Supplementary Information

A Supramolecular Polymeric Heterojunction Composed of All-Carbon Conjugated Polymer and Fullerenes

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1. General Methods and Apparatus

NMR spectra were recorded on Bruker BioSpin (^{1}H 400 MHz, ^{13}C 100 MHz) spectrometer. Chemical shifts for ^{1}H NMR are expressed in parts per million (ppm) relative to $CDCl_3$ (δ 7.26 ppm). High resolution mass spectrometry (HR-MS) analyses were carried out using MALDI-TOF-MS techniques. Data were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, br = broad signal), coupling constant (Hz), and integration. Samples were characterized with Raman spectroscopy (RM3000, Renishaw, UK) and Infrared spectroscopy (IR, FTS-7000, Varian, USA). UV-vis absorption spectra were performed on a UNIC-3802 spectrophotometer. All solvents for syntheses were dried by distillation under nitrogen prior to use tetrahydrofuran (THF) and 1,4-dioxane were distilled after reflux with sodium). Other chemicals were obtained from commercial suppliers (Innochem or Acros). Air-sensitive reactions were all carried out under argon. The molecular weight distribution, relative number-average and weight-average molecular weights were determined at 40 °C by gel permeation chromatography (GPC, Waters 1525) equipped with a refractive index detector (Waters 2414) and Agilent PLgel 5 μm MIXED-C column with the eluent at 1.0 mL/min. The calibration was built on polystyrene standards. Analytical thin-layer chromatographies (TLC) were performed with silica gel HSGF 254. Flash chromatography was performed on silica gel (300~400 mesh).

2. Synthetic procedures

Synthesis of compound 2',5'-dibromo-4,4''-dichloro-1,1':4',1''-terphenyl (1).

2',5'-dibromo-4,4''-dichloro-1,1':4',1''-terphenyl was prepared according to the published procedures.[S1]

Synthesis of compound 2,2'-(2',5'-bis(4-chlorophenyl)-[1,1':4',1''-terphenyl]-4,4''-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (2).

To a mixture of 3 (2.2 g, 4.8 mmol) and 1,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene (8.3 g, 33.8 mmol) dispersed in 1,4-diaxane(30 mL), ethanol (15 mL), and deionized water (15 mL) in a round-bottom flask (250mL) , then degassed for 15 minutes by bubbling Ar through the solution. To the mixture were added tetrakis(triphenylphosphine)palladium (100 mg, 0.09 mmol) and Na_2CO_3 (5.1 g, 48.0 mmol), which was further purged with Ar for another 15 minutes. Thereafter, the mixture was then stirred at 80 °C for 36 h, the reaction was quenched with methanol (10 mL). The crude product was recrystallization from CH_2Cl_2/MeOH to afford 4 as white solid (2.03 g, 60%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.70 (d, J = 7.6 Hz, 4H), 7.46 (s, 2H), 7.20 (d, J = 7.8 Hz, 8H), 7.12 (d, J = 8.2 Hz, 4H), 1.35 (s, 24H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) 143.30, 139.80, 139.09, 138.74, 134.60, 132.94, 132.87, 131.10, 129.19, 128.35, 83.88, 24.91. HR-MS (MALDI-TOF) *m/z* calcd. for $C_{42}H_{42}B_2Cl_2O_4$ $[Ag]^+$: 809.1698, found: 809.1634

Synthesis of compound 4.

To a degassed suspension of 3 [S2] (163.32 mg, 0.2 mmol), 2 (130.72 mg, 0.19 mmol), and KOH (134 mg, 2.39 mmol) in THF (250 mL) and H_2O (10 mL) was added

$Pd(PPh_3)_4$ (30 mg, 0.026 mmol), then the mixture was degassed for 20 min. Then the mixture was heated up to 77 °C for 48 h under nitrogen atmosphere. After cooling down to room temperature, water was added and the mixture was extracted with DCM. The combined organic layer was dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure to afford crude product 6 as a white solid for the next step without further purification.

Synthesis of compound 5.

To a 50-mL round-bottom flask (vessel A) containing a magnetic stirring bar were added $SnCl_2 \cdot 2H_2O$ (274 mg, 1.21 mmol), THF (25 mL) and concentrated HCl/H_2O (0.21mL, 12 mol/L) were added, and the resultant mixture was further stirred at room temperature for 30 min. To another 200-mL round-bottom flask (vessel B) containing a magnetic stirring bar were added the above crude product 6 and dry THF (10 mL). A solution of H_2SnCl_4/THF (18 mL, 0.72 mmol, 0.04 M in THF) in vessel A was added. After stirring the mixture at room temperature for 2 h, the mixture was quenched with aqueous sodium hydroxide, extracted with CH_2Cl_2, dried over Na_2SO_4, and concentrated under reduced pressure. The crude product was purified by column chromatography (hexane/CH_2Cl_2 = 4/1) to afford compound **5** (18.2 mg, ~10% over two steps) as a pale yellow solid. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.63-7.52 (m, 24H), 7.42 (d, J = 8.5 Hz, 4H), 7.35 (s, 2H), 7.28 (d, J = 8.4 Hz, 4H), 7.21 (d, J = 8.3 Hz, 4H), 7.11 (dd, J = 8.4, 6.9 Hz, 8H); ^{13}C NMR (100 MHz, $CS_2/CDCl_3$ (1:1)): δ (ppm) 139.24, 138.87, 138.64, 138.55, 138.33, 138.24, 138.19, 138.16, 138.07, 138.05, 137.98, 137.80, 133.15, 132.74, 130.66, 130.31, 128.29, 127.67, 127.42, 127.36, 127.28, 127.19, 127.09. HR-MS (MALDI-TOF) *m/z* calcd. for $C_{72}H_{46}Cl_2$ $[M]^+$: 980.2977, found: 980.2923. IR (KBr) cm^{-1}: 3026, 2963, 2921, 2850, 2156, 1860, 1688,1586, 1476, 1340, 1095, 813, 757. Raman spectra (cm^{-1}): 1203, 1275, 1597.

Synthesis of SPh.

To a mixture of compound **5** (64 mg, 65.0 μmol), 2,2′-bipyridyl (119 mg, 0.76 mmol), and 1,5-cyclooctadiene (94 μL, 0.76 mmol) in a round-bottom flask (25 mL) was added anhydrous DMF (5 mL). The mixture was bubbled with Ar for 0.5 h before bis(1,5-cyclooctadiene)nickel(0) (210 mg, 0.763 mmol) was added in one portion. Thereafter, the mixture was heated up to reflux for 120 h to give a deep purple suspension. Upon cooling to room temperature, the solvent was removed by rotary evaporator. The resulting precipitate was filtered, washed intensively with 0.5 M HCl solution in water, and saturated EDTA solution methanol, filtered and washed with water, methanol, acetone, methanol, and hexane. The precipitate was collected, giving 40 mg of polymer **SPh** as a yellow solid (yield: 67%): M_n =10768 g·mol^{-1}, M_w =28655 g·mol^{-1} by GPC. IR (KBr) cm^{-1}: 2963, 2913, 2853, 1413, 1260, 1093, 1017, 800, 706. Raman spectra (cm^{-1}): 1206, 1276, 1600.

3. Methods for STM measurements

Drop casting method: STM experiments were performed using Createc LT-STM in an UHV chamber with base pressure of 1 × 10^{-10} mbar. Atomically flat Au(111) single crystal was used as the substrate which was cleaned by repeated cycles of Ar^+ sputtering (2 keV) and annealing at 700 K for 10 min. The sample was then deposited onto the freshly-prepared Au(111) surface by casting a small drop (~2 μL) of the solution in CH_2Cl_2 (1 × 10^{-4} M) and then transferred back into the UHV chamber immediately after the solvent evaporated. Before subjected to scanning, the sample was further annealed at ~400 K for 15 min in order to desorb the contaminations possibly introduced from the solution. Related STM images (Figures 3e and 3f) were acquired at liquid-nitrogen temperature using an electrochemically etched gold tip in the constant-current mode.

4. Physical characterizations and photophysical properties

Photophysical studies

UV-Vis absorption spectra of **SPh** and compound **5** were performed on a UNIC-3802 spectrophotometer at room temperature. The fluorescent emission experiments were performed on a Fluoromax-4 spectrofluorometer at room temperature and the fluorescence spectra of **SPh** and compound **5** were collected under an excitation wavelength at 320 nm and 300 nm, respectively. The fluorescent time-resolved decays were measured on a Mini-tau spectrometer (Edinburgh, U.K.) using time-correlated single-photon counting technique (TCSPC). The sample was excited at 390 nm with a picosecond pulsed diode laser (EPL-390, Edinburgh, U.K.) triggered at 5 MHz repetition rate. The emission was detected at 469 nm. The detected fluorescence intensity decays were analyzed using a monoexponential model. The measurements were performed at least twice for consistency. **SPh** and compound **5** were measured in CH_2Cl_2 with a concentration of 0.1 $mg \cdot mL^{-1}$ and 1.0×10^{-5} M, respectively.

Fluorescence quenching experiment. To a solution of compound **5** (8.33×10^{-6} $mol \cdot L^{-1}$) were titrated by C_{60} (2.50×10^{-5} $mol \cdot L^{-1}$) in toluene at room temperature. The changes in the fluorescent intensity of compound **5** at different ratios between them were recorded. The K_a was determined by the equation [S3-S5]: $F/F_0 = (1+ (k_f/k_s)K_a[C_{60}])/(1 + K_a[C_{60}])$. F, F_0, k_f, k_s, K_a, $[C_{60}]$ are fluorescence intensity, fluorescence of compound **5** before the addition of C_{60}, a proportionality constant of the complex, a proportionality constant of the host, the binding constant, and the concentration of C_{60}, respectively. A solution of **SPh** (1.67×10^{-3} $mg \cdot mL^{-1}$) were titrated by C_{60} (from 0.0 to 5.50×10^{-6} $mol \cdot L^{-}$

^{1}) in toluene at room temperature. The changes in the fluorescent intensity of **SPh** at different ratios between them were recorded.

UV-vis Titrations. To a solution of **SPh** (1.67×10^{-3} mg·mL^{-1}) were titrated by C_{60} (from 0.0 to 5.50×10^{-6} mol·L^{-1}) in toluene at room temperature. The resulting solutions were measured by UV-vis spectroscopy at room temperature. These spectra were corrected with background subtraction. [S6]

5. SCLC measurements.

Electron-only devices (ITO/ZnO/Active layer/Ca/Al) were fabricated as follows: 0.1 M zinc acetate in a solution mixture of 2-methoxy ethanol and ethanolamine was spin-coated onto the ITO substrates at 3000 rpm for 30 s, followed by heating at 200 °C for 30 min in air to form a ZnO film. The o-dichlorobenzene solution of C_{60} (4 mg/mL), **SPh** (4 mg/mL), **SPh** in the presence of C_{60} (4 mg/mL) were spin-coated onto the ZnO layer at 1000 rpm for 40s, respectively. Then the devices were annealed at 125 °C for 10 min. Finally, 10 nm Ca/80 nm Al was deposited sequentially atop the active layer in a vacuum chamber ($\sim 10^{-5}$ Pa) with a defined active area of 2×5 mm^2.

Hole-only devices (ITO/PEDOT: PSS/Active layer /MoO_3/Ag) were fabricated as follows: ITO was treated in an ultraviolet-ozone chamber for 15 min. Then PEDOT: Samples were spin-coated onto the ITO substrates at 3500 rpm for 40 s and was heated at 150 °C for 15 min. The o-dichlorobenzene solution of C_{60} (4 mg/mL), **SPh** (4 mg/mL), **SPh** in the presence of C_{60} (4 mg/mL) were spin-coated onto the PEDOT: Samples layers at 1000 rpm for 40s, and the devices were annealed at 125 °C for 10 min. Finally, 8 nm Ca/80 nm Ag was deposited atop the **SPh** layer in a vacuum chamber ($\approx 10^{-5}$ Torr). The current density-voltage (*J*-*V*) characterization of the devices were carried out by using a Keithley 2400 source measurement. The thickness of samples is 50 nm, which was measured by using a KLA-Tencor P6 surface profilometer.

The μ_e / μ_h value is calculated from Mott-Gurney equation (1):

$$J_{SCLC} = \frac{9}{8}\varepsilon_0 \varepsilon_r \mu_{e/h}\left(\frac{V^2}{L^3}\right) \quad (1)$$

where J_{SCLC} stands for current density, V is the applied potential, L is the thickness of the C_{60} (50 nm), **SPh** (50 nm), **SPh** with C_{60} (50 nm), ε_r is the relative dielectric constant of the blend, ε_0 is the permittivity of free space (8.85×10^{-12} C V^{-1} s^{-1}).

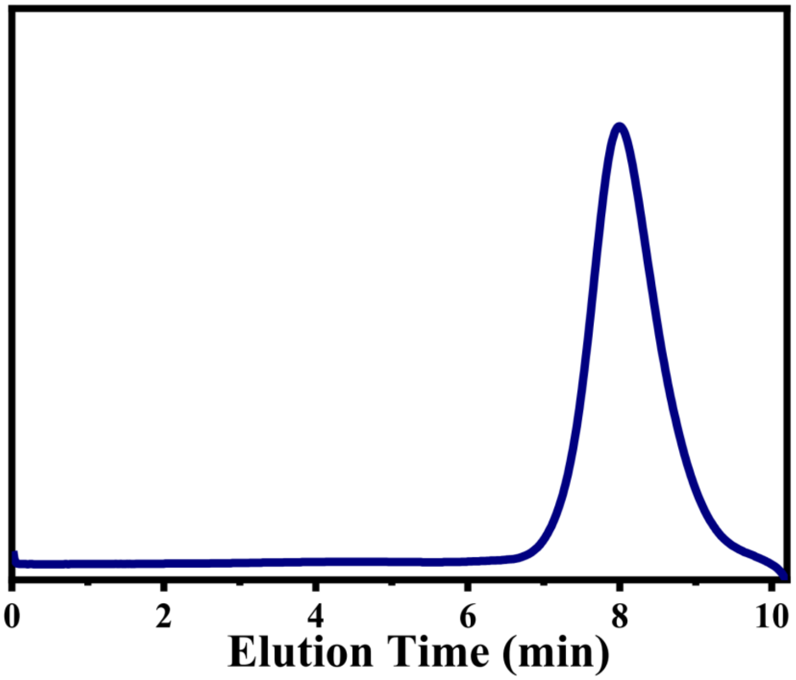


Figure S1. GPC trace of **SPh** using $CHCl_3$ as the solvent.

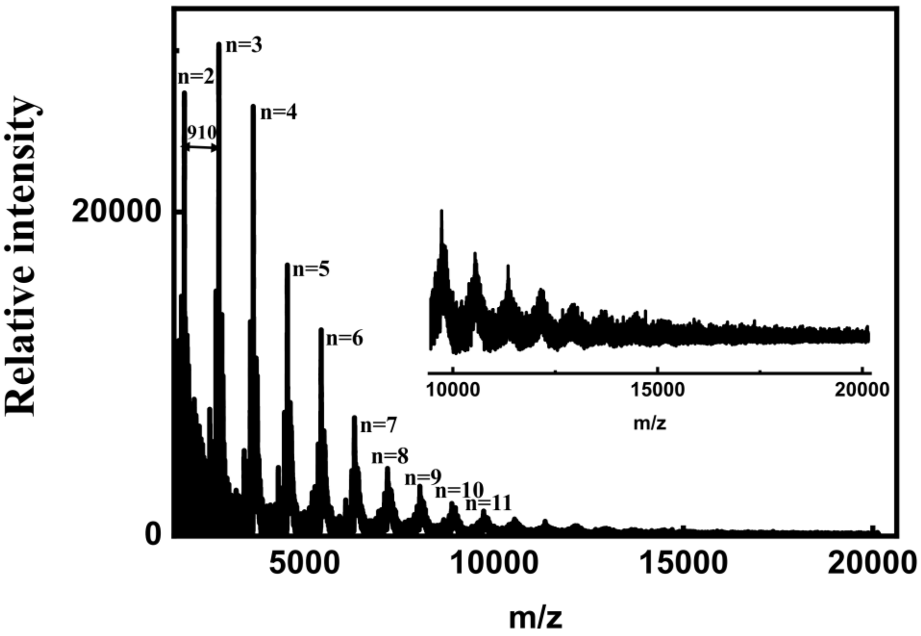


Figure S2. MALDI-TOF-MS spectrum for **SPh**.

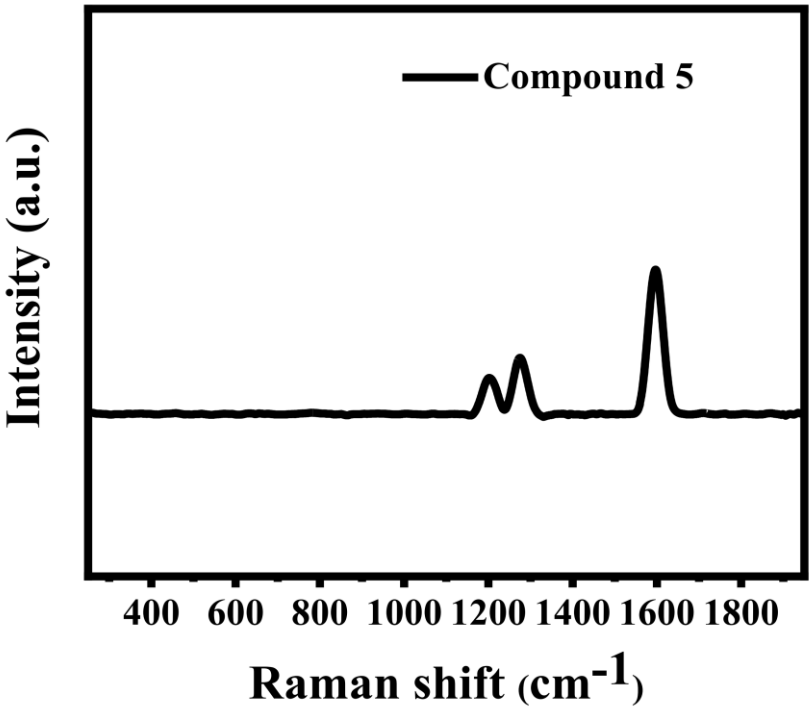


Figure S3. Raman spectra (excited at 785 nm) of compound **5**.

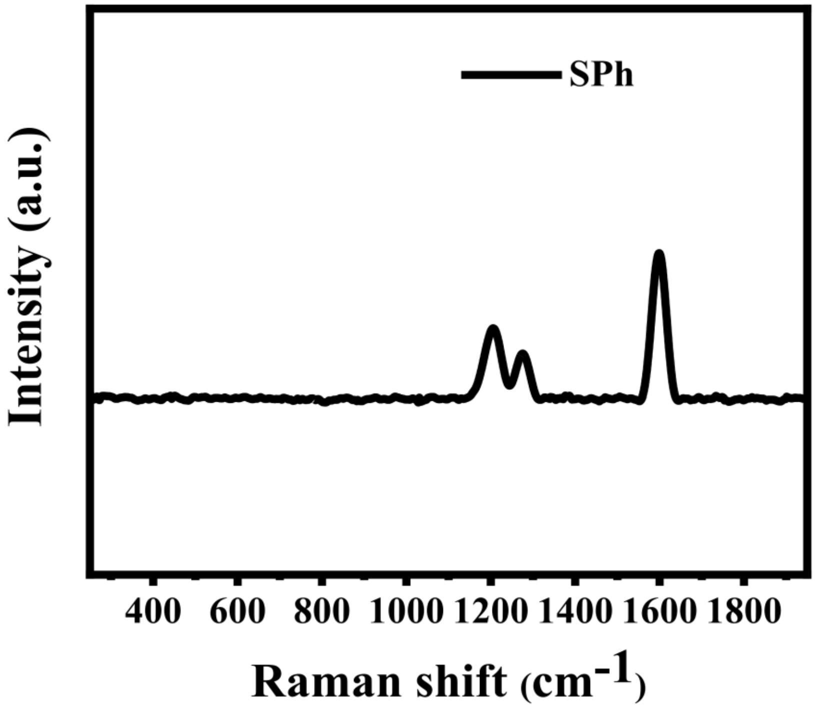


Figure S4. Raman spectra (excited at 785 nm) of **SPh**.

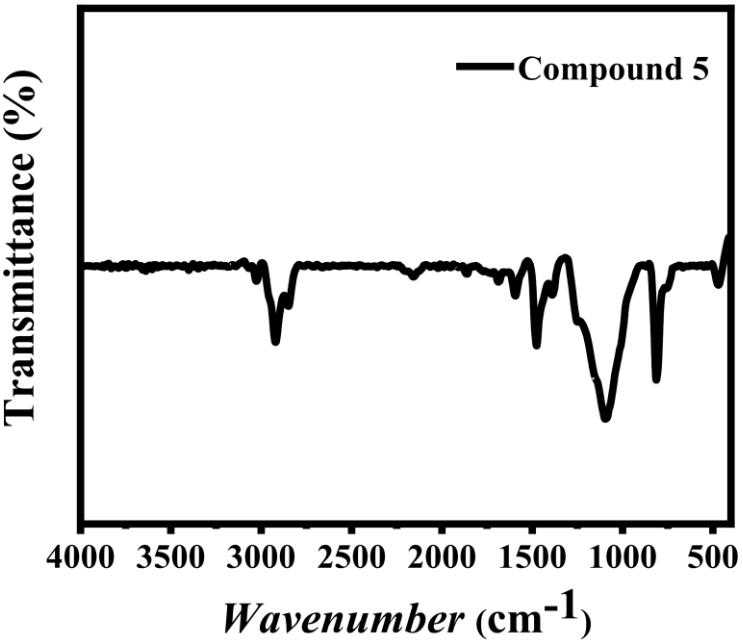


Figure S5. FTIR spectra of compound **5**.

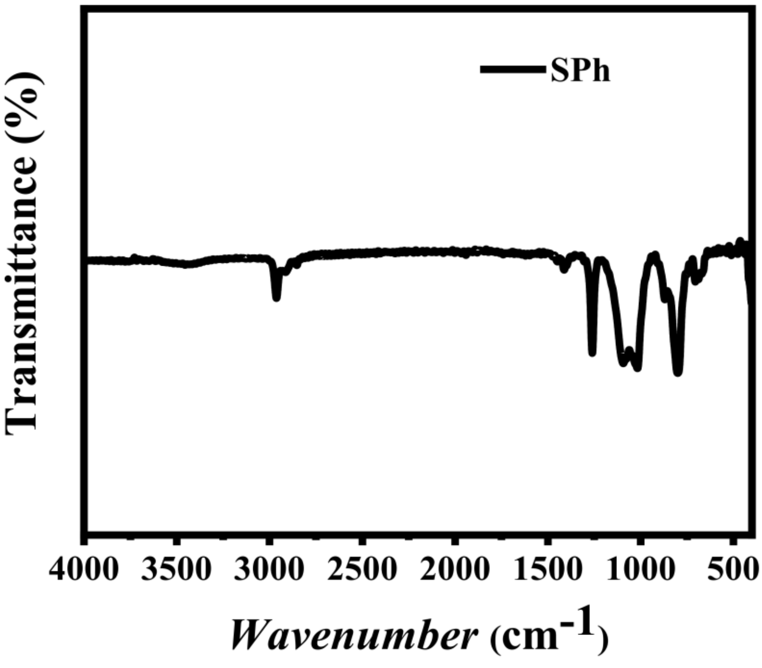


Figure S6. FTIR spectrum of **SPh**.

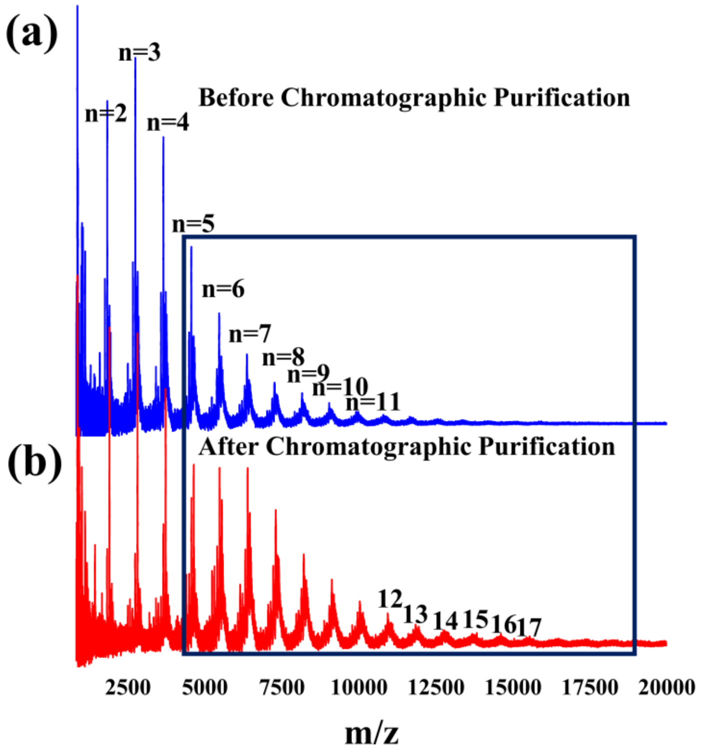


Figure S7. MALDI-TOF spectra of **SPh** before (a) and after (b) chromatographic purification.

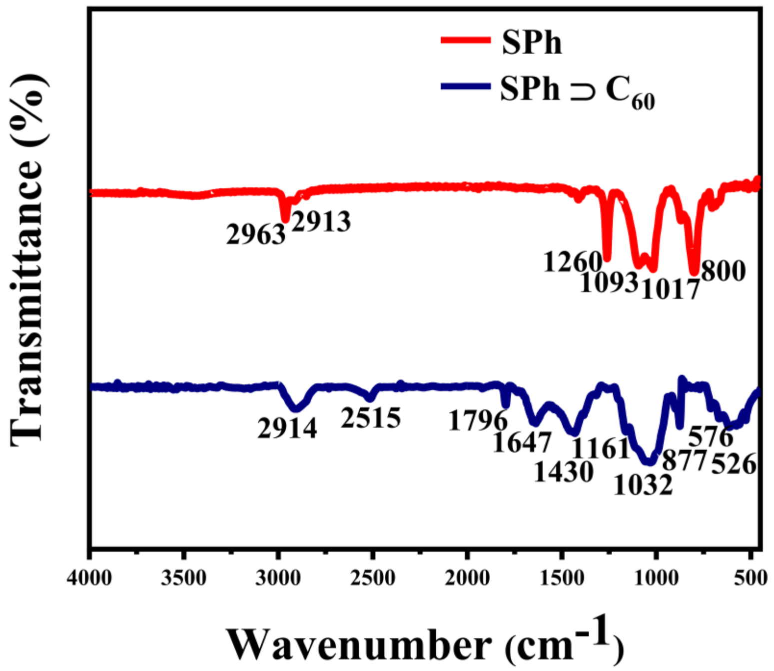


Figure S8. FTIR spectra of **SPh** (red) and **SPh**$\supset$C$_{60}$ (navy).

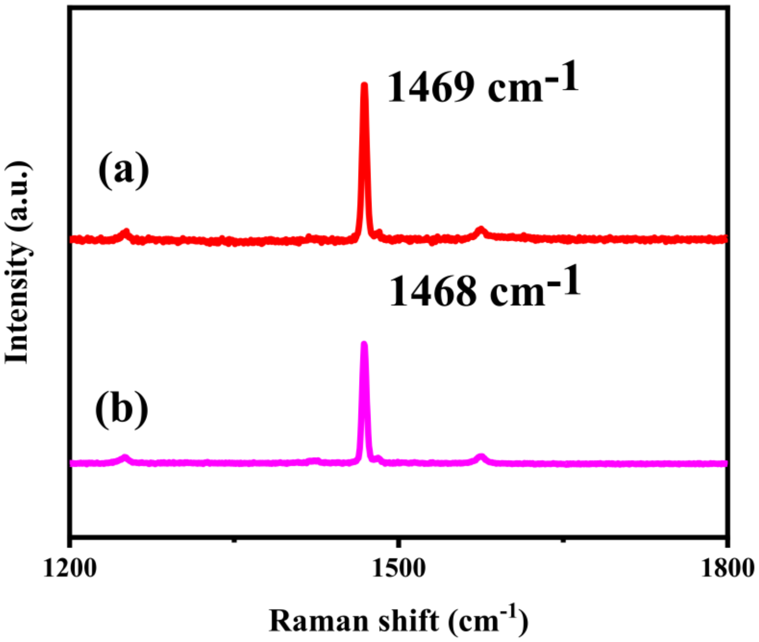
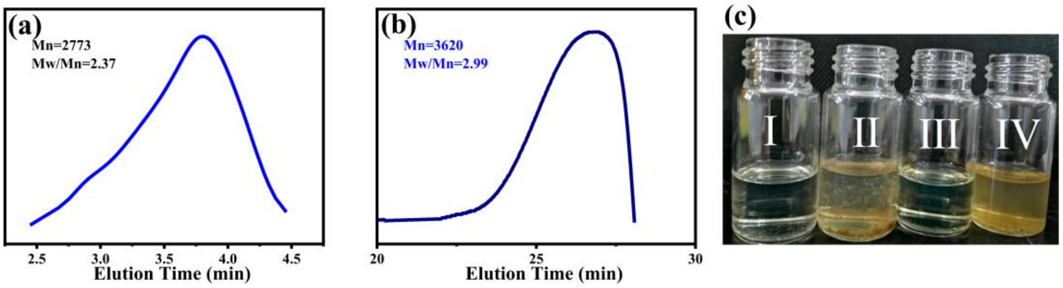


Figure S9. Raman spectra of **SPh**⊃C_{60} (a) and C_{60} (b).



(eluent: CHCl$_3$)

(eluent: DMF)

Figure S10. (a) GPC trace of **SPh**⊃C$_{60}$ (eluent: CHCl$_3$). (b) GPC trace of **SPh**⊃C$_{60}$ (eluent: DMF). (c) Photographs of S**Ph** dissolved in CHCl$_3$ (I), **SPh**⊃C$_{60}$ dissolved in CHCl$_3$ (II), **SPh** dissolved in DMF (III), **SPh**⊃C$_{60}$ dissolved in DMF (IV).

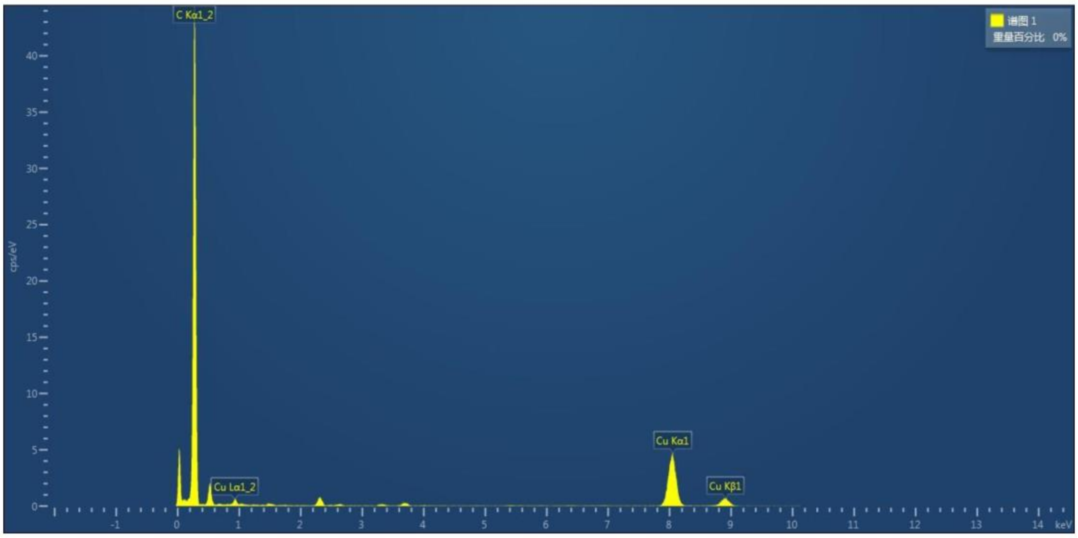


Figure S11. Electron microscopy energy-dispersive X-ray spectroscopy (EDS) mapping image of **SPh**.

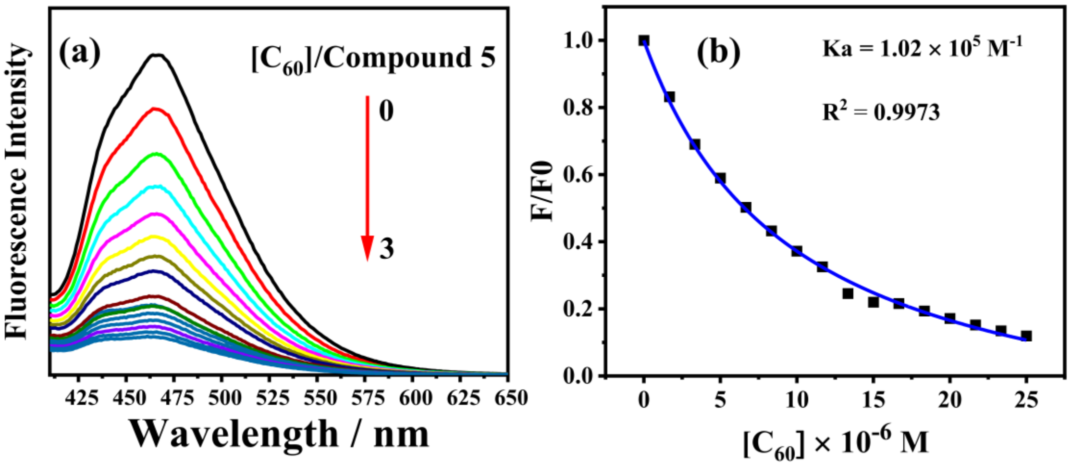


Figure S12. (a) Fluorescence spectra of compound **5** (8.33×10^{-6} mol·L-1) titrated with C_{60} in toluene at room temperature. The concentrations of C_{60} are 0.00 - 2.5×10^{-5} mol·L^{-1} from the top to the bottom. (b) Correlation of [C_{60}] on the fluorescence intensity of compound **5** in toluene for calculating the Ka. R^2 is the standard deviation.

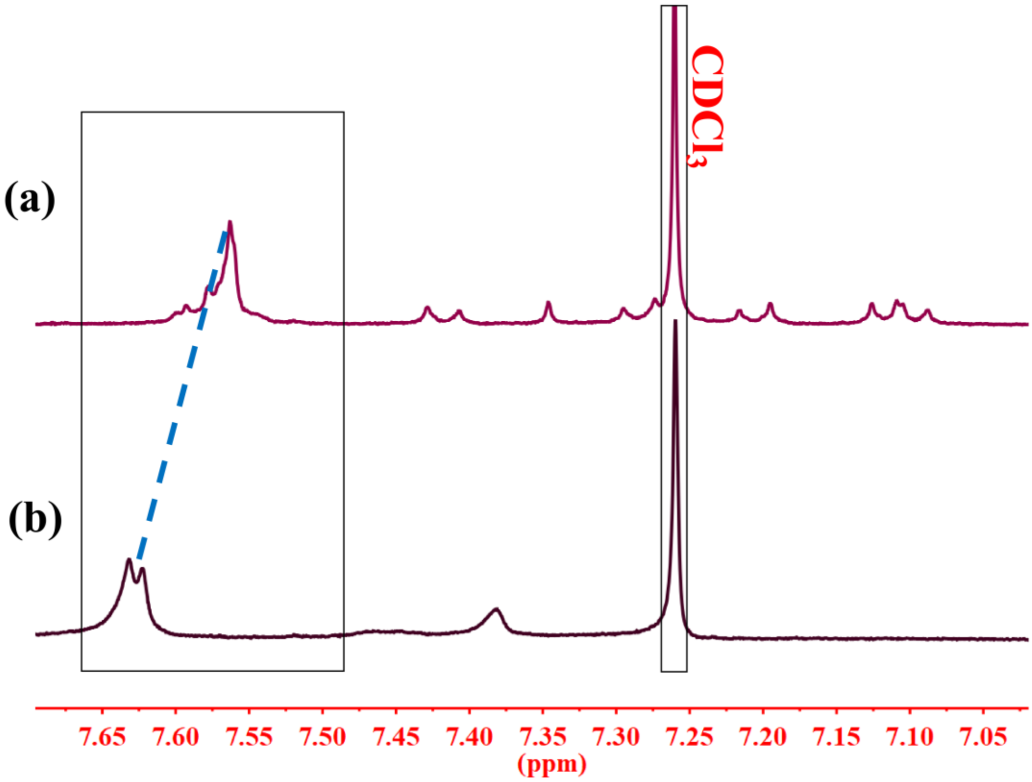


Figure S13. ^{1}H NMR spectra in $CDCl_3$ at room temperature of compound **5** before (a) and after (b) the addition of C_{60}.

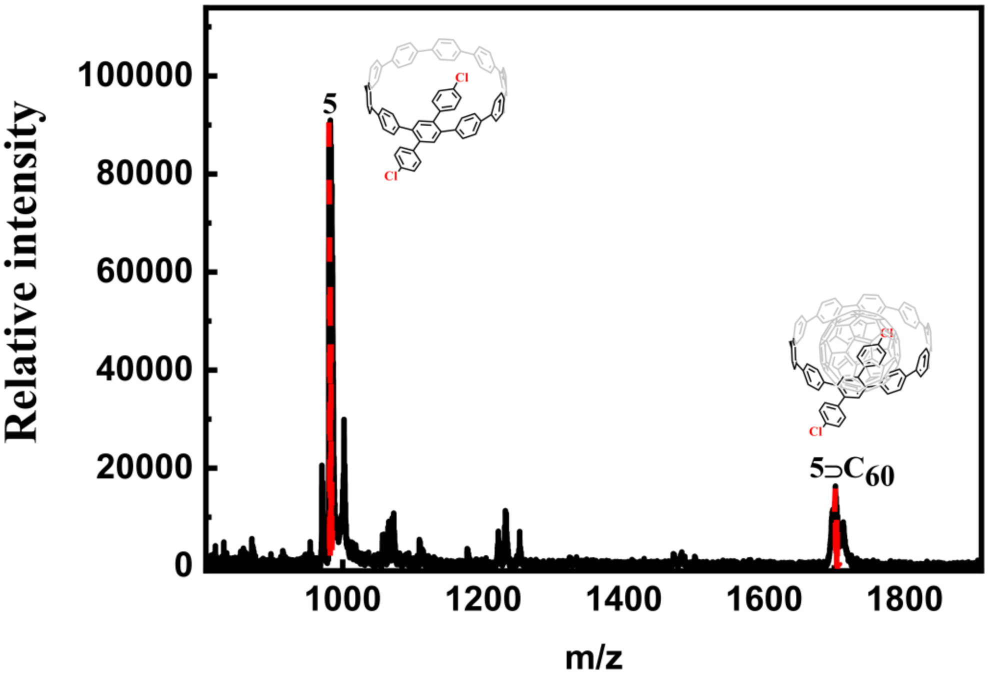


Figure S14. Mass spectrometry data for the compound **5**⊃C_{60} complex.

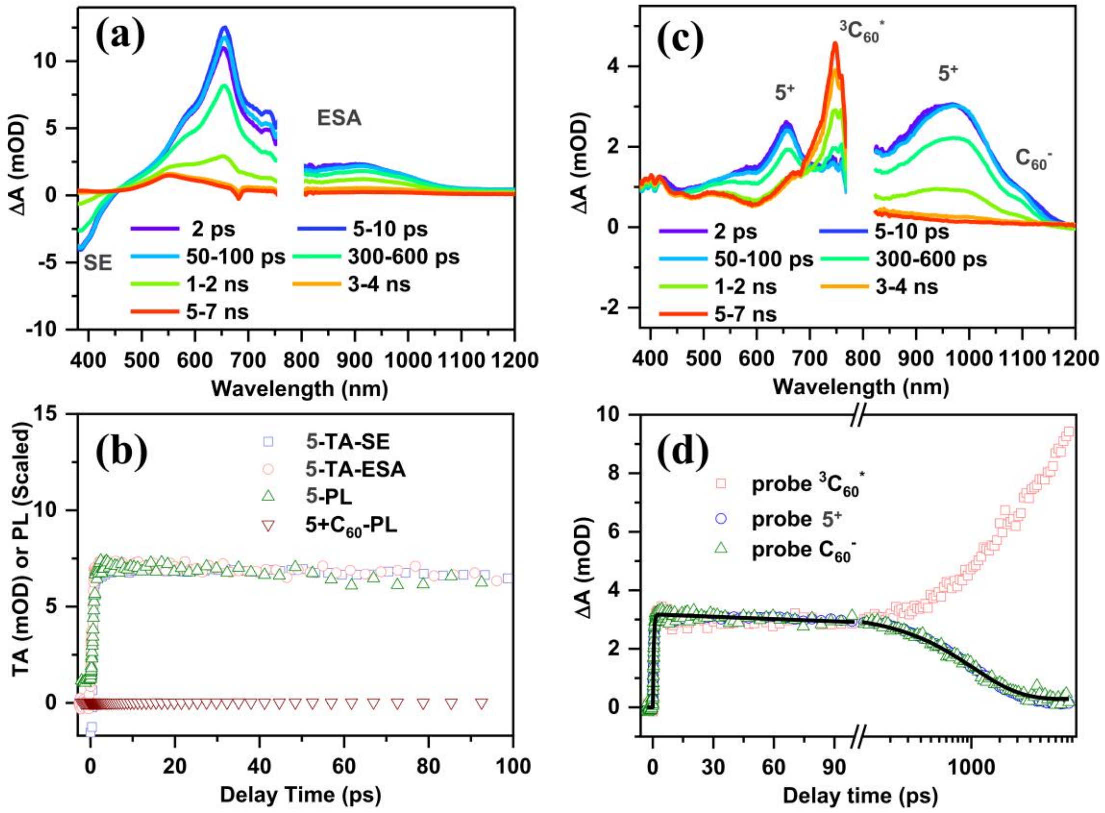


Figure S15. TA results for compound **5**. (a) TA spectra of compound **5** probed at indicated time delays following 350 nm excitation. The SE and ESA features of compound **5** are indicated. (b) Normalized FU kinetics (green triangles) and TA kinetics of compound **5** probed at SE (blue squares) and ESA (red circles) peaks. The FU kinetics of compound **5**$\supset C_{60}$ is also shown with wine triangles. (c) TA spectra of compound **5**$\supset C_{60}$ probed at indicated time delays following 350 nm excitation. The absorptions of compound **5**$^{+}$, $^{3}C_{60}^{*}$ and C_{60}^{-} are also indicated. (d) Normalized TA kinetics of compound **5**$\supset C_{60}$ probed at the $^{3}C_{60}^{*}$ (red squares), compound **5**$^{+}$ (blue circles) and C_{60}^{-} (green triangles) and their fits (black line).

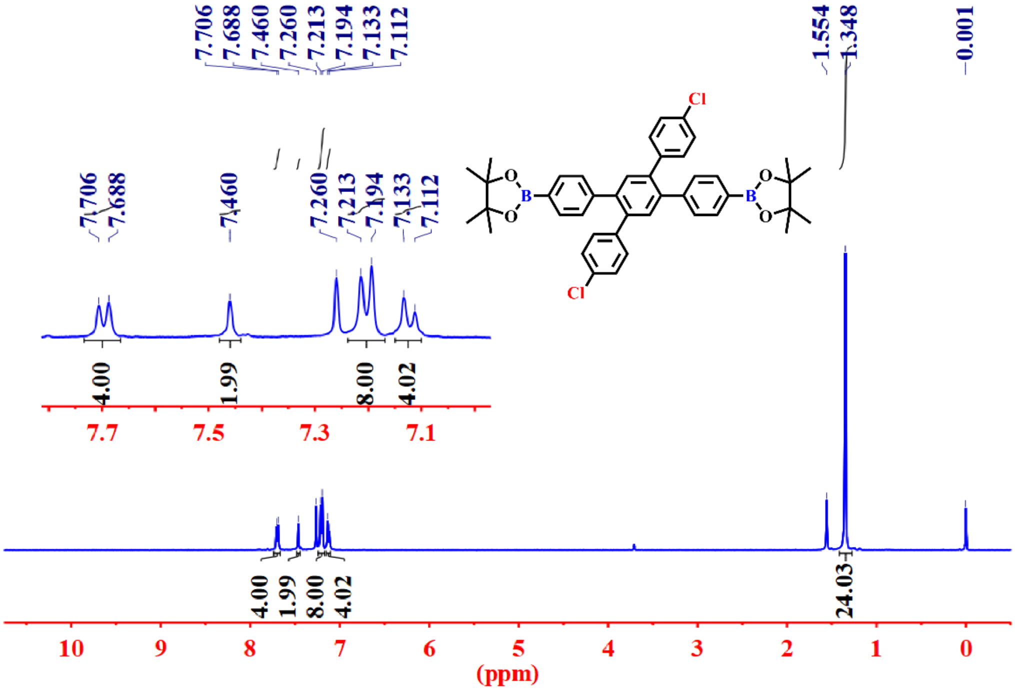


Figure S16. ^{1}H NMR spectrum of compound **2** in $CDCl_3$.

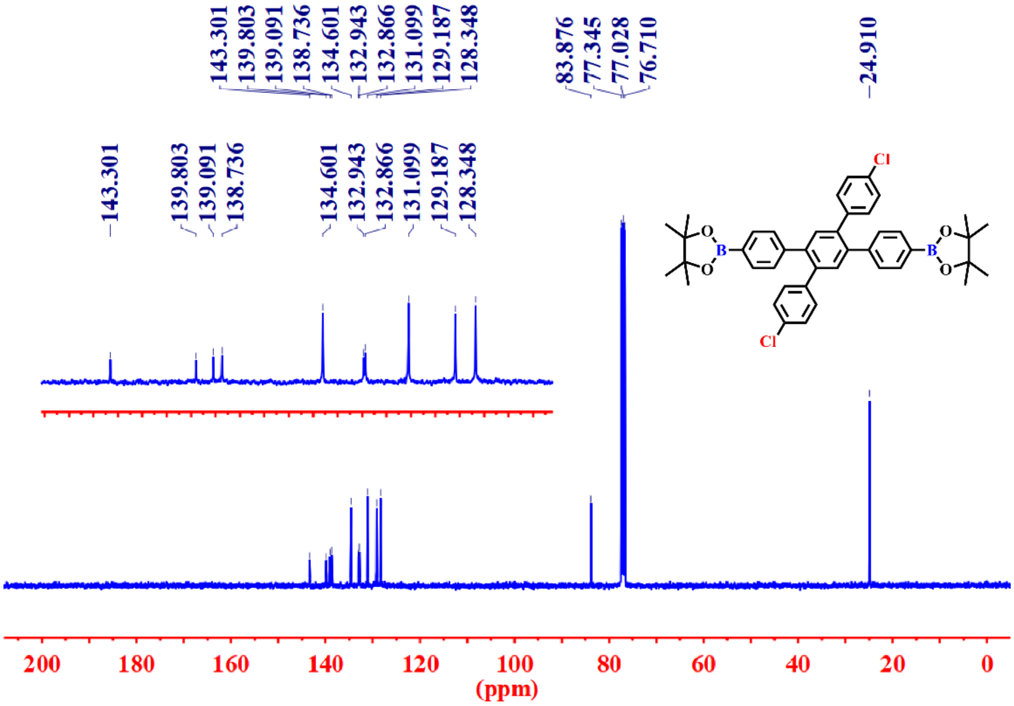


Figure S17. ^{13}C NMR spectrum of compound **2** in CDCl$_3$.

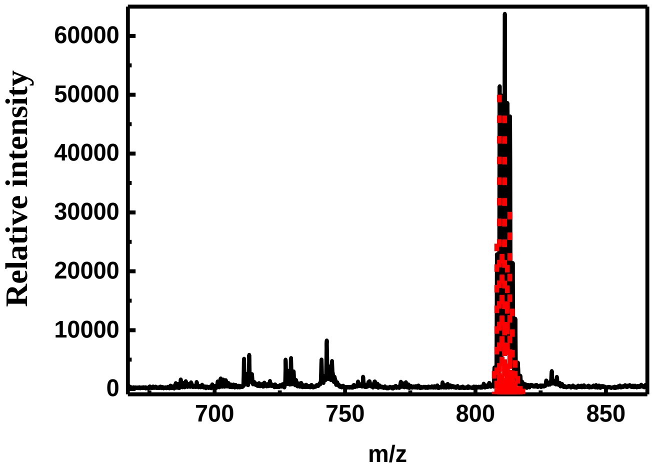


Figure S18. MALDI-TOF-MS spectrum (black) and simulated data (red) for compound **2**.

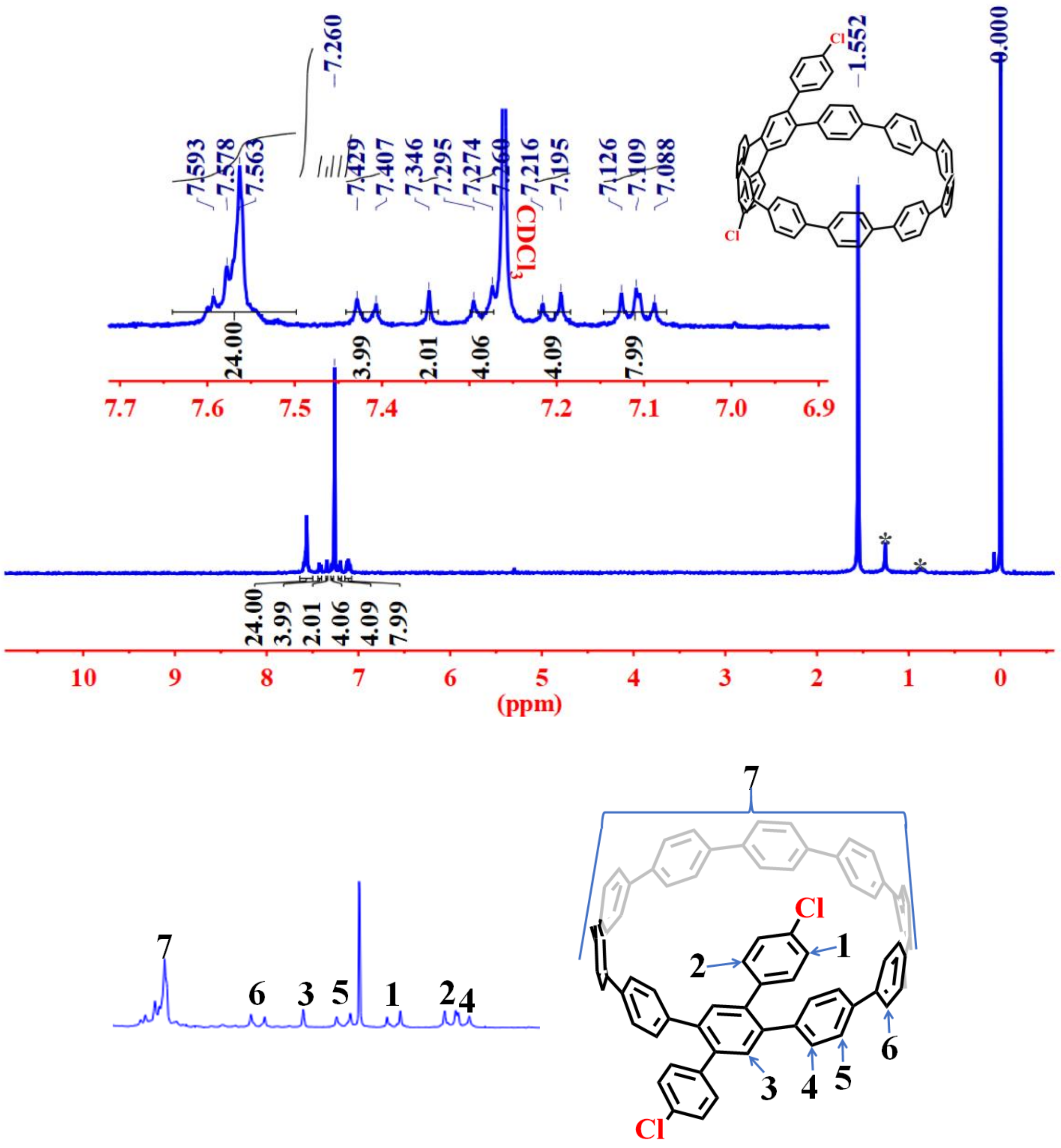


Figure S19. ^{1}H NMR spectrum of compound **5** in $CDCl_3$. (* grease residual signals).

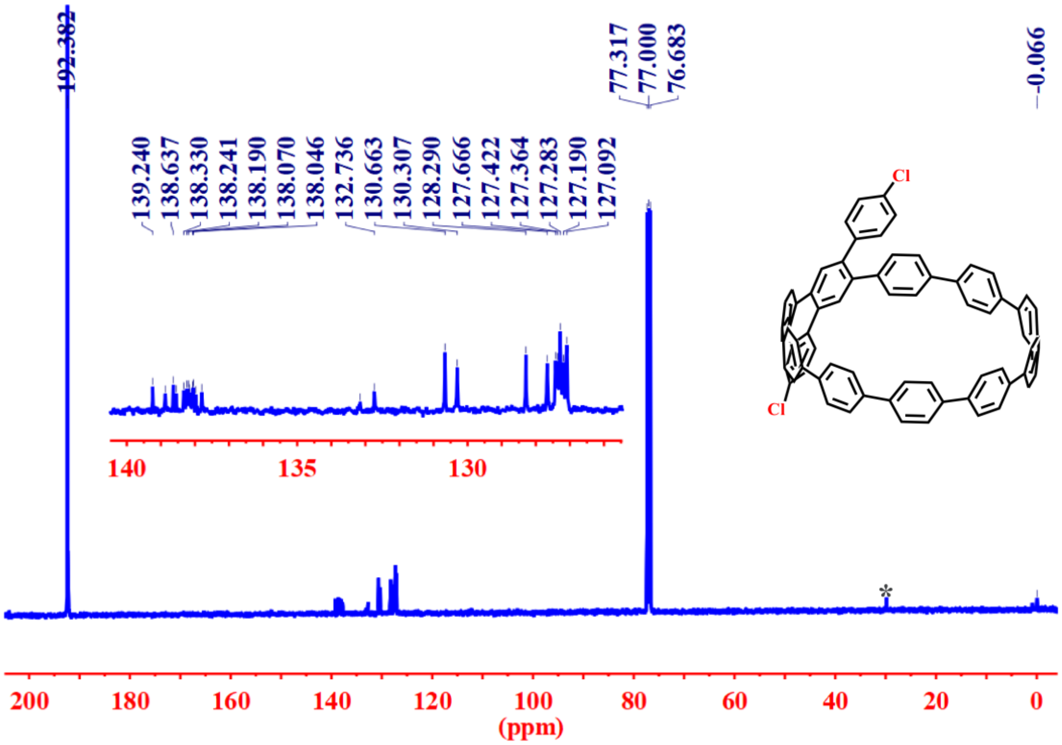


Figure S20. ^{13}C NMR spectrum of compound **5** in $CS_2/CDCl_3$ (1:1). (* grease residual signals).

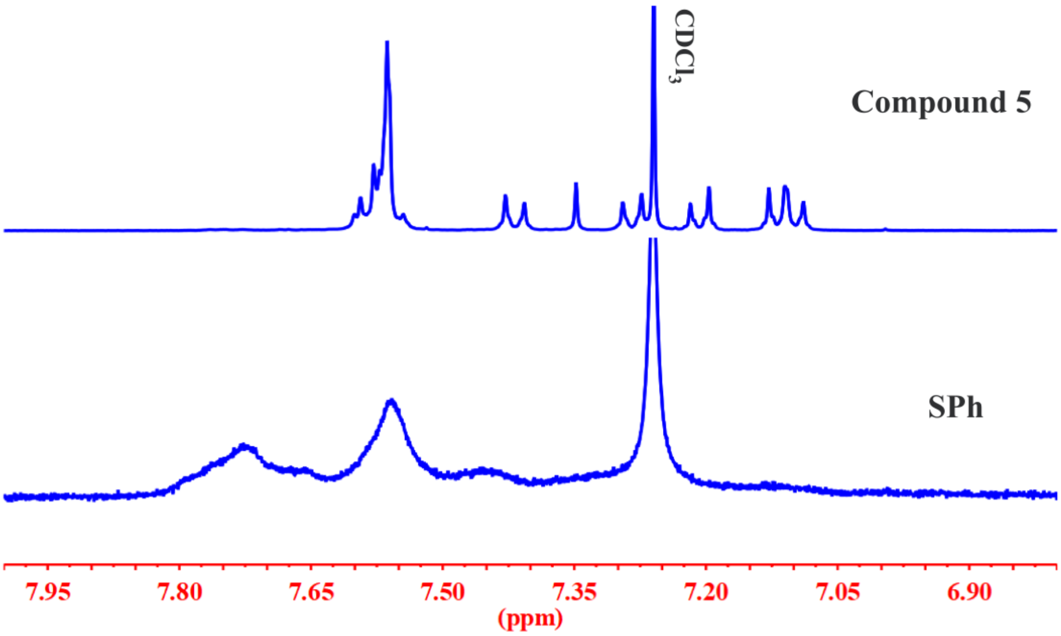


Figure S21. ^{1}H NMR spectra of **SPh** and compound **5** in CDCl$_3$.

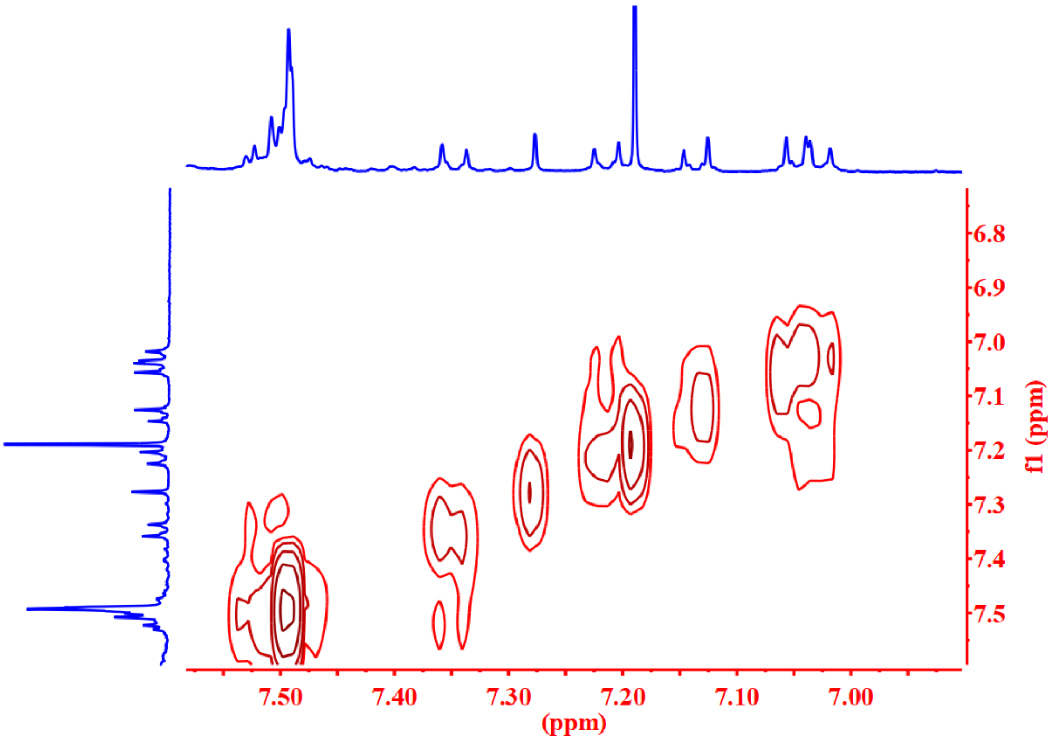


Figure S22. Expanded 2D ^{1}H-^{1}H COSY NMR spectrum (400 MHz, $CDCl_3$) of compound **5**.

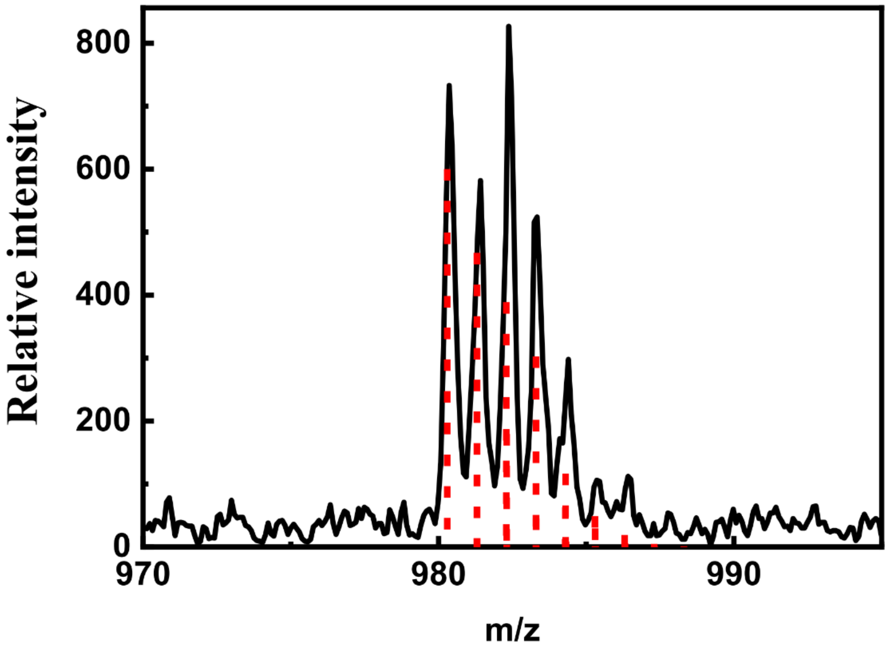


Figure S23. MALDI-TOF-MS spectrum (black) and simulated data (red) for compound **5**.

References

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