

Supporting Information

Side-Chain *meta*[6]Cycloparaphenylene-Based Nanoring-Containing Polymers

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1. General Information

1.1 Materials

All reagents were purchased from the *Sigma-Aldrich*, *Alfa Aesar*, *J&K Chemicals*, *Energy Chemicals*, *Aladdin Reagents*, *Meryer Chemicals* or *Leyan Chemicals* and used without further purification unless otherwise stated. The third-generation Grubbs catalyst (G3) refers to Grubbs Catalyst® M37a. *m*[6]CPP-alkyne was prepared based on a previously work.^[1] All the synthetic steps were carried out under an inert argon atmosphere using standard Schlenk technique unless otherwise stated. All solvents were extra dry for reactions unless otherwise stated.

1.2 Characterizations

Nuclear magnetic resonance (NMR) experiments (^1H and ^{13}C) were recorded on a Bruker Avance NEO 400 instrument by using deuterated chloroform as a solvent. Chemical shifts were calibrated to the proton resonance of solvent (7.26 and 77.0 ppm for ^1H NMR and ^{13}C NMR spectroscopies, respectively).

High-resolution mass spectra (HRMS) were recorded by a Waters Xevo G2-XS QToF mass spectrometer which utilized an ESI ionization source.

Gel permeation chromatography (GPC) curves were measured with Waters 1525 by using chloroform as the mobile phase at 35 °C. The flow rate was 1 mL/min, and the injection volume was 10 μL . A refractive index detector was employed to characterize the number average molecular weight (M_n) and molecular weight distribution (D) through conventional calibration by using narrow-distributed polystyrene as an internal standard.

UV-Vis absorption spectra were recorded with Shimadzu UV-2700 spectrophotometers with a 10.00 mm quartz cuvette using dichloromethane as the solvent and monochromatic light of various wavelengths over a range of 300–600 nm.

Fluorescence spectra were obtained by using Edinburgh FLS980 fluorescence spectrophotometer equipped with a 450 W xenon arc lamp, the extinction wavelength was fixed at 328 nm, the fluorescence emission spectra were collected over a range of 350–700 nm. The band-pass excitation and band-pass emission slits were both 1 nm.

The absolute fluorescence quantum yields of samples were collected on HORIBA FluoroMax-4 fluorescence spectrophotometer with integrating sphere and a supplied reference plug was used as a reference sample. The extinction wavelength was fixed at 328 nm, the signal were collected over a range of 400–640 nm.

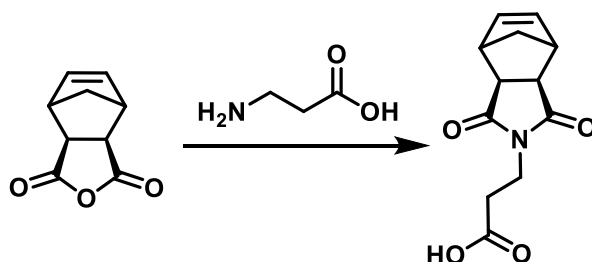
Fluorescence decay curves were obtained on HORIBA FluoroMax-4 fluorescence spectrophotometer using an IBH 369 nm NanoLED as the excitation source. Samples were excited at a wavelength of 369 nm and the signal was detected at 510 nm. The fluorescence decays were acquired over 4096 channels using a time-per-channel of 5.338672E-11 sec/ch with 10,000 counts at the maximum for the decay curves. The decay curves were fitted from a single-exponential function.

Glass transition temperature (T_g) was characterized with a Netzsch differential scanning calorimeter (DSC) calibrated with an indium standard. The heating and cooling rates were fixed at 10 °C/min from 25 °C to 200 °C.

2. Synthesis

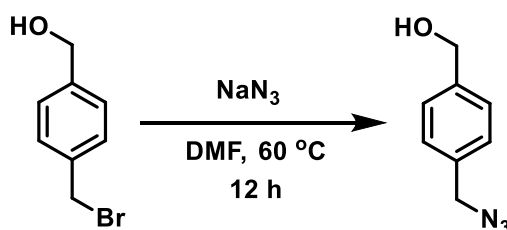
2.1 Monomer synthesis

2.1.1 Synthesis of N-[3-propanoic acid]-*cis*-5-norbornene-*exo*-2,3-dicarboximide



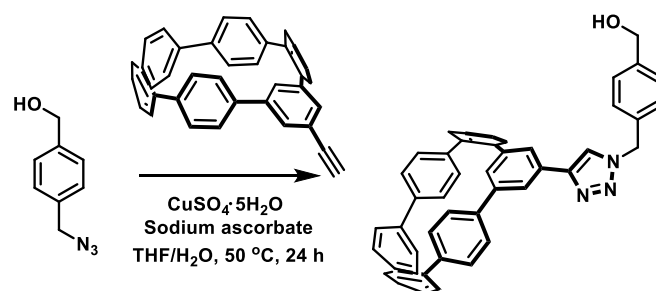
Cis-5-norbornene-*exo*-2,3-dicarboxylic anhydride (1 g, 6.090 mmol) and 3-aminopropanoic acid (0.6780 g, 7.711 mmol) and TEA (77.02 mg, 102.4 μ L, 0.7629 mmol) were dissolved in 4 mL toluene. The mixture was heated to reflux and maintained overnight. After the reaction was finished, the mixture was dispersed in ethyl acetate, washed with dilute hydrochloric acid (pH=1), water, saturated brine and dried over anhydrous Na_2SO_4 . The product was obtained as white solid without further purification (0.8969 g, 58.1% yield). ^1H NMR (400 MHz, CDCl_3) δ = 10.51 (br, 1H), 6.27 (s, 2H), 3.77 (t, $J=7.3$, 2H), 3.26 (s, 2H), 2.70 – 2.60 (m, 4H), 1.49 (d, 1H), 1.22 (d, 1H).

2.1.2 Synthesis of (4-(azidomethyl)phenyl)methanol 2



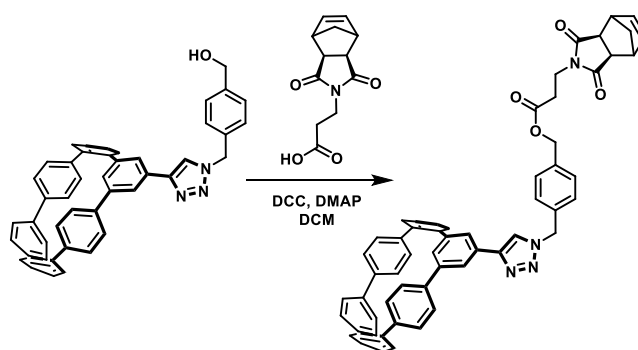
4-Bromomethylbenzyl alcohol (700 mg, 3.482 mmol), sodium azide (300 mg, 4.615 mmol), and KI (100 mg, 0.6024 mmol) were dispersed in 50 mL DMF solution. The mixture was stirred at room temperature overnight. After the reaction was finished, the mixture was dispersed in ether, washed with water, saturated brine and dried over anhydrous Na_2SO_4 . The product was obtained as colorless liquid without further purification (0.5587 g, 98.3% yield). ^1H NMR (400 MHz, CDCl_3) δ = 7.37 (d, $J=7.5$, 2H), 7.29 (d, $J=7.6$, 2H), 4.67 (s, 2H), 4.32 (s, 2H), 2.15 (br, 1H).

2.1.3 Synthesis of 3



2 (6.791 mg, 0.04161 mmol), meta[6]cycloparaphenylenes acetylene (20 mg, 0.04161 mmol), sodium ascorbate (14.49 mg, 0.08322 mmol), $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (10.39 mg, 0.04161 mmol) were mixed together, then a mixture of THF/water (5:1, v/v) solution (480 μL) was injected. The reaction was stirred at 50 °C for 24 h. The reaction mixture was then filtered, the filtrate was extracted with ethyl acetate and washed with water, brine and dried over anhydrous Na_2SO_4 . The crude product was concentrated with a rotary evaporator. The residue was purified by silica flash chromatography (EA: PE=1:1 as eluent). The product was obtained as yellowish solid (24.8 mg, 92.4% yield). ^1H NMR (400 MHz, CDCl_3) δ = 7.86 (s, 2H), 7.74 (s, 1H), 7.53 – 7.30 (m, 20H), 7.16 (d, $J=8.0$, 4H), 5.58 (s, 2H), 5.56 (s, 1H), 4.70 (s, 2H), 2.20 (br, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ = 143.18, 142.16, 139.37, 139.12, 137.38, 136.33, 136.22, 133.71, 131.25, 129.38, 128.32, 128.01, 127.78, 127.63, 127.50, 127.15, 119.55, 64.57, 54.04. HRMS m/z (ESI) calcd for $\text{C}_{46}\text{N}_3\text{OH}_{33}\text{Na}$ ($\text{M} + \text{Na}$)⁺ 666.2516, found 666.2522.

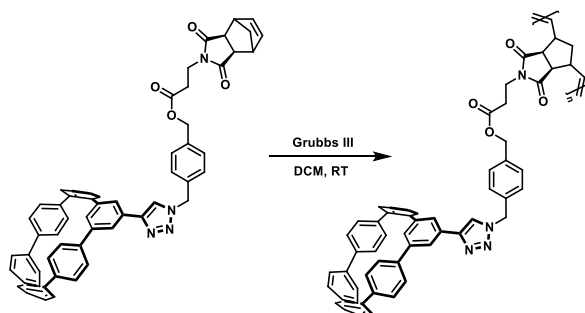
2.1.4 Synthesis of 4



3 (22.50 mg, 0.03495 mmol), *N*-[3-carboxylpropyl]-*cis*-5-norbornene-*exo*-2,3-dicarboximide (8.222 mg, 0.03495 mmol), and DMAP (4.270 mg, 0.03495) were dissolved in dichloromethane. Then DCC (7.211 mg, 0.03495 mmol) was added in one batch. The reaction was stirred overnight at room temperature. The reaction mixture was filtered and the filtrate was concentrated with a rotary evaporator. The residue was

purified by silica flash chromatography (EA: PE=2: 1 as eluent). The product was obtained as yellowish solid (25.6 mg, 85.0% yield). ^1H NMR (400 MHz, CDCl_3) δ = 7.88 (s, 2H), 7.75 (s, 1H), 7.56 – 7.31 (m, 20H), 7.17 (d, $J=7.6$, 4H), 6.26 (s, 2H), 5.61 (s, 2H), 5.57 (s, 1H), 5.11 (s, 2H), 3.77 (t, $J=7.1$, 2H), 3.21 (s, 2H), 2.70 – 2.60 (m, 4H), 1.42 (d, $J=9.9$, 1H), 1.19 (d, $J=9.9$, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ = 177.64, 170.45, 143.20, 142.21, 139.42, 139.15, 137.81, 137.41, 136.35, 136.25, 134.74, 131.30, 129.40, 129.19, 128.35, 128.04, 127.81, 127.53, 127.17, 119.60, 66.08, 53.96, 47.79, 45.15, 42.71, 34.39, 32.16. HRMS m/z (ESI) calcd for $\text{C}_{58}\text{N}_4\text{O}_4\text{H}_{44}\text{Na}$ ($\text{M} + \text{Na}$) $^+$ 883.3255, found 883.3257.

2.2 Polymer synthesis



2.2.1 Synthesis of P1

Monomer 4 (25 mg, 0.02900 mmol, 100 equiv.) was dissolved in 0.95 mL chloroform. The solution was fully degassed. A solution of third-generation Grubbs catalyst (G3, 0.2562 mg, 0.29 μmol , 1 equiv.) in 0.05 mL chloroform was added to initiate the polymerization. The reaction was conducted at room temperature for 30 min and then quenched with several drops of EVE. The product mixture was dissolved in chloroform, precipitated into methanol three times and dried, yielding 23 mg yellowish solid ($M_n = 59000$ Da, $D = 1.22$).

2.2.2 Synthesis of P2

The synthetic procedure is similar to the synthesis of P1, the only difference is that the feeding ratio of monomer to catalyst was modified into 50:1 ($M_n = 28700$ Da, $D = 1.19$).

2.2.3 Synthesis of P3

The synthetic procedure is similar to the synthesis of P1, the only difference is that the feeding ratio of monomer to catalyst was modified into 500:1 ($M_n = 316000$ Da, $D =$

1.28).

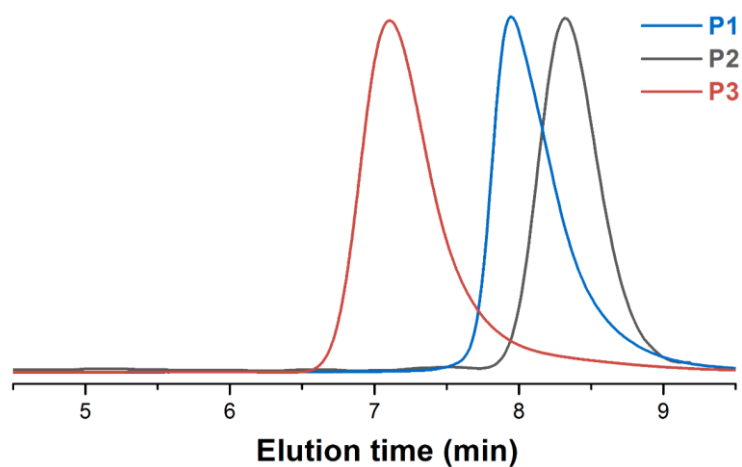


Figure S1. GPC elution curves of different polymers.

2.3 Polymerization kinetic study

Monomer **4** (25 mg, 0.02900 mmol, 100 equiv.) was dissolved in 0.95 mL chloroform. The solution was fully degassed at 0 °C. A solution of G3 catalyst (0.2562 mg, 0.29 μ mol, 1 equiv.) in 0.05 mL chloroform was added, and a stopwatch was started. Aliquots of 100 μ L were withdrawn at different intervals and added to a vial with EVE (100 μ L) and thoroughly mixed. Then the vial was subjected to rotary evaporator. CDCl_3 was added to each vial and ^1H NMR spectra were obtained to determine monomer conversion. The solution in NMR tube was subsequently evaporated for GPC measurement to determine the molecular weight and dispersity.

3. Property comparison of different polymers

3.1 Photophysical properties

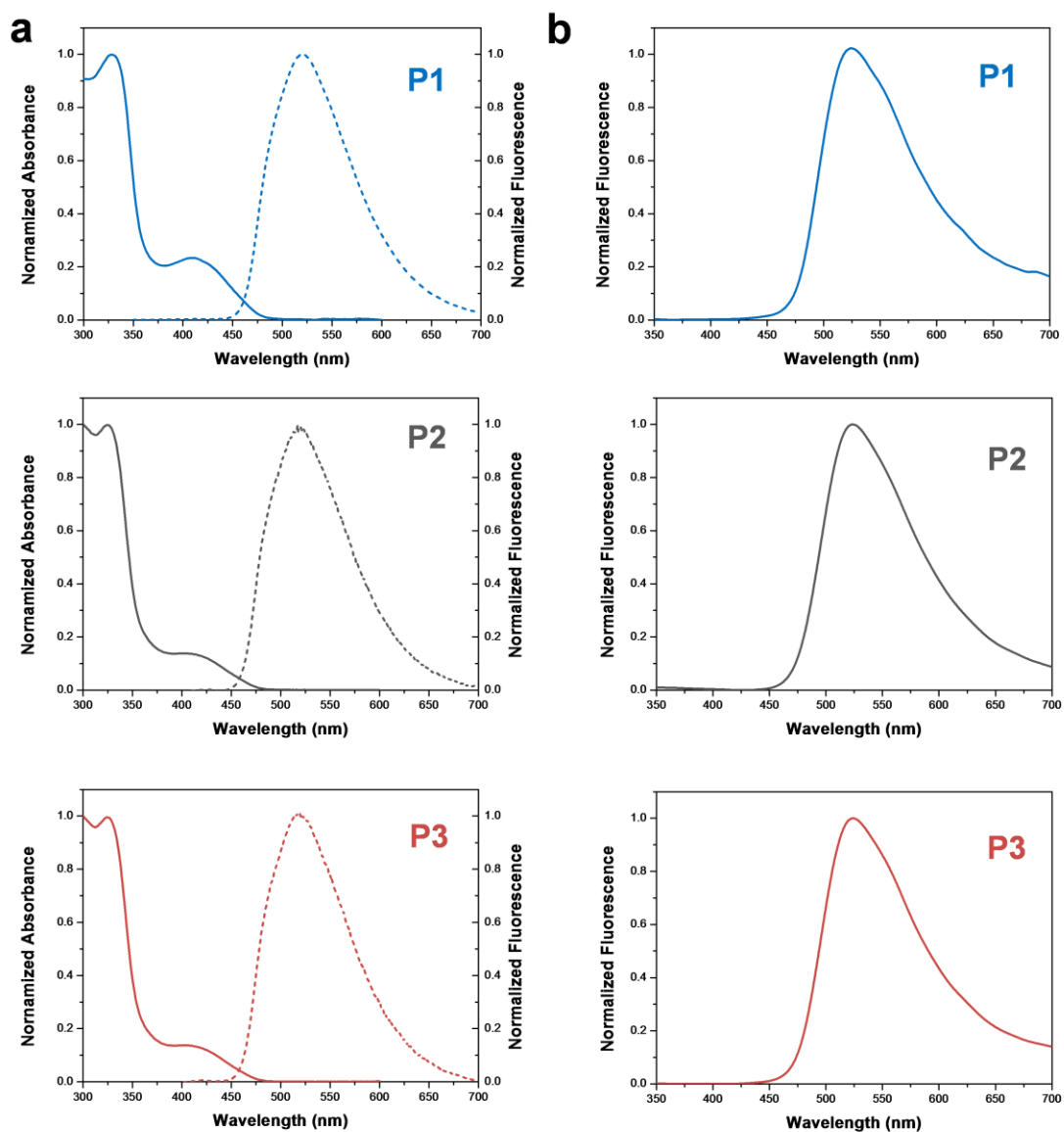


Figure S2. (a) Absorbance and fluorescence emission spectra of different polymers in dichloromethane. (b) Fluorescence-emission spectra of polymers under solid powder state.

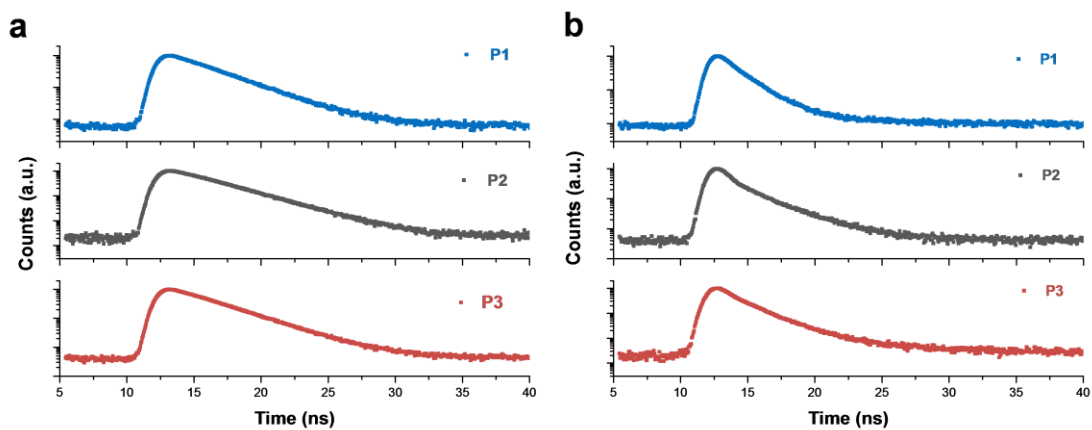


Figure S3. Emission lifetimes for different polymers in dichloromethane (a) and solid powder state (b).

3.2 Calorimetric properties

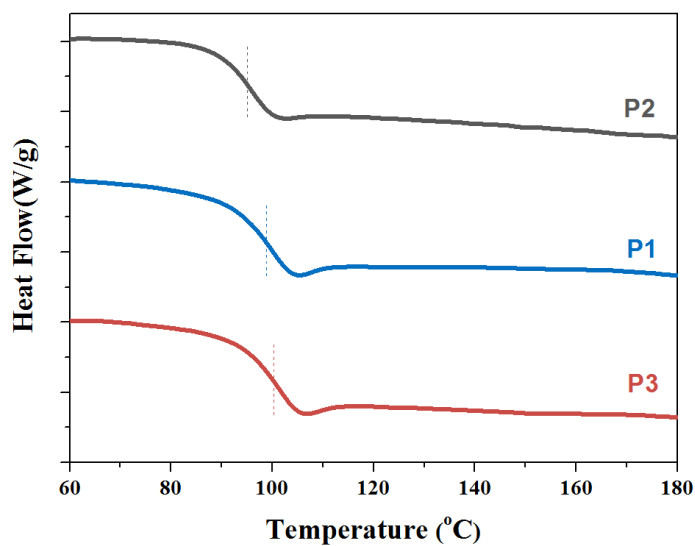


Figure S4. Differential scanning calorimetry (DSC) traces of different polymers at a heating rate of 10 K/min.

4. NMR spectra

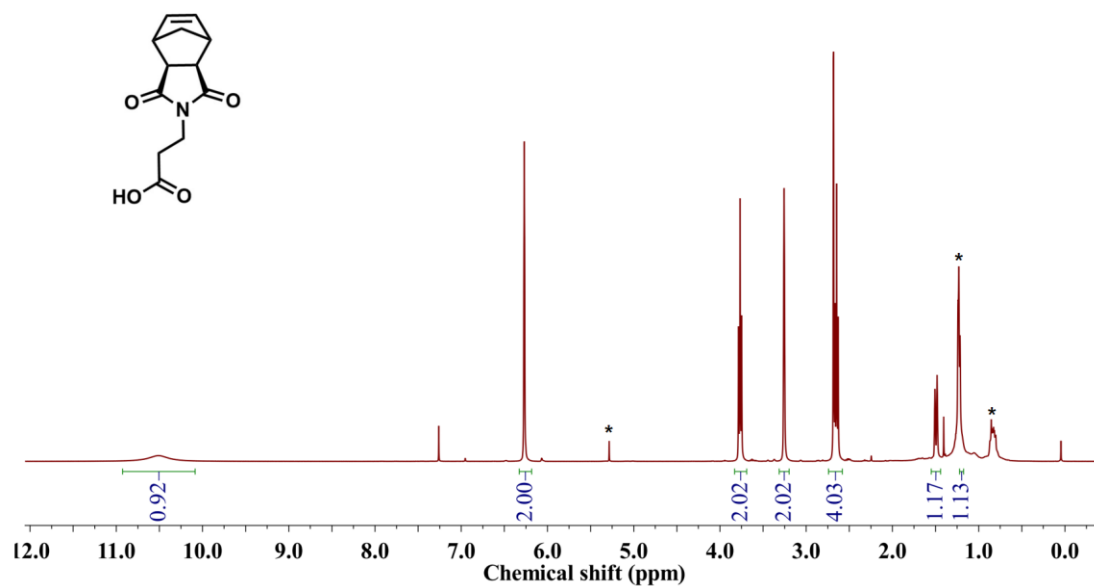


Figure S5. ^1H NMR spectrum of *N*-[3-propanoic acid]-*cis*-5-norbornene-*exo*-2,3-dicarboximide in CDCl_3 .

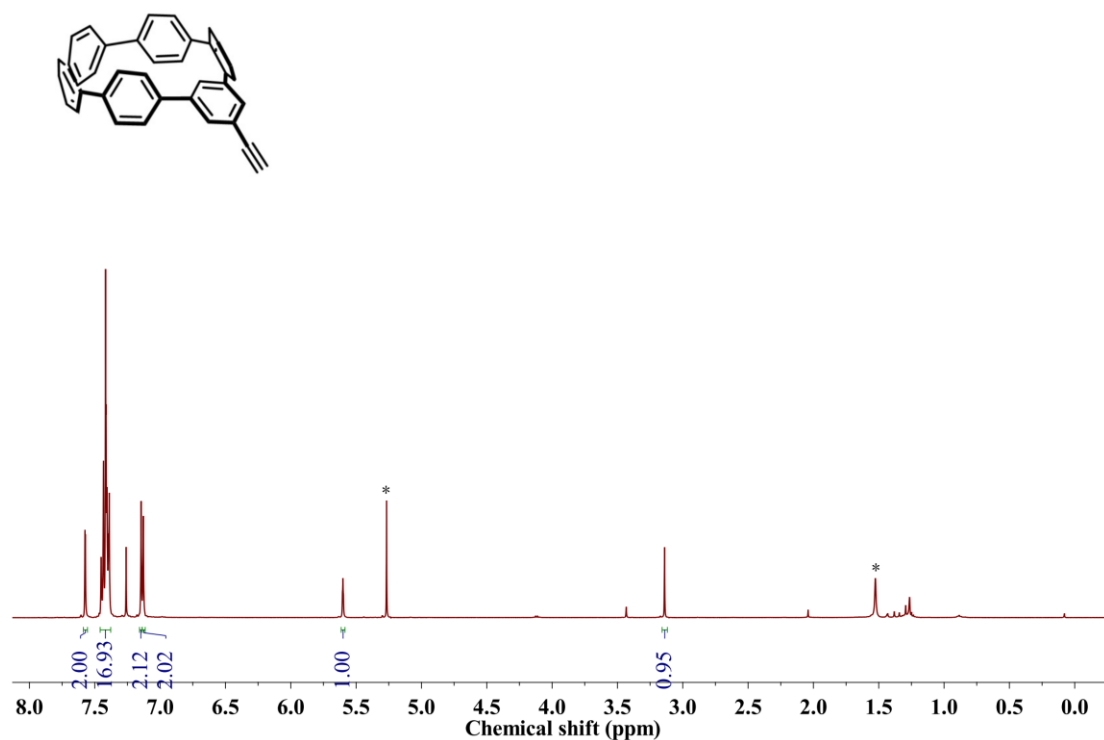


Figure S6. ^1H NMR spectrum of alkyne-incorporated *m*[6]CPP in CDCl_3 .

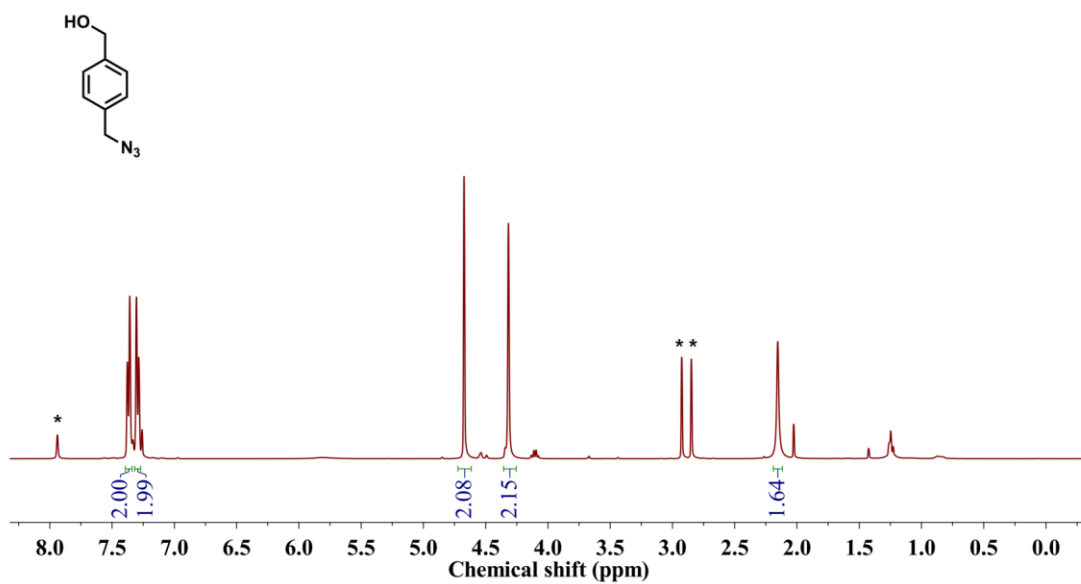


Figure S7. ¹H NMR spectrum of **2** in CDCl₃.

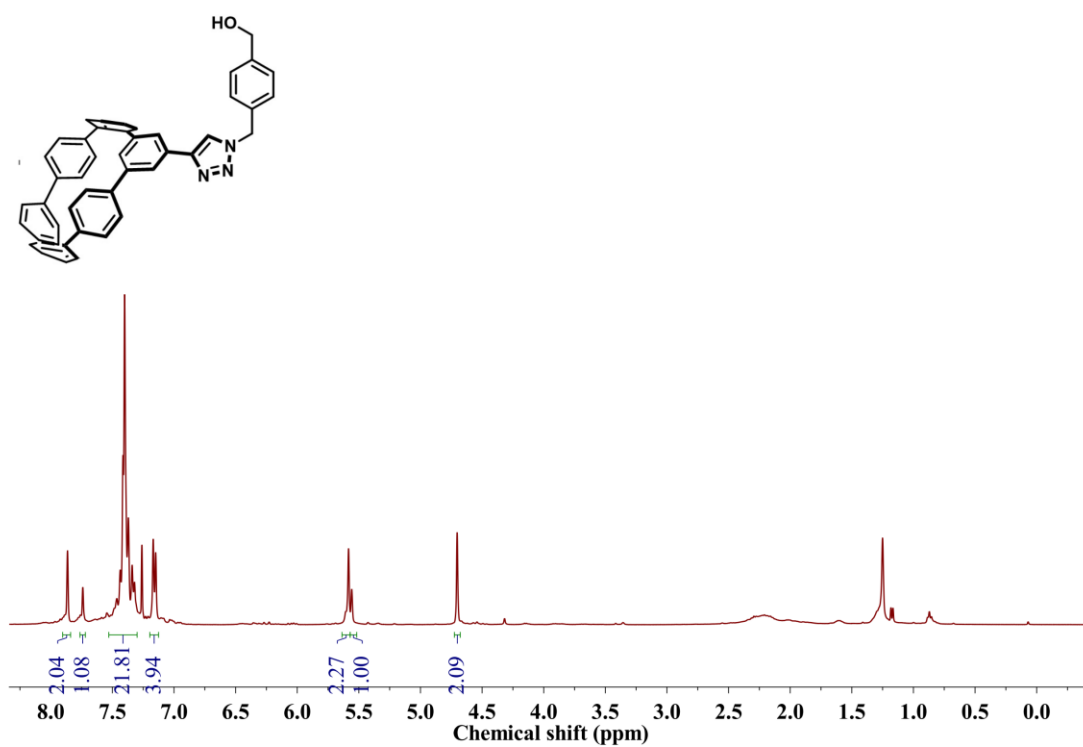


Figure S8. ¹H NMR spectrum of **3** in CDCl₃.

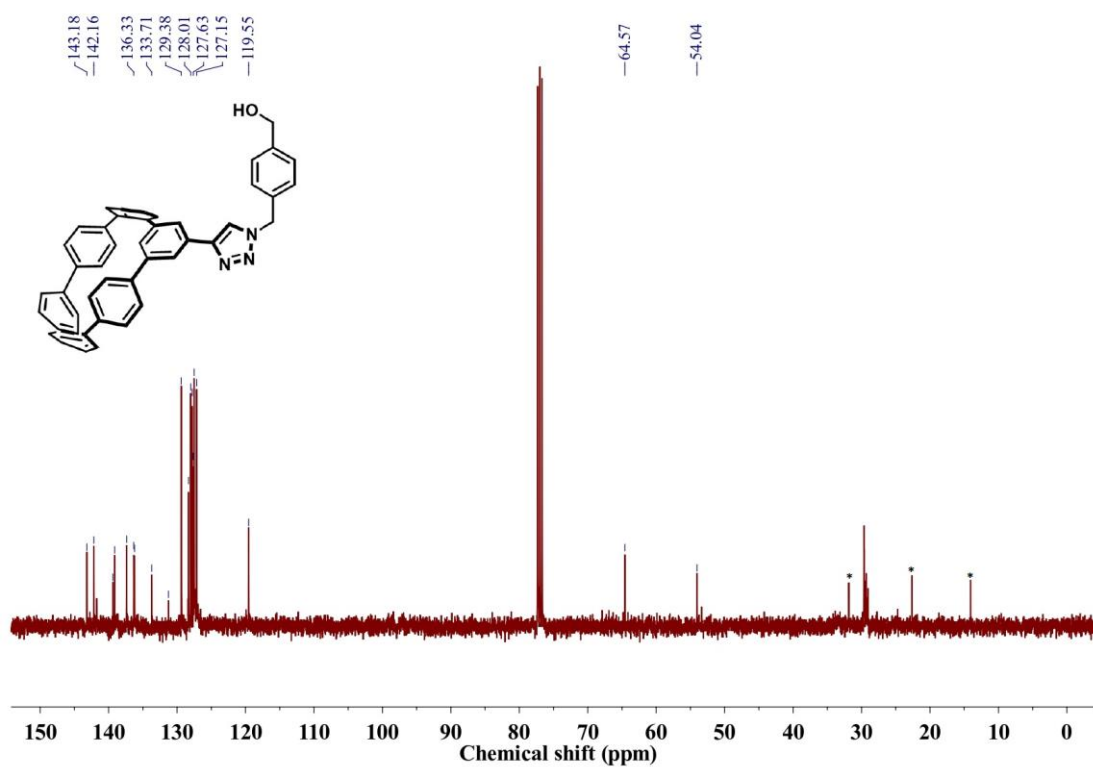


Figure S9. ^{13}C NMR spectrum of **3** in CDCl_3 .

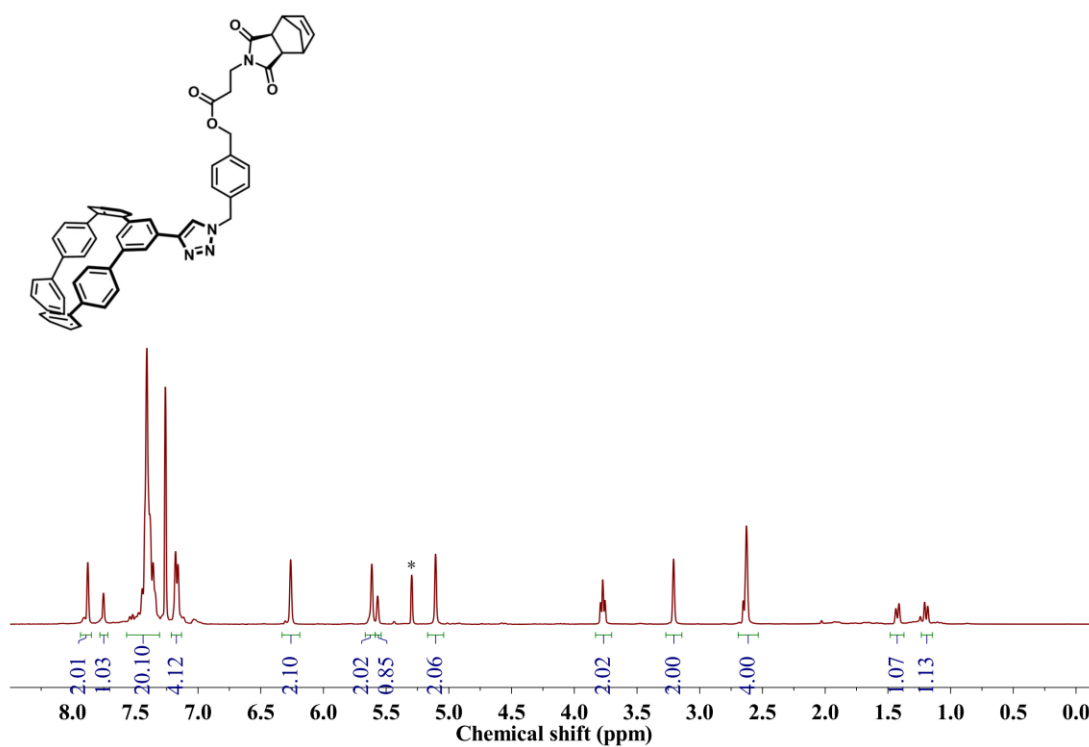


Figure S10. ^1H NMR spectrum of **4** in CDCl_3 .

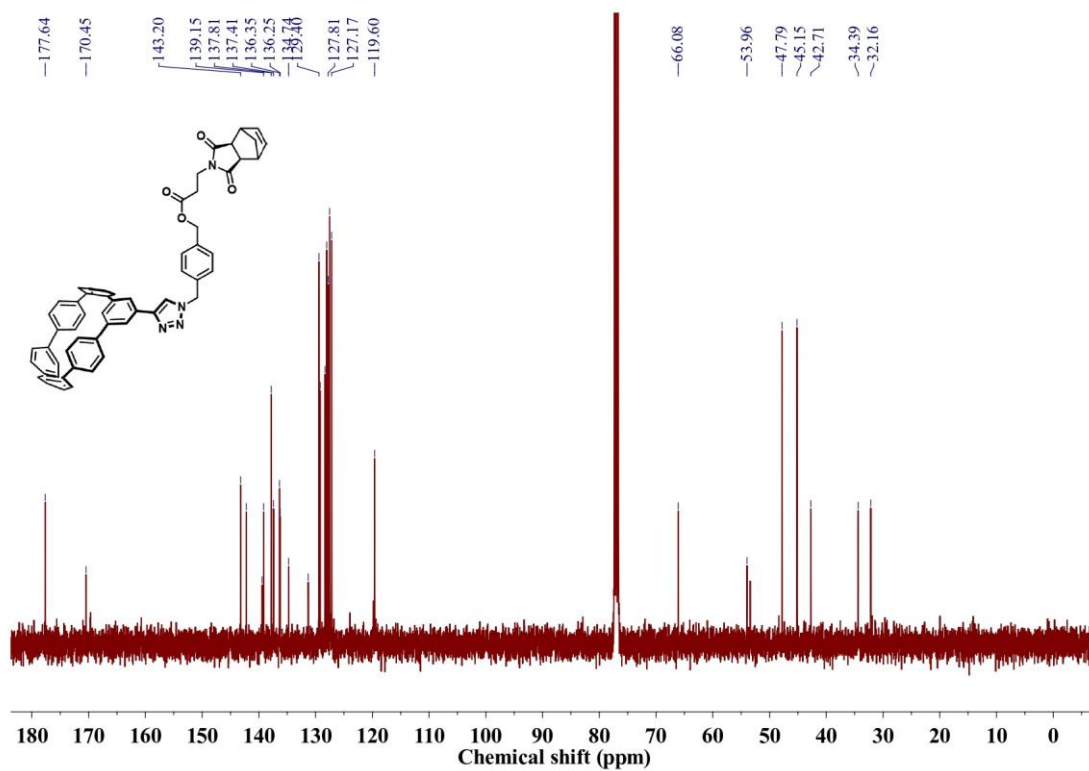


Figure S11. ^{13}C NMR spectrum of **4** in CDCl_3 .

References

- [1] Lovell TC, Bolton SG, Kenison JP, Shangguan J, Otteson CE, Civitci F, Nan X, Pluth MD, Jasti R, *ACS Nano*, 2021, 15, 15285.