

Supporting Information for

Synthesis of bead-like multicyclic polymer by UV-induced coupling of anthracene-telechelic monocyclic precursor and its reversible topological conversion

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Experimental Section

Materials

Propargyl alcohol was distilled under reduced pressure and stored in dark. Styrene (St, 99%) was distilled under reduced pressure and stored at -20 °C. Copper(I) bromide [Cu^IBr, 95%] was stirred overnight in acetic acid, filtered, washed with ethanol three times successively, and dried in vacuo. Sodium azide (NaN₃), 2-bromoisobutyryl bromide (98%), p-toluenesulfonic acid, 2,2-dimethylol propionic acid, 2,2'-bipyridine (bpy), *N,N'*-dicyclohexylcarbodiimide (DCC), 4-(dimethylamino) pyridine (DMAP), and triethylamine (99.5%) were purchased from Aladdin Reagent of China and used as received. Poly(ethylene oxide) (PEO, $M_n = 2000$ g/mol), 9-anthracenecarboxylic acid, sym-dibenzo-1,5-cyclooctadiene-3,7-diyne (DIBOD), p-toluene sulfonyl chloride (TsCl), and *N,N',N'',N''*-pentamethyldiethylenetriamine (PMDETA) were purchased from TCI of China and used as received. Sodium hydroxide (NaOH), sodium chloride (NaCl), anhydrous sodium sulfate (Na₂SO₄), 2,2-dimethoxypropane, concentrated hydrochloric acid (HCl), thionyl chloride (SOCl₂), *N,N*-dimethylformamide (DMF) and other solvents were purchased from Sinopharm Chemical Reagent Co. and used without further purification.

Characterization

Nuclear Magnetic Resonance (NMR). All NMR spectra were recorded on a Bruker NMR spectrometer (resonance frequency of 400 MHz for ¹H and 100 MHz for ¹³C) operated in the Fourier transform mode. The samples were dissolved in chloroform-d with tetramethylsilane (TMS) as an internal reference.

Fourier transform infrared (FT-IR). FT-IR spectra were recorded on a Bruker VECTOR-22 IR spectrometer. The polymer samples were dissolved in dry THF and then cast onto a KBr disk to form the film by solvent evaporation under an infrared lamp.

UV/Vis Spectroscopy. UV spectra were recorded on a PerkinElmer Lambda2 UV-vis spectrometer in the wavelength range from 300 to 600 nm.

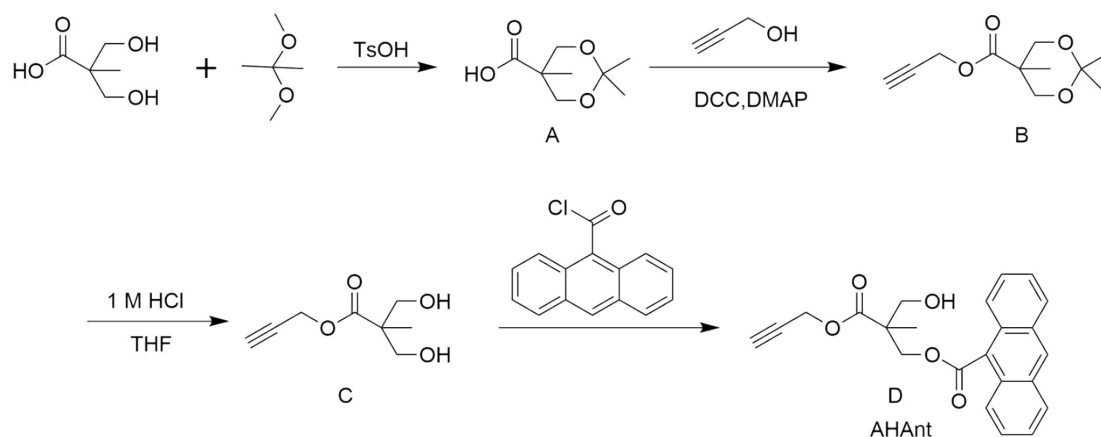
Gel permeation chromatographic (GPC). Molecular weights and molecular weight distributions were determined by gel permeation chromatography (GPC, Waters 1515) equipped with RI 2414 detector at 35 °C and microstyragel columns calibrated with monodisperse polystyrene standards. Tetrahydrofuran (THF) was used as the eluent at a flow rate of 1.0 mL/min.

MALDI-TOF MS. The matrix-assisted laser desorption ionization time-of-flight mass spectrometry measurements were conducted on a Perspective Biosystem Voyager-DESTR MALDI-TOF Mass spectrometer.

Elemental Analysis (EA). The contents of elements were measured on Vario EL cube. The instrument was equipped with liquid loading parts and autosampler. Under 950 °C conditions, the content of carbon, hydrogen, nitrogen (C, H, N) elements in organic compound samples could be measured quickly and accurately simultaneously. Under the circumstance of 1150 °C, the percentage of oxygen (O) elements in organic compound samples could be measured quickly and accurately.

UV radiation was performed by using a spot light source (NICHIAD SX, 033B/233A), and UV intensity was about 0.2 W/cm².

Experimental Section



Scheme S1. The synthetic route of AHAnt.

Synthesis of 2,2,5-trimethyl-1,3-dioxane-5-carboxylic acid (compound A)

In a 250 mL round-bottomed flask, 2,2-dimethylol propionic acid (13.41 g, 10 mmol), 2,2-dimethoxypropane (18.40 mL, 15 mmol) and p-toluenesulfonic acid monohydrate (0.86 g, 5 mmol) were added successively, then acetone (100 mL) was poured as the solvent. The reaction mixture was kept at room temperature for approximately 30 minutes, and the turbid mixture became clear. The mixture was kept stirring at room temperature for 2 h, and the mixed solution of aqueous ammonia and ethanol (v:v = 1:1, 5 mL) were added. Continuous stirring for 5 minutes, the insoluble salt was removed by filtration, and the solvent was removed by rotary evaporation to obtain white solid. The residue was dissolved using dichloromethane, then washed with brine for 2 times (2×100 mL). The organic layer was dried over anhydrous Na_2SO_4 for 12 hours, and the solvent was evaporated, then the product was obtained as white solid (15.68 g, 90%) after drying in vacuo under room temperature for 24 hours.

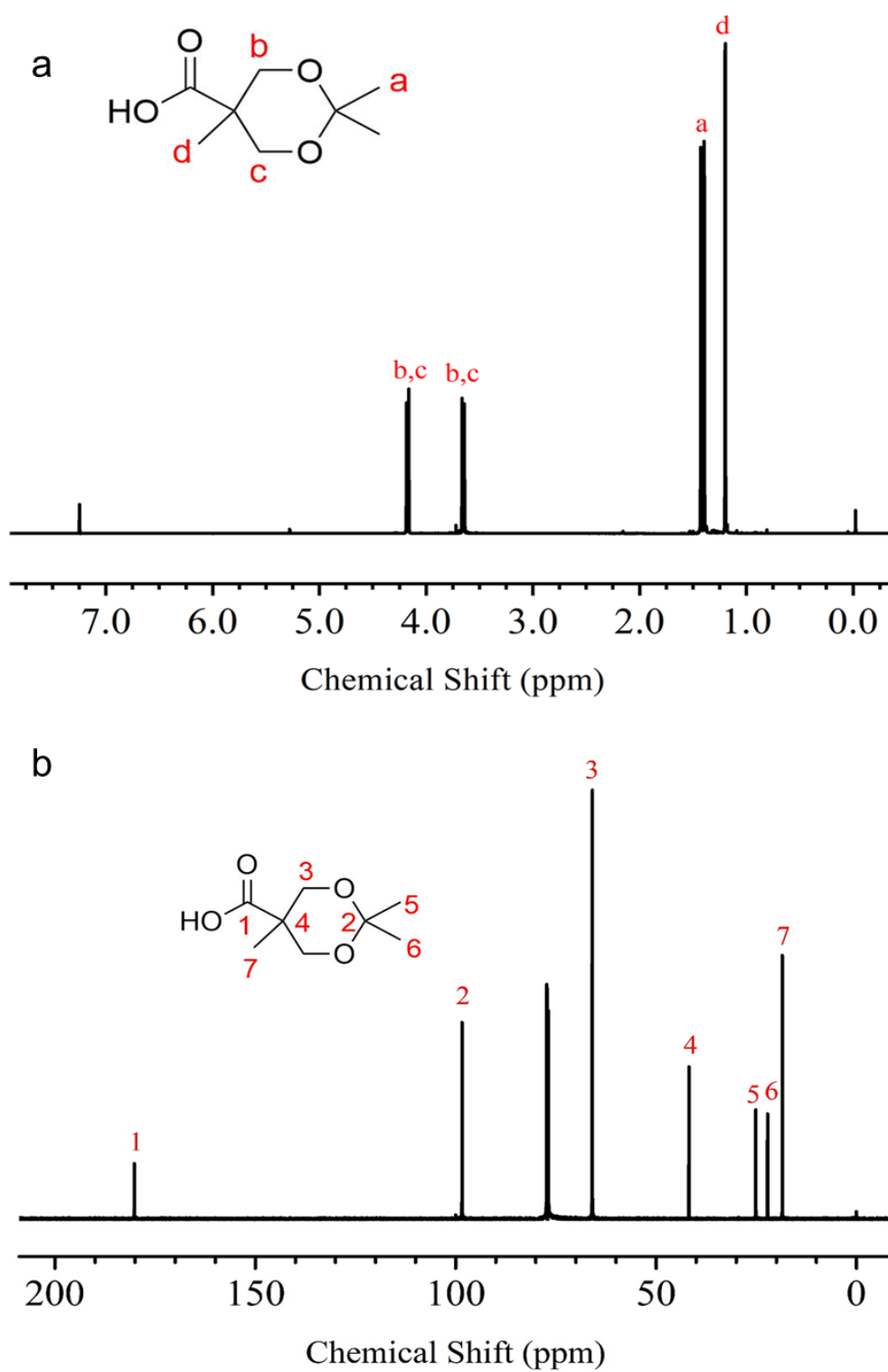
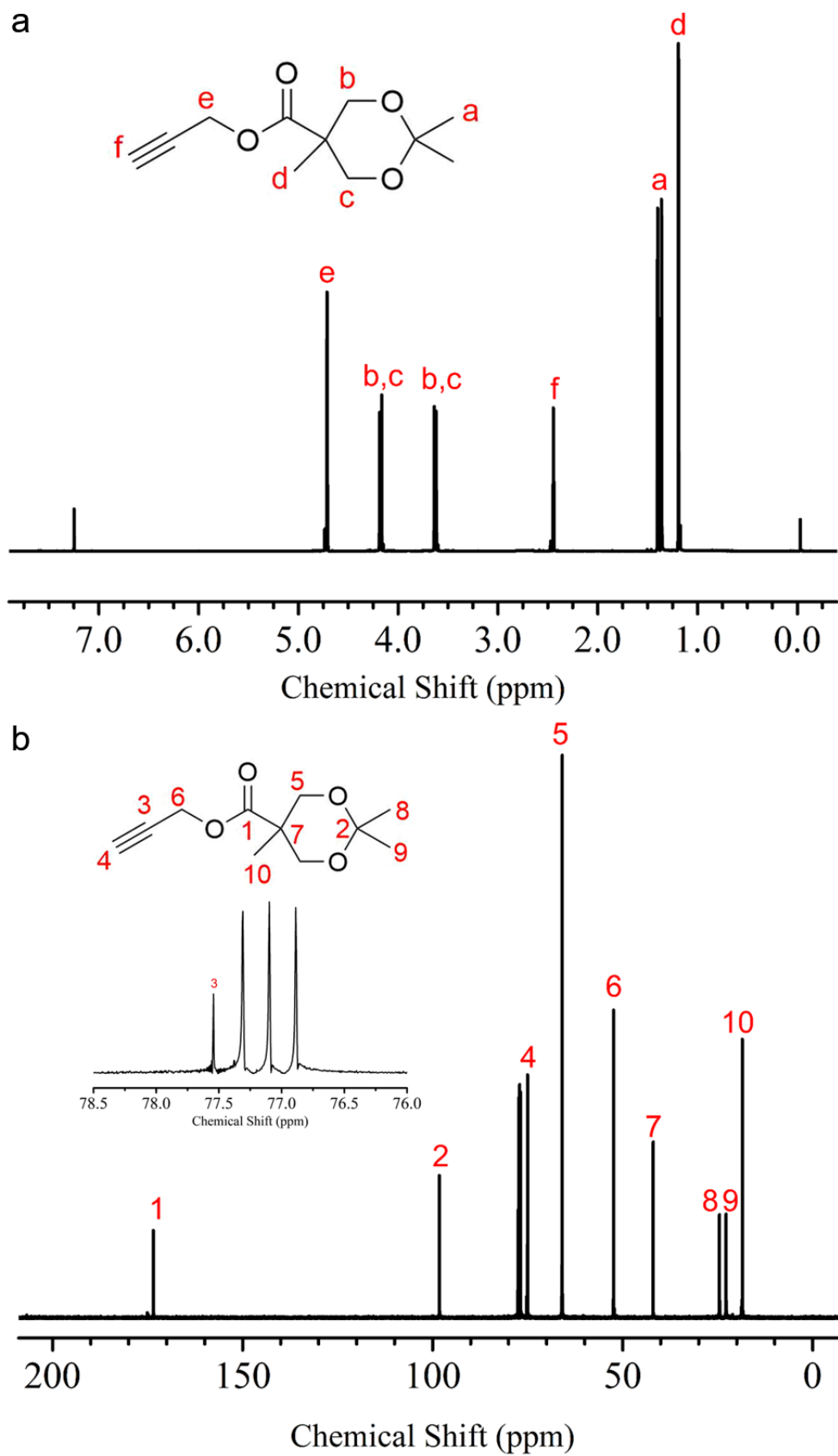


Fig. S1 ^1H NMR (a) and ^{13}C NMR (b) spectra of the compound A in CDCl_3 .

Synthesis of prop-2-yn-1-yl 2,2,5-trimethyl-1,3-dioxane-5-carboxylate (compound B)

Compound A (15.68 g, 90 mmol), propargyl alcohol (6.70 mL, 120 mmol), and DMAP (5.50 g, 45 mmol) were added into a 250 mL round-bottomed flask successively. Dichloromethane (150 mL) was added to dissolve the reactant, then the mixture was cooled by ice bath. DCC (21.66 g, 105 mmol) dissolved in dichloromethane (50 mL) was added drop-wise. After completion of the addition, the mixture reacted for 12 h at room temperature. The mixture was filtered, and washed with brine for 3 times (3 × 100 mL). The organic layer was dried over anhydrous Na₂SO₄ for 12 hours, and the solvent was evaporated. The residue was further purified by passing through a silica column (ethyl acetate: petroleum ether = 1:25, v/v) to give yellow viscous liquid (17.27 g, yield: 90.4%).



**Synthesis of prop-2-yn-1-yl 3-hydroxy-2-(hydroxymethyl)-2-methylpropanoate
(compound C)**

In a 250 mL round-bottomed flask, the compound B (21.23 g, 100 mmol) was dissolved in THF (53 mL), then HCl (53 mL, 1M) was added. The reaction was conducted at the room temperature. After 6 hours, the mixture was extracted with dichloromethane and dried over anhydrous Na₂SO₄, then filtering and concentrating, the crude product was further purified by passing through a silica column (ethyl acetate: petroleum ether = 2:1, v/v) to give viscous liquid (13.02 g, yield: 75.6 %).

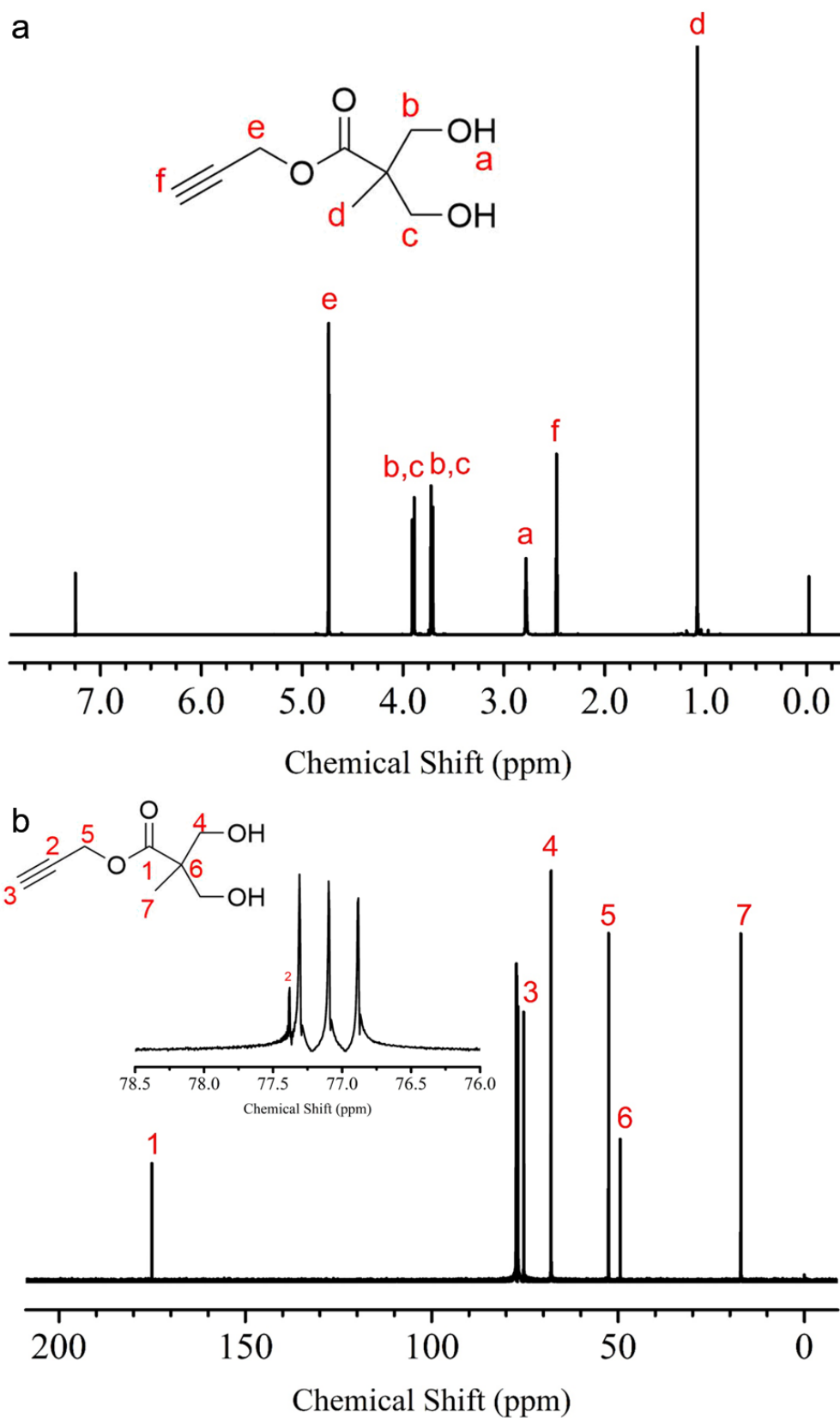


Fig. S3 ^1H NMR (a) and ^{13}C NMR (b) spectra of the compound C in CDCl_3 .

Synthesis of 2-(hydroxymethyl)-2-methyl-3-oxo-3-(prop-2-yn-1-yloxy) propyl anthracene-9-carboxylate (AHAnt)

According to previous literature, 9-anthracenoyl chloride was synthesized.¹

In a 500 mL round-bottomed flask, compound C (7.74 g, 45 mmol) and TEA (4.20 mL, 30 mmol) were added successively, then dried dichloromethane (400 mL) was poured as solvent. Under the ice bath, 9-anthracenoyl chloride dissolved with dichloromethane (50 mL) were added to the mixture drop-wise. After completion of addition, the mixture reacted overnight. The solvent was removed in vacuo, and the residue was further purified by passing through a silica column (dichloromethane as eluent) to give yellow viscous liquid (9.36 g, yield: 55.2 %). The result of elemental analysis was C: 71.54%, H: 5.83%, and O: 21.43%, respectively.

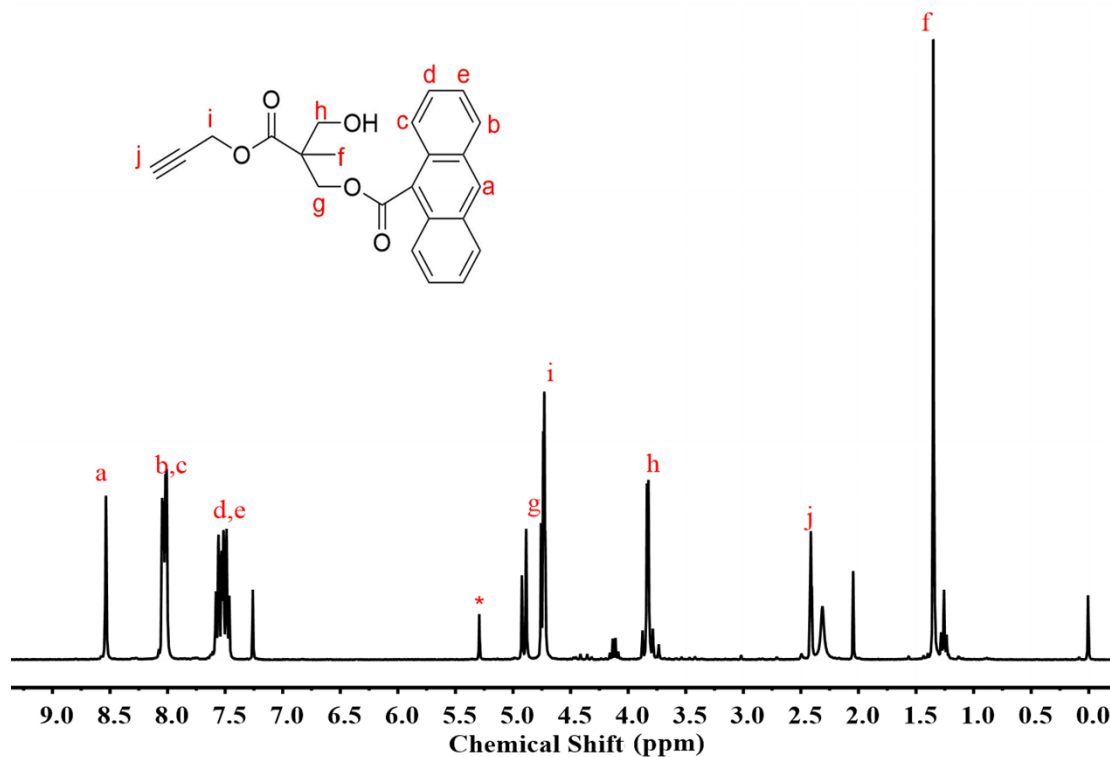


Fig. S4 ¹H NMR spectrum of AHAnt in CDCl₃. (*: dichloromethane)

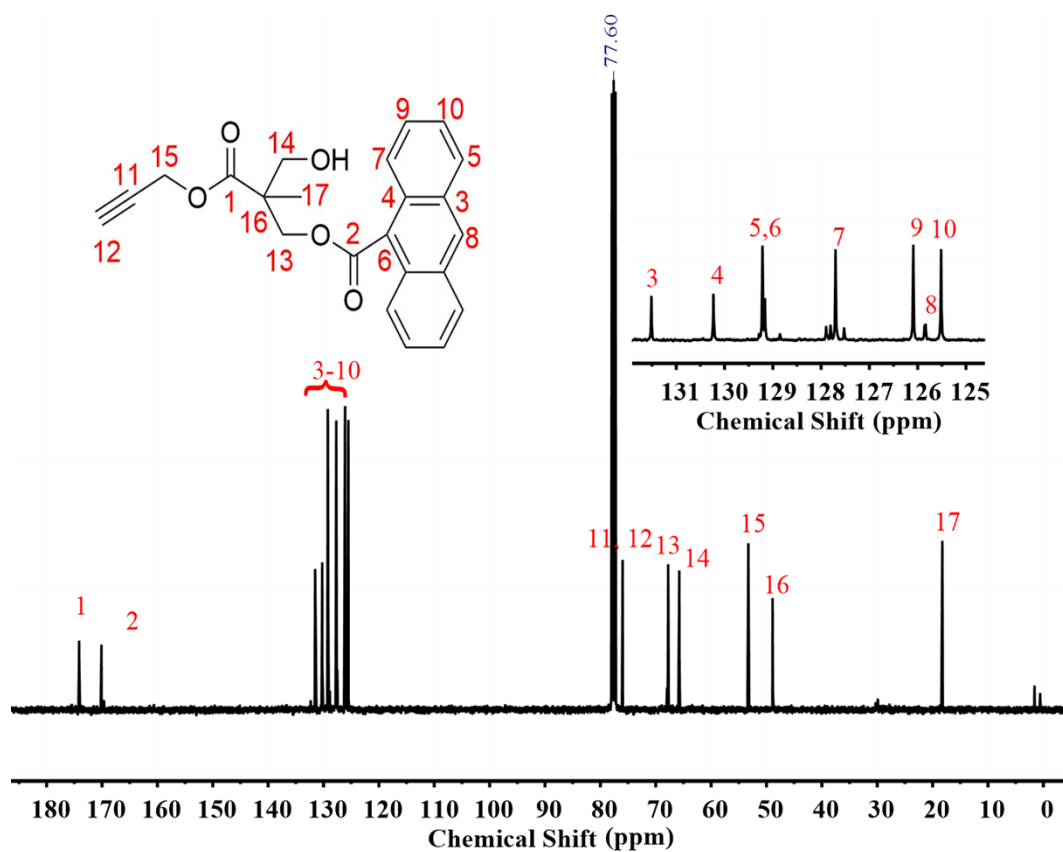


Fig. S5 ^{13}C NMR spectrum of AHAnt in CDCl_3 .

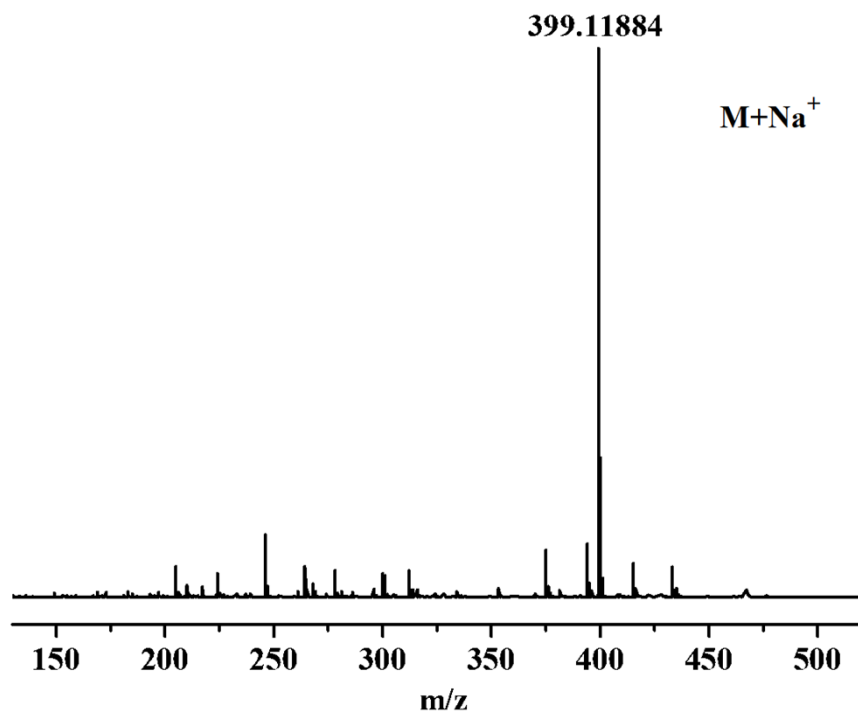


Fig. S6 ESI-MS spectrum of AHAnt.

Synthesis of PEO-Ts

In a 250 mL round-bottomed flask, anhydrous dichloromethane (50 mL) was added to dissolve PEO (15.00 g, 7.5 mmol), and then TEA (21 mL, 150 mmol) was added. After stirring vigorously for 10 min under the room temperature, TsCl (2.85 g, 15 mmol) dissolved in dichloromethane (25 mL) was added drop-wise into the reaction system under the ice bath. The mixture was kept stirring for 12 hours under 50 °C, the solution was washed with 1M HCl for three times (3×100 mL), and dried with anhydrous Na_2SO_4 and anhydrous Na_2CO_3 , followed by filtering and concentrating. PEO-Ts (14.05 g, yield: 90.0%) was obtained as white solid by precipitating in ice diethyl ether.

Synthesis of PEO-N₃

In a 250 mL round-bottomed flask, PEO-Ts (7.02 g, 3 mmol), sodium azide (3.54 g, 60 mmol) and DMF (60 mL) were added successively. The reaction mixture was kept at 90 °C overnight. After completion of the reaction, DMF was removed by vacuum distillation, and the residual was dissolved in THF followed by passing through a neutral alumina column to remove the excess NaN_3 , then the polymer solution was concentrated and precipitated in iced diethyl ether to afford PEO-N₃ (6.80 g, yield: 85%) as yellow solid.

Synthesis of PEO-ant

In a 100 mL reaction bottle, PEO-N₃ (5.30 g, 2.5 mmol), AHAnt (2.07 g, 5.5 mmol), PMDETA (1.04 mL, 5 mmol), $\text{Cu}^{\text{I}}\text{Br}$ (7.17 g, 5 mmol) and DMF (40 mL) were added successively. The mixture was bubbled with N_2 for 30 min, then the flask was sealed

and kept stirring at 60 °C for 12 h. After the completion of reaction, DMF was removed by vacuum distillation, and the residue was dissolved in dichloromethane followed by passing through a neutral alumina column to remove the copper salt. The polymer solution was concentrated by a rotary evaporator and precipitated into iced diethyl ether, PEO-ant (5.80 g, yield: 84.3%) was obtained as yellow solid after filtration and drying under vacuum for 24 h.

Synthesis of ATRP macroinitiator PEO-Br

In a 100 mL round-bottomed flask, PEO-ant (2.75 g, 1 mmol), TEA (1.39 mL, 10 mmol) and dichloromethane (30 mL) was added successively, and the mixture was stirred under the ice bath, then 2-bromoisobutyryl bromide (2.39 g, 10 mmol) dissolved in dichloromethane (20 mL) was added dropwise. The mixture was kept stirring for 12 h under ice-water bath, and then reacted at room temperature for another 12 hours. After the completion of the substitution, the solution was washed with brine for three times and dried with anhydrous sodium sulfate for 12 h. PEO-Br was obtained as pale yellow solid (2.52 g, yield: 80%) after precipitating in iced diethyl ether.

Synthesis of PEO-PS-Br

The typical ATRP process was as follows: PEO-Br (600 mg, 0.2 mmol), Cu^IBr (58 mg, 0.4 mmol), bpy (187 mg, 1.2 mmol), styrene (3.12 g, 30 mmol) and anisole (3.60 mL) were added to a 10 mL tube with magnetic bar. After three freeze-vacuum-thaw cycles, the tube was sealed under freezing and vacuum conditions, then it was immersed in an oil bath at 105 °C for 3 hours. After the completion of polymerization, the tube was taken out and placed in liquid nitrogen to quench the polymerization. The polymer

solution was exposed to air and diluted with THF, and the copper salt was removed by passing through neutral alumina column. Then the solution was concentrated by a rotary evaporator and was precipitated in a large amount of ice n-hexane for three times. After centrifugation, the precipitate was collected and dried in a vacuum drying oven for 24 hours to obtain PEO-PS-Br (990 mg, yield: 24%) as a pale yellow solid.

Synthesis of PEO-PS-N₃

PEO-PS-Br (940 mg), sodium azide (1.01 g) and dried DMF (30 mL) were added to a 100 mL round bottom flask, and reaction was performed at 60 °C for 24 hours. After the reaction was completed, the unreacted sodium azide was removed by filtration, and DMF was removed by a rotary evaporator. The crude product was dissolved in THF, and followed by passing through a neutral alumina column to remove residual sodium azide. Then the polymer solution was concentrated, and precipitated twice in a large amount of ice n-hexane. After filtration, the precipitate was collected and dried overnight in a vacuum drying oven to afford PEO-PS-N₃ (900 mg, yield: 96%) as a pale yellow solid.

Synthesis of anthracene-telechelic monocyclic precursor (C(PEO-PS)-ant)

PEO-PS-N₃ (80 mg, 0.01 mmol) was dissolved in dry THF (500 mL), and bubbled with nitrogen for 30 mins, then DIBOD (100 mg, 0.5 mmol) dissolved in THF (1 mL) was added slowly to the above system, and the mixture was kept at room temperature for 12 hours. After the completion of reaction, the polymer solution was concentrated and precipitated three times in a large amount of ice-cold n-hexane, followed by centrifugation, and the precipitate was collected and dried overnight in a vacuum drying

oven to obtain C(PEO-PS)-ant (75 mg, yield: 93%) as an orange solid.

Synthesis of bead-like multicyclic polymer

C(PEO-PS)-ant (12 mg) was dissolved in THF (120 μ L), then the solution was transferred to a 5 mL quartz tube and irradiated with 365 nm UV. At predetermined intervals, a small portion of solution was taken for analysis. After 8 hours of irradiation, the polymer solution was precipitated in a large amount of ice-cold n-hexane, followed by centrifugation, and the precipitate was collected and dried overnight in a vacuum drying oven to afford bead-like multicyclic polymer as a dark yellow solid (10.5 mg, yield: 87%).

Topological conversion between bead-like multicyclic polymer and monocyclic polymer

Bead-like multicyclic polymer (10 mg) was dissolved in THF (100 μ L), then the solution was transferred to a 5 mL quartz tube and irradiated under 254 nm ultraviolet light for 2 hours. After the reaction was completed, the solution was precipitated in ice-cold n-hexane followed by centrifugation, the precipitate was collected, and dried in a vacuum drying oven overnight to obtain a pale yellow solid (8.5 mg, yield: 85%).

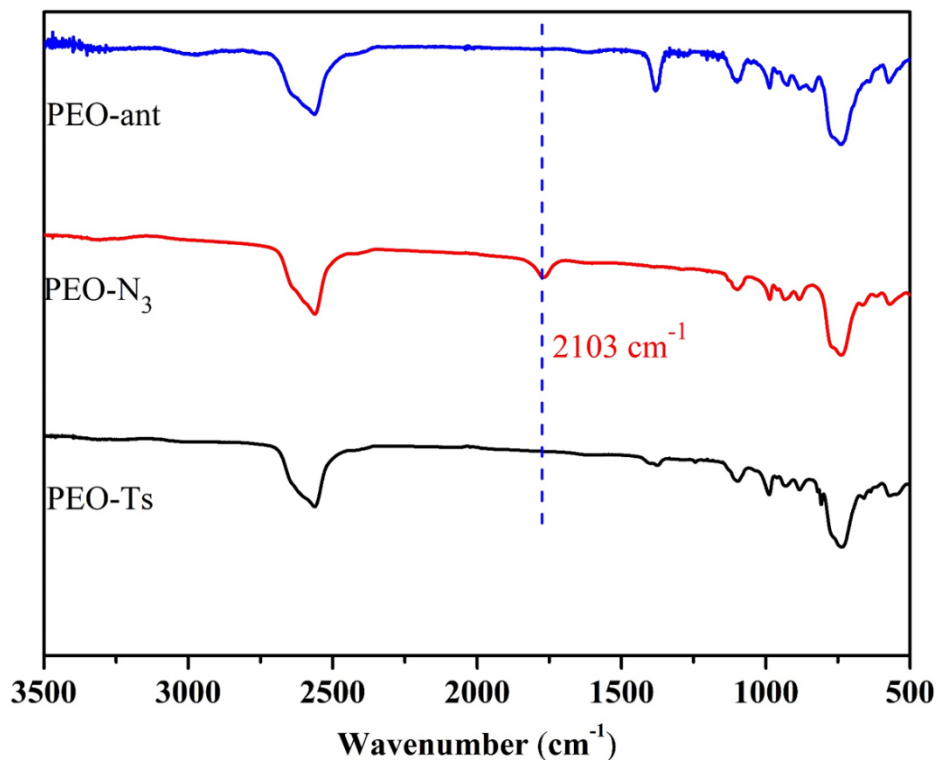


Fig. S7 FT-IR spectra of PEO-Ts (black line), PEO-N₃ (red line) and PEO-ant (blue line).

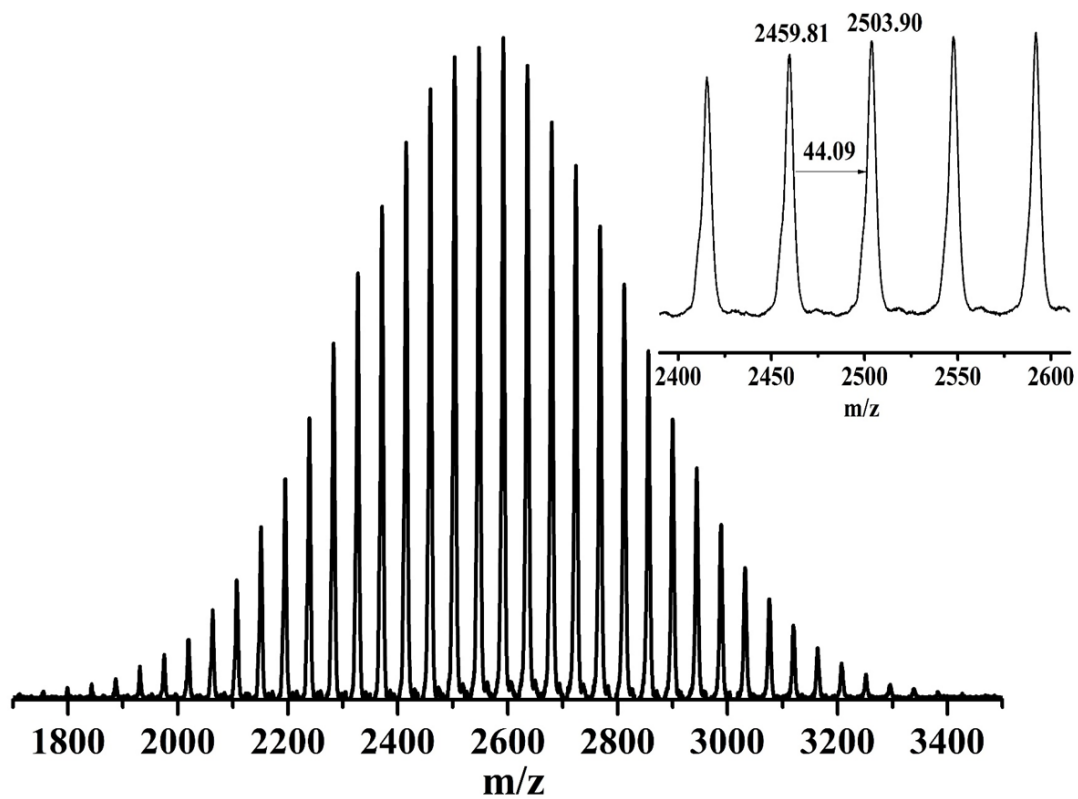


Fig. S8 MALDI-TOF MS spectrum of PEO-ant.

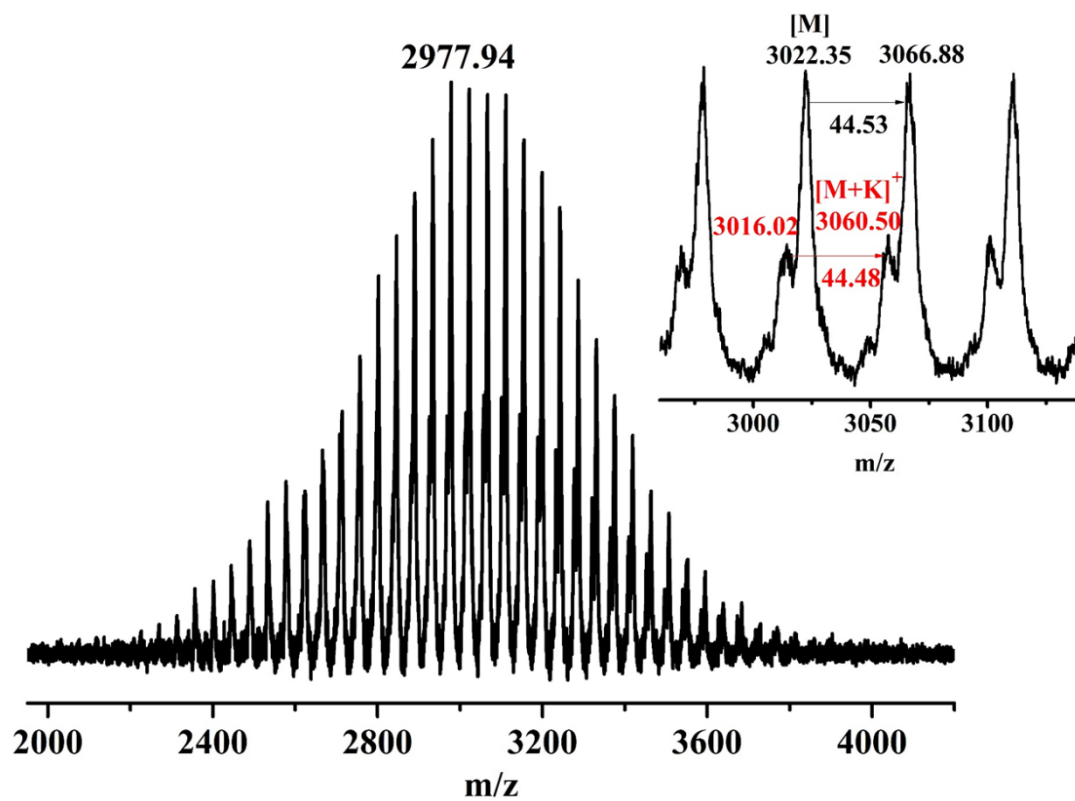


Fig. S9 MALDI-TOF MS spectrum of PEO-Br.

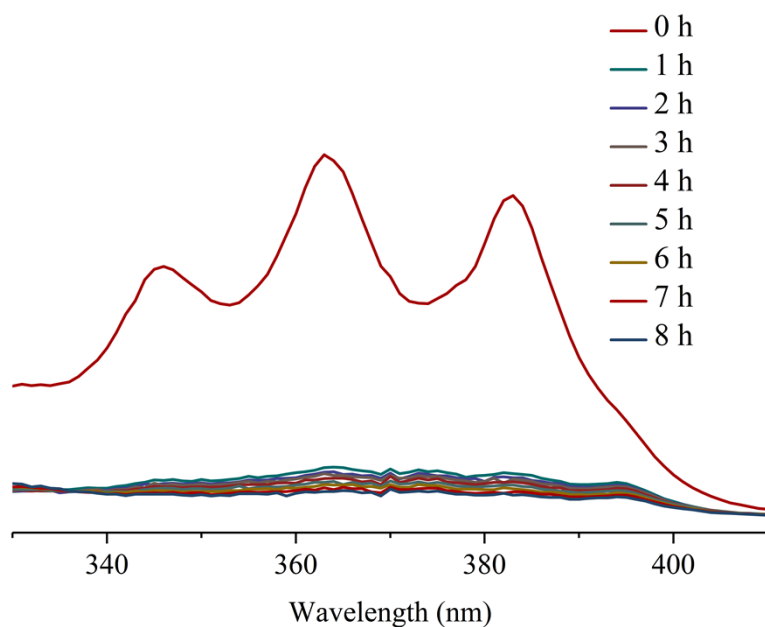


Fig. S10 Time-course UV-Vis spectra of C(PEO-PS)-ant upon irradiation at 365 nm in THF.

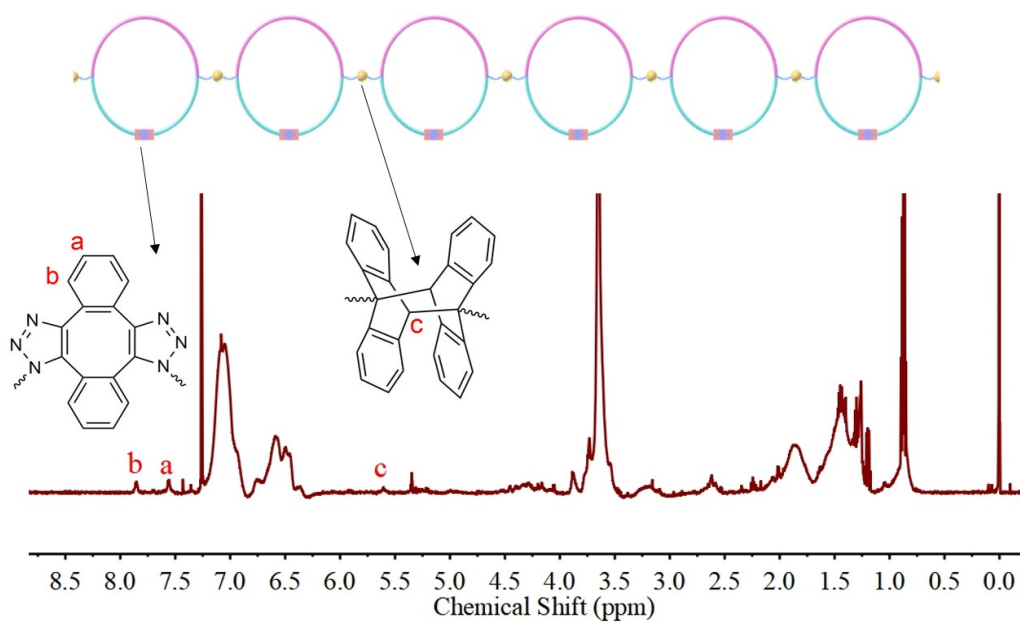


Fig. S11 ^1H NMR spectrum of the bead-like multicyclic polymer in CDCl_3 .

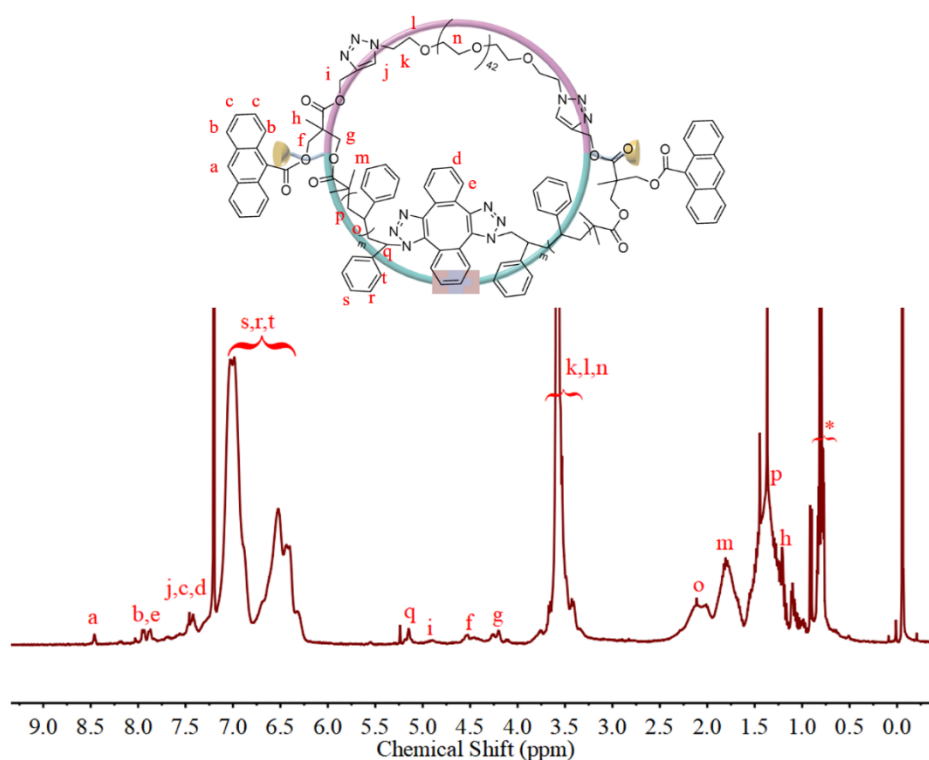


Fig. S12 ^1H NMR spectrum of bead-like multicyclic polymer after irradiation with 254 nm UV for 2 h (in CDCl_3). (*: n-hexane)

Reference

- 1 J. Karthikeyan and N. Yoshikai, *Org. Lett.*, 2014, **16**, 4224-4227.