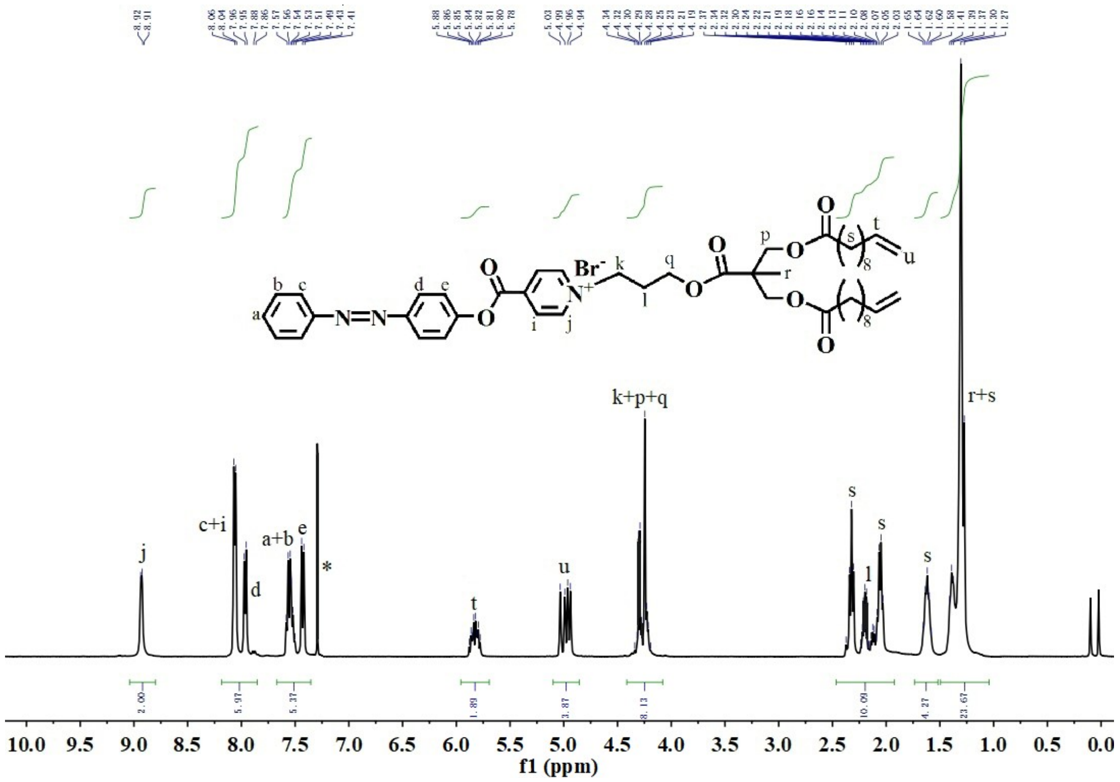


Figure S7. ^{1}H NMR spectrum of ionic azo-diene monomer, **IAzoC$_0$M**.

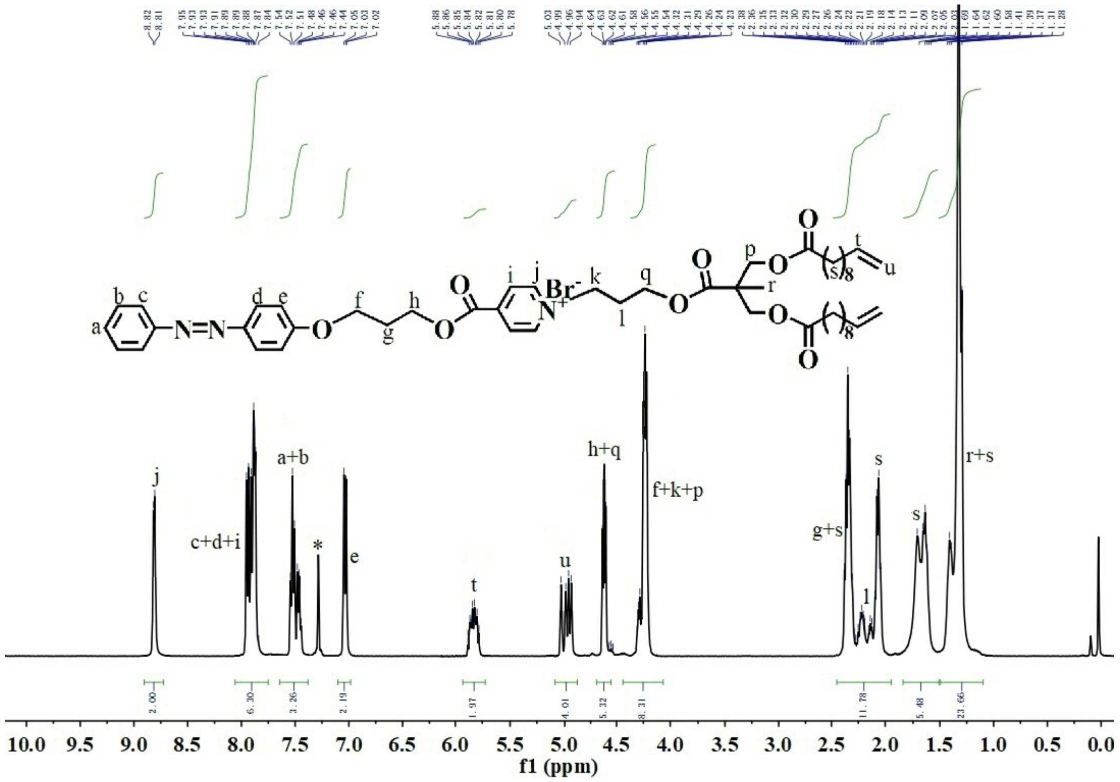


Figure S8. ^{1}H NMR spectrum of ionic azo-diene monomer, **IAzoC$_3$M**.

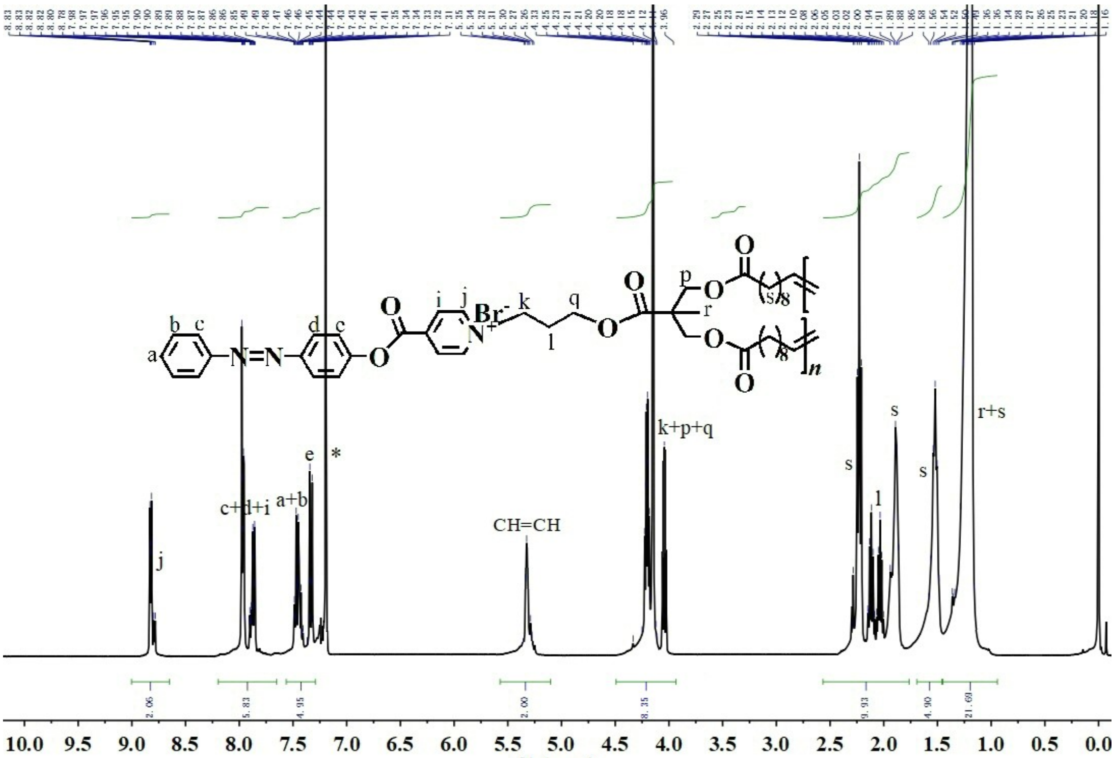


Figure S9. ^{1}H NMR spectrum of ionic azo-homopolymer, **IAzoC$_0$HP**.

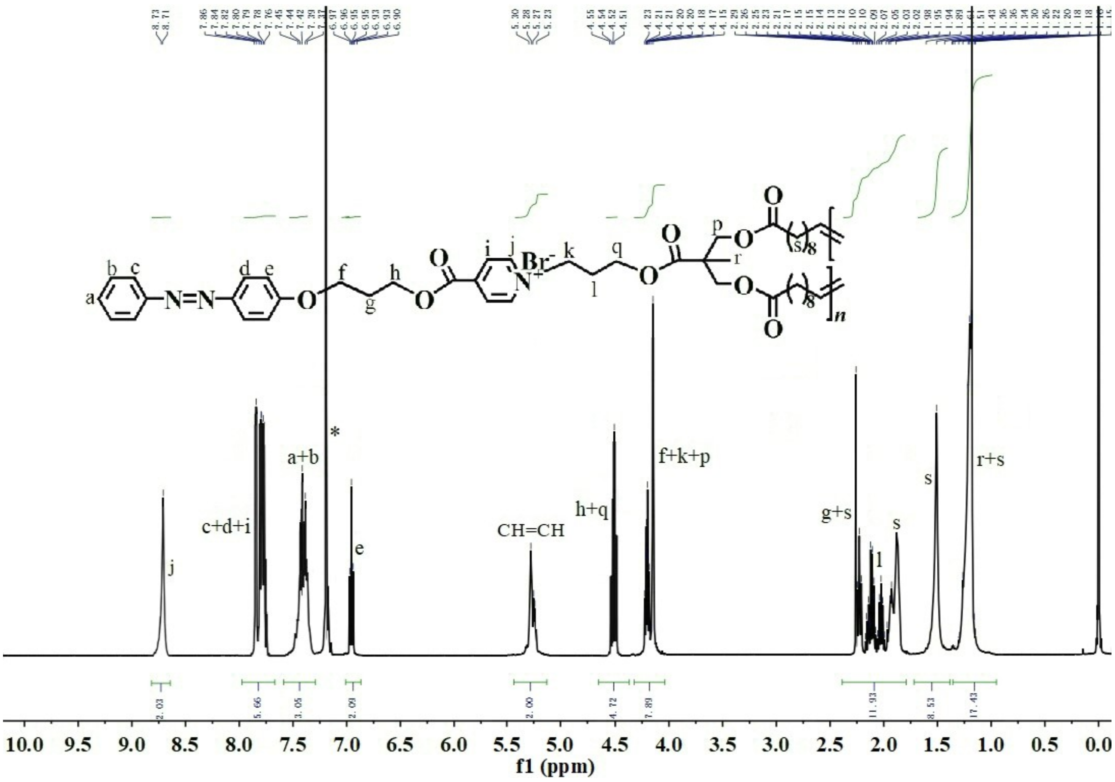


Figure S10. ^{1}H NMR spectrum of ionic azo-homopolymer, **IAzoC$_3$HP**.

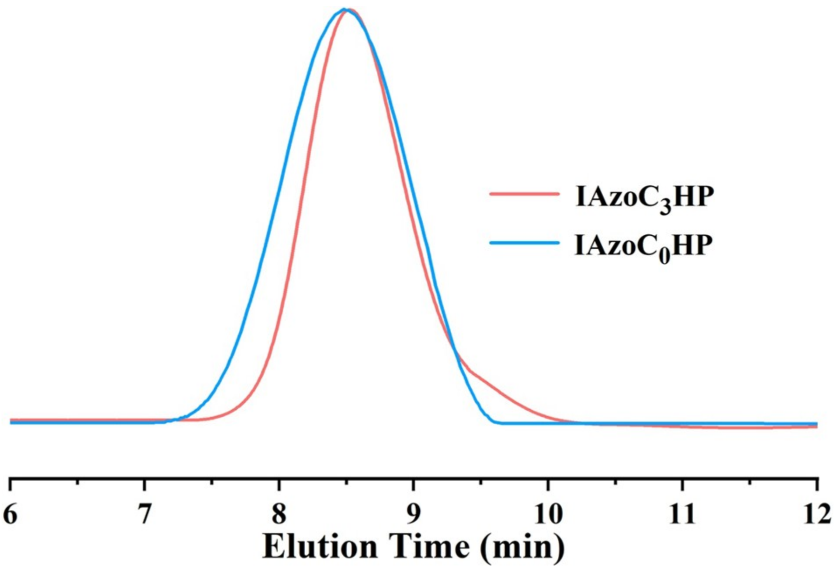


Figure S11. GPC traces of ionic azo-homopolymers, **IAzoC$_p$HPs**.

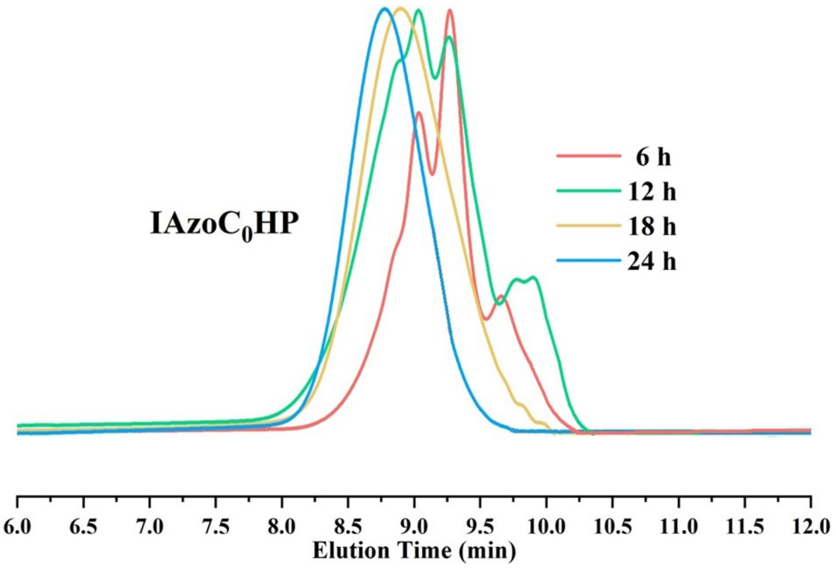


Figure S12. GPC traces of ionic azo-homopolymer, **IAzoC$_0$HP** with different ADMET polymerization times.

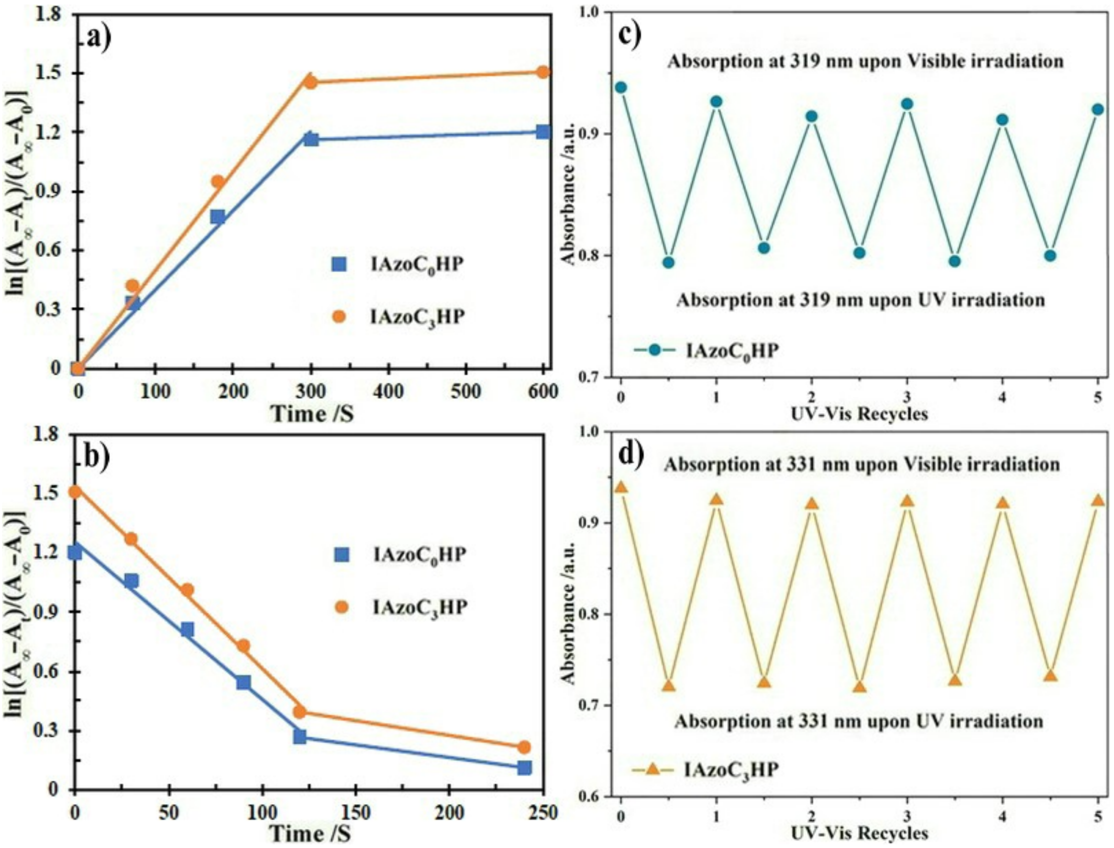


Figure S13. First-order kinetics for (a) *trans→cis* and (b) *cis→trans* photoisomerization transition of **IAzoC$_p$HPs**, corresponding to UV–Vis spectra of **IAzoC$_p$HPs** in **Figure 1**. Absorption changes of (c) **IAzoC$_0$HP**and (d) **IAzoC$_3$HP** under alternating UV- and Vis-light irradiation for 5 cycles.

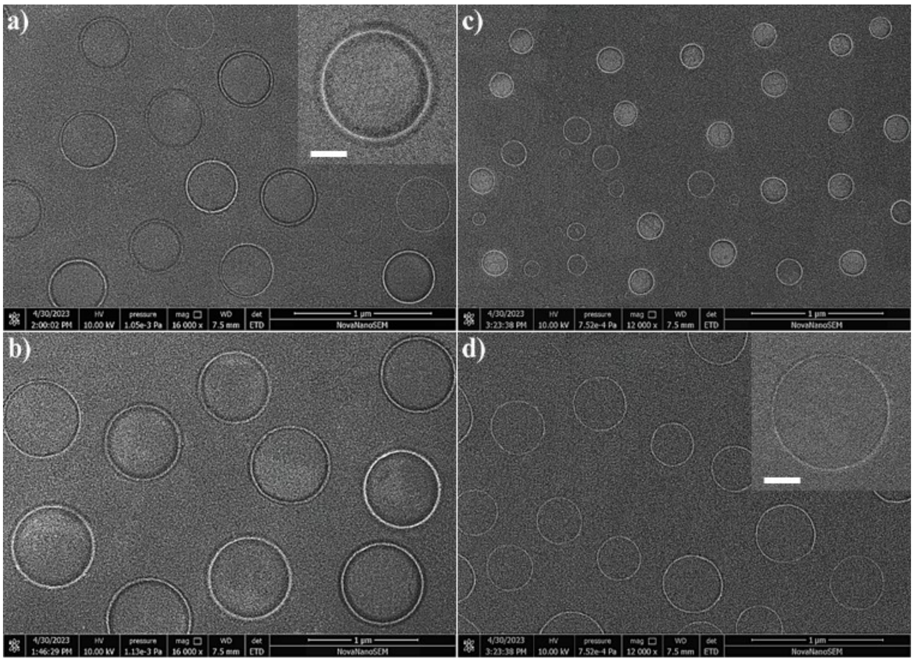


Figure S14. SEM images displaying self-assembled nanostructures of **IAzoC$_p$HPs**

prepared in THF with different initial concentrations: (a, b) 0.03 and 0.06 M for **IAzoC$_3$HP**, (c, d) 0.01 and 0.03 M for **IAzoC$_0$HP**.

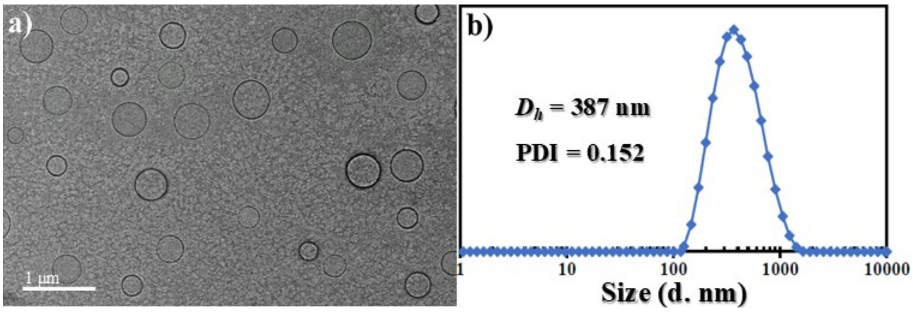


Figure S15. (a) TEM image and (b) corresponding DLS result of polymeric toroid self-assembled from **IAzoC$_0$HP** solution stored for two weeks with the initial concentration of 0.03 M.

Table S1. Self-Assembly of **IAzoC$_p$HPs** in Different Solvents.

Code	Hompolymer	$M_{n,GPC}$ (kDa)	$D_{h,DLS}$ (nm)	PDI	$D_{h,TEM}$ (nm)	Concentration (mol/L)	Solvent
1	**IAzoC$_3$HP**	18.5	140	0.124	95	0.01	CH_2Cl_2
2			155	0.127	133		$CHCl_3$
3			191	0.138	168		Acetone
4	**IAzoC$_0$HP**	19.8	157	0.159	142	0.01	CH_2Cl_2
5			178	0.152	169		$CHCl_3$
6			236	0.143	221		Acetone

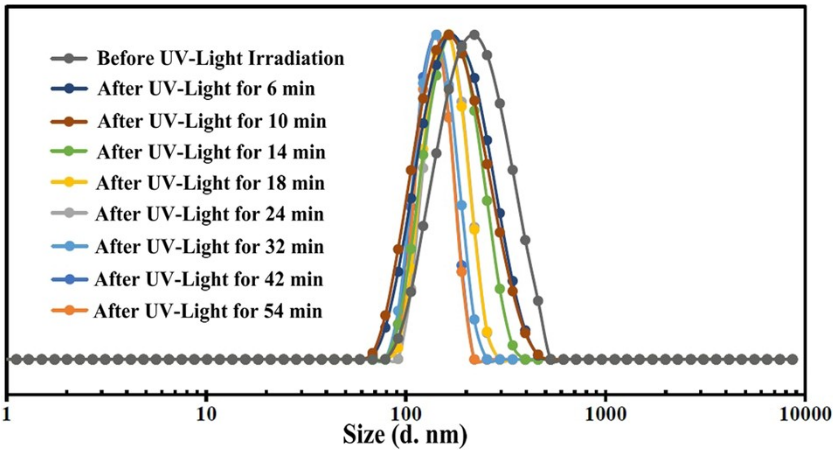


Figure S16. DLS curves of the morphology evolution of toroids from **IAzoC$_0$HP** after UV-light irradiation with different time, corresponding to TEM images in Figure 3.

In DLS plots, **IAzoC$_0$HP** initially formed the preformed spheres with the hydrodynamic diameter (D_h) of 220 nm. Subsequently, D_h decreased to ~163 nm after UV-light irradiation until 24 min and changed from a wider distribution (PDI = 0.276) to the relatively narrow distributions (PDI = 0.189~0.175). After further irradiating UV-light, the particle size became somewhat smaller (D_h = ~152 nm) with similar distributions (PDI = 0.172~0.163), demonstrating that the more uniform assemblies were formed. Thus, the DLS characterization for self-assemblies was consistent with the TEM results in Figure 3. These three D_hs correspond to TEM images in Figure 3a, 3b-f and 3g-i respectively.

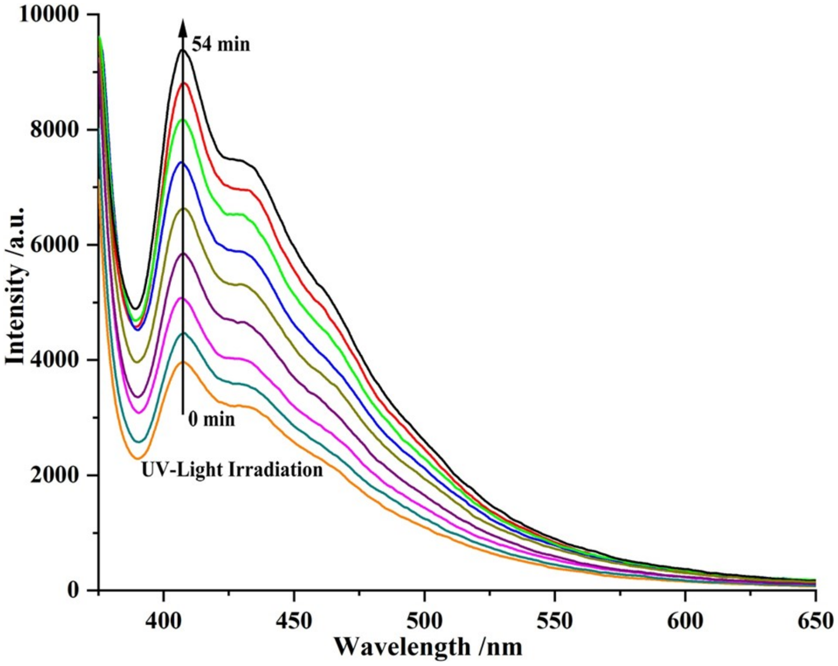


Figure S17. Fluorescence spectrum (λ_{ex} = 390 nm) of ionic azo-homopolymer, **IAzoC$_0$HP** dissolved in THF solution with the concentration of 0.005 M before and after UV-light irradiation, corresponding to the irradiation time in Figure 3.

As shown in Figure S16, the intensity of the fluorescence emission increased considerably with the irradiation of UV-light, corresponding to the various morphology evolution process in Figure 3. Generally, the nonplanar bent-shaped *cis*-isomers hamper the photoinduced electron transfer of azo chromophores, thereby enhancing the fluorescence emission. Moreover, the strong fluorescence would also be exhibited upon spontaneous formation of self-assembled nanoaggregates.[S1] That is to say, *cis*-isomers formed by the shackling isomerization process was insufficient to improve the fluorescence emission significantly, the diverse morphology formed in Figure 3 under different UV-light irradiation times is all that counts for fluorescence enhancement.

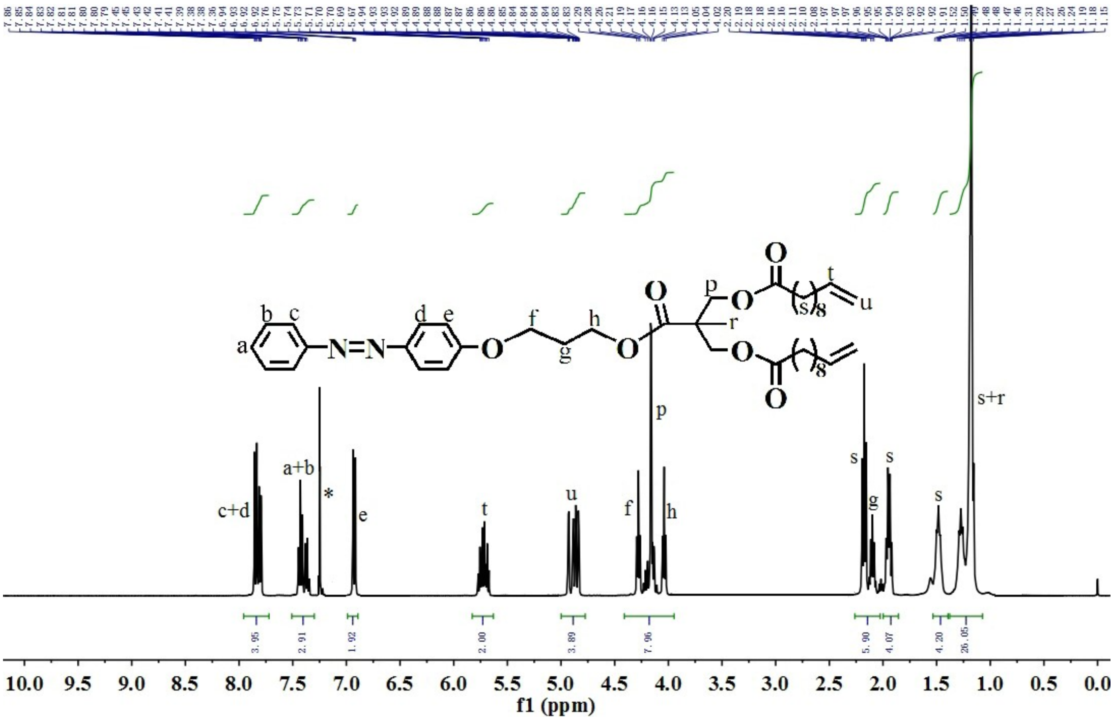


Figure S18. ^{1}H NMR spectrum of azo-diene monomer, **AzoM**.

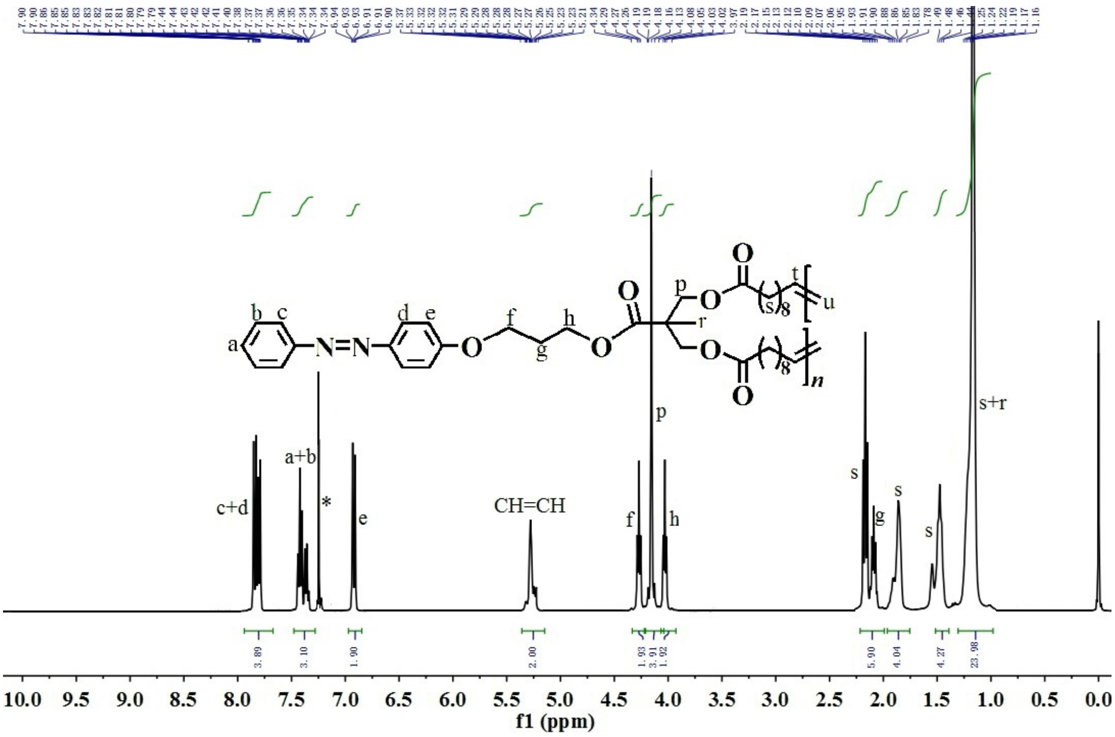


Figure S19. ^{1}H NMR spectrum of azo-homopolymer, **AzoHP**.

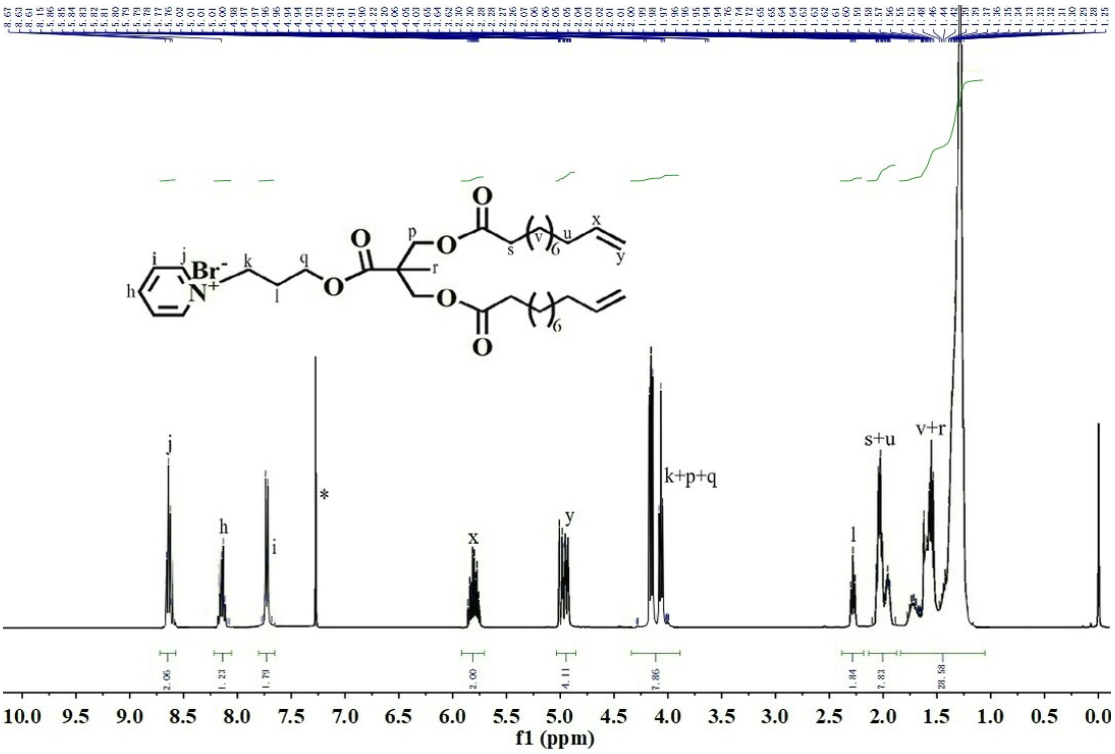


Figure S20. ^{1}H NMR spectrum of ionic diene monomer, **Py-BrM**.

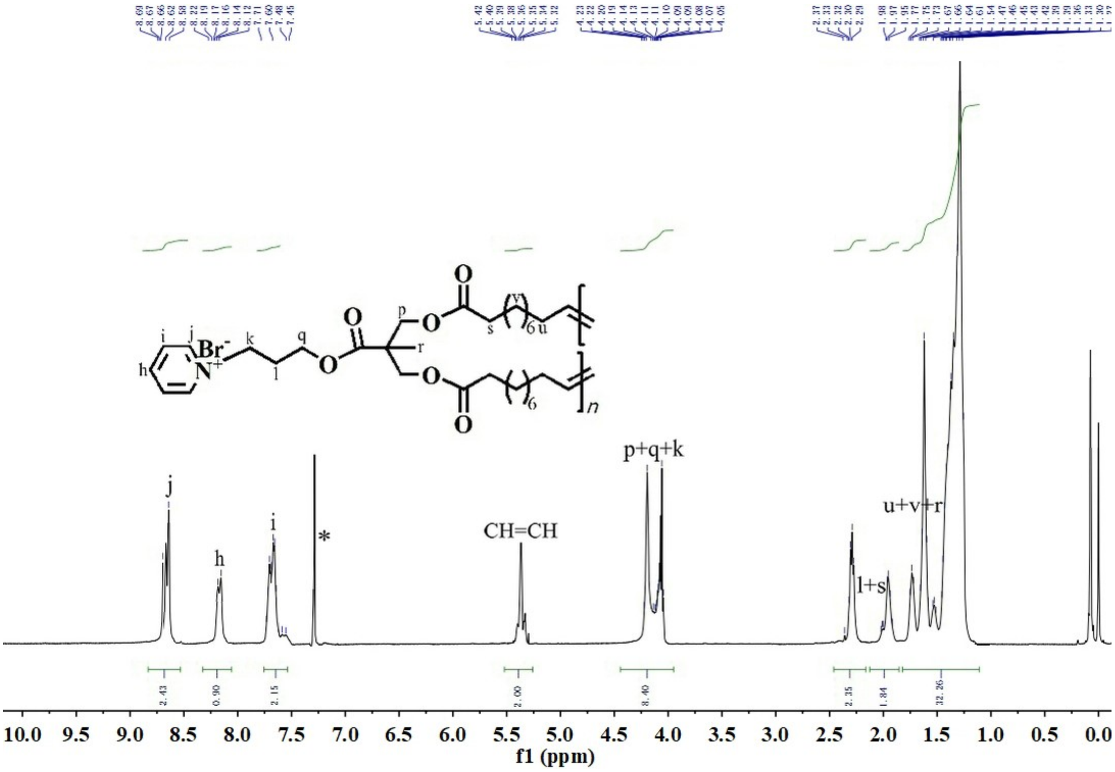


Figure S21. ^{1}H NMR spectrum of pyridinium bromide-homopolymer, **Py-BrHP**.

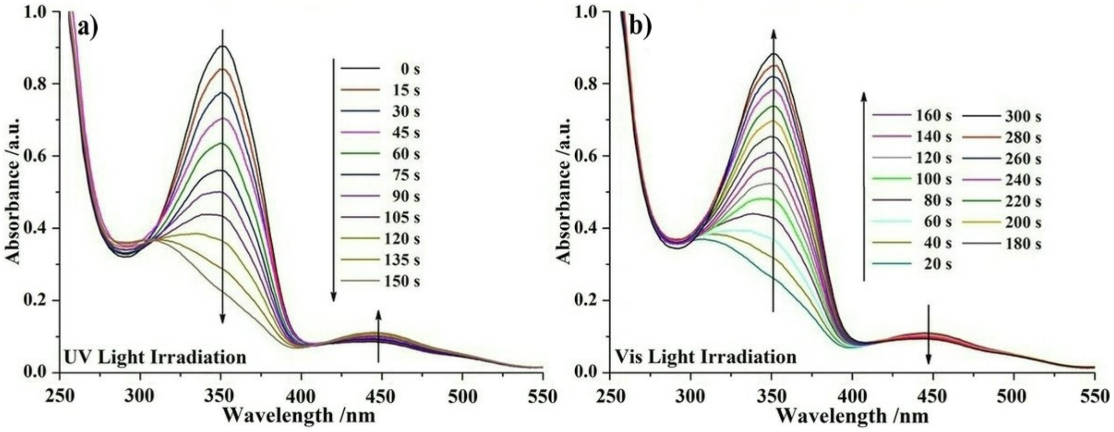


Figure S22. UV–Vis spectra of azo-homopolymer, **AzoHP** in diluted THF solutions with the concentration of 2.5 × 10^{-5} mol/L. Absorbance changes with (a) UV-light and (b) Vis-light irradiation times.

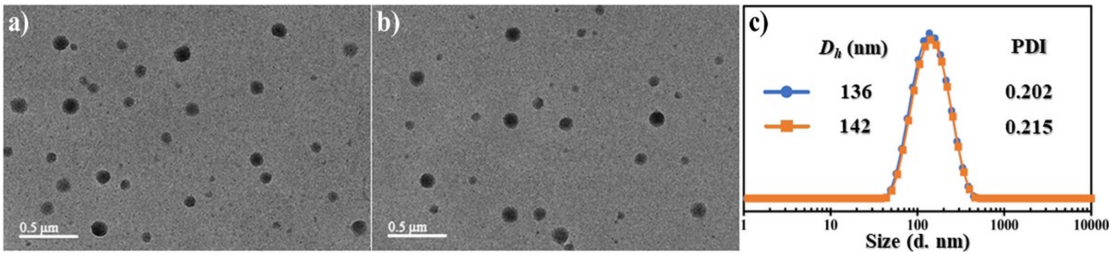


Figure S23. The self-assembly of pyridinium bromide-homopolymer, **Py-BrHP** to form micelles at initial concentration of 0.005 M. (a, b) TEM images of micelles before and after UV-light irradiation. (c) DLS analysis of the corresponding micelles in (a, b).

Table S2. Non-covalent interaction-dependent morphologies from **AzoHP** and **Py-BrHP** in THF with the initial concentration of 0.005 M.

Hompolymer	$M_{\mathrm{n,GPC}}$ (kDa)	M_w/M_n	Morphology	$D_{h,DLS}$ (nm)	PDI	$D_{h,TEM}$ (nm)
AzoHP	20.3	1.41	Amorphous	–	–	–
Py-BrHP	21.2	1.59	Spherical Micelles	136	0.202	106

To prove that the synergistic effect between electrostatic force and π–π interaction plays a critical role in the formation of the stable morphology and tunable size of toroidal assemblies,[S2,S3] we designed and synthesized the homopolymers with different pendants that can provide non-covalent interactions. The synthesis (see Experimental Part), structure and molecular weight characterization (Figure S18–21), and photoisomerization behavior (Figure S22) of the corresponding homopolymer followed the same protocols as **IAzoC$_p$HPs**. As shown in Table S2, the molecular weights of homopolymers, **AzoHP** and **Py-BrHP** were 20.3 and 21.2 kDa, respectively, which were similar to those of **IAzoC$_p$HPs**. However, there is only one non-covalent interaction for **AzoHP** (π–π interaction), meanwhile, UV−Vis analysis of **AzoHP** in Figure S22 displayed that more than 90% of *trans*-isomer converted to *cis*-isomer which can't form π–π stacking after UV light irradiating and reaching photostationary state, thus the non-covalent interaction of **AzoHP** was not strong enough to drive self-assembly and form the regular morphology under the same self-assembly conditions as **IAzoC$_p$HPs**. Differently, TEM image and DLS analysis (Figure S23a and c) showed that the spherical micelles with D_h of 136 nm were formed from **Py-BrHP** as in the presence of electrostatic force, hydrophobic polyolefin backbone and hydrophilic pyridinium cation side-group during the self-assembly process,[S4] however, was insufficient to induce the self-assembly to form vesicle, nanotoroid or other nanostructures. Importantly, these spherical micelles were stable (morphology and size) after UV-light irradiation (Figure S23b and c). These results strongly confirmed our speculation that the effect between multiple non-covalent interactions is essential for the formation of diverse nanostructures.

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