Electronic Supplementary Information

Self-assembly of β-cyclodextrin-pillar[5]arene molecules into supramolecular nanoassemblies: Morphology control by stimuli-responsiveness and host–guest interactions

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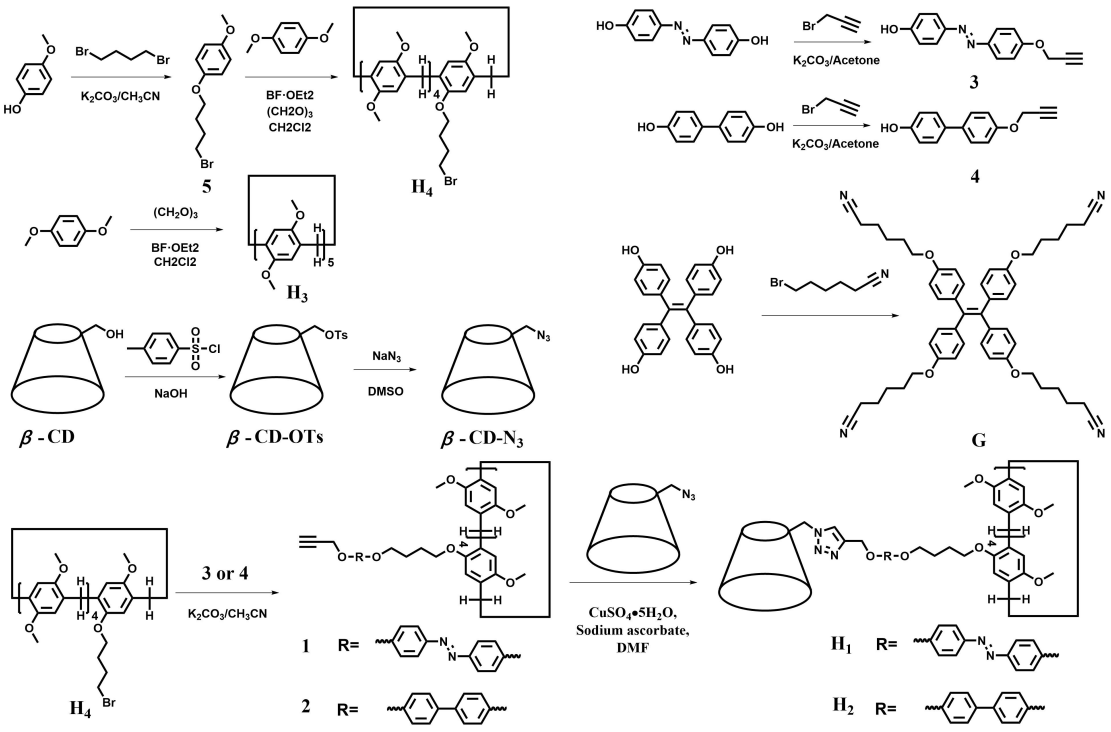
General Materials and Techniques.

General Materials: Toluene-p-sulfonyl chloride, 1,4-Dimethoxybenzene, Boron trifluoride ether, 1,4-Dibromobutane, 4-Methoxyphenol, Copper sulfate pentahydrate, Sodium ascorbate, 6-Bromohexanenitrile, Sodium hydroxide, β-Cyclodextrin, Tetrakis(4-hydroxyphenyl)ethylene, Polyformaldehyde, Sodium azide, Propargyl bromide, Potassium carbonate and conventional reagents were used as received.

Techniques: ^{1}H-NMR (300, 500 MHz), ^{13}C-NMR (75, 125 MHz) and ^{1}H NOESY NMR (500 MHz) spectra were recorded on a Bruker AM-300 and AM-500 instrument. The Uv-vis and FL spectra were obtained with JASCO UV-V650 UV-vis and FP-8200 FL spectrometers, respectively. Mass spectroscopy was performed with a Shimadzu AXIMA-CFR matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometer. A zetasizer Nano-ZS was used to analyze the size distributions of molecules in aqueous solution. ATR-IR spectra were obtained using a Bruker VERTEX 70 spectrometer. Transmission electron microscope (TEM) experiments: A glow discharge instrument (15mA, 60s) was used to carry out hydrophilic treatment on the carbon support membrane (ordinary carbon support membrane, 200 mesh, Beijing China Lens Science and Technology Co., LTD.), and then 3 μL samples of H_2O/DMSO solution and $CHCl_3$/DMSO solution were added to the treated and untreated carbon support membranes by drops respectively, standing at room temperature. After drying, 3 μL uranyl acetate aqueous solution (0.4 wt %) was used for staining. After standing for one minute, absorb the excess dye solution, and dry again at room temperature, the carbon support membrane can be placed in the sample

tank for testing. Transmission electron microscope (TEM) images were measured by JEOL's high resolution TEM (JEM-2100 Plus), using an accelerated voltage of 120kV. Atomic force microscope (AFM) experiments: The whole layer of mica was completely peeled off with plastic tape (Scotch), and the freshly peeled mica (10×20 mm) was placed on the surface dish, drop 5μL of the solution to be tested was added to the mica by drip casting method, and the mica was taken out and placed on the sample table for testing after being dried at room temperature for 12 hours. The test mode was adopted ACAFM mode.

Synthesis of the molecules $H_{1\text{-}2}$, 1-4 and G:



Scheme S1 Synthetic routes of the molecules $H_{1\text{-}2}$, **1-4** and **G**.

Compounds **5, H_3**, **H_4**, **β-CD-OTs**, **β-CD-N_3** were synthesized based on previous literature reports.[1-3]

Synthesis **3** and **4**. These compounds were synthesized according to the same procedure, a representation example is described for **3**. 4,4′-dihydroxyazobenzene

(2.00 g, 9.34 mmol) and potassium carbonate (4.50 g, 32.6 mmol) were dispersed in 50 ml acetone, the mixture was degassed and stirred at room temperature for 2 hours. Next, propargyl bromide (0.925 g, 7.78 mmol) was added dropwise to the mixture, refluxed 24 hours under a nitrogen environment. After the organic solution was removed and water was added, extracted with dichloromethane and ethyl acetate. At last, 0.635 g pure target molecule **3** was obtained through column chromatography.

Compound **3**: (Yellow solid, yield 34.3%, M.p.: 134 ℃), ^{1}H NMR (300 MHz, DMSO-d_6, δ, ppm): 10.22 (s, 1H), 7.79 (dd, J = 19.2, 8.7 Hz, 4H), 7.16 (d, J = 8.7 Hz, 2H), 6.93 (d, J = 8.7 Hz, 2H), 4.91 (d, J = 2.4 Hz, 2H), 3.64 (t, J = 2.4 Hz, 1H). ^{13}C NMR (75 MHz, DMSO-d_6, δ, ppm): 160.90, 159.50, 147.18, 145.69, 124.93, 124.26, 116.33, 115.84, 79.38, 79.06, 56.26. Elemental analysis for $C_{15}H_{12}N_2O_2$ (252.27 g/mol): C: 71.42%, H: 4.79%, N: 11.10%, found: C: 71.37%, H: 4.99%, N: 10.91%.

Compound **4**: (White solid, yield 43.5%, M.p.: 135 ℃), ^{1}H NMR (300 MHz, DMSO-d_6, δ, ppm): 9.45 (s, 1H), 7.45 (dd, J = 25.2, 8.7 Hz, 4H), 7.02 (d, J = 8.7 Hz, 2H), 6.82 (d, J = 8.7 Hz, 2H), 4.81 (d, J = 2.4 Hz, 2H), 3.58 (t, J = 2.4 Hz, 1H). ^{13}C NMR (75 MHz, DMSO-d_6, δ, ppm): 157.09, 156.52, 133.98, 131.07, 127.78, 127.45, 116.13, 115.66, 79.84, 78.65, 55.91. Elemental analysis for $C_{15}H_{12}O_2$ (224.25 g/mol): C: 80.34%, H: 5.39%, found: C: 80.28%, H: 5.59%.

Compound **G**: tetrakis(4-hydroxytetraphenyl)ethene (0.150 g, 0.378 mmol) and potassium carbonate (0.174 g, 1.26 mmol) were dispersed in 50 ml acetone, the mixture was degassed and stirred at room temperature for 2 hours. Next, 6-bromohexanenitrile (0.333 g, 1.89 mmol) was added dropwise to the mixture, refluxed 24 hours under a nitrogen environment. After the organic solution was removed and water was added, extracted with dichloromethane and ethyl acetate. At last, 0.258 g pure target molecule **G** was obtained through column chromatography. (White solid, yield 87.7%, M.p.: 83 ℃), ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 6.92 (d, J = 9.0 Hz, 8H), 6.62 (d, J = 9.0 Hz, 8H), 3.90 (t, J = 6.0 Hz, 8H), 2.38 (t, J = 6.0 Hz, 8H), 1.83-1.69 (m, 16H), 1.67-1.59 (m, 8H). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 157.08, 138.33, 136.93, 132.57, 119.66, 113.50, 67.11, 28.54, 25.47, 25.22, 17.17. MALDI-TOF-MS: m/z $[M-H]^+$ 776.36. Elemental analysis for $C_{50}H_{56}N_4O_4$ (777.00

g/mol): C: 77.29%, H: 7.26%, N: 7.21%, found: C: 76.98%, H: 6.96%, N: 7.14%.

Synthesis **1** and **2**. These compounds were synthesized according to the same procedure, a representation example is described for **1**. **3** (0.1 g, 0.396 mmol) and potassium carbonate (0.27 g, 1.96 mmol) were dispersed in 60 ml acetonitrile, the mixture was degassed and stirred at room temperature for 2 hours. Next, **H_4** (0.41 g, 0.47 mmol) was added dropwise to the mixture, refluxed 24 hours under a nitrogen environment. After the organic solution was removed and water was added, extracted with dichloromethane and ethyl acetate. At last, 0.232 g pure target molecule **1** was obtained through column chromatography.

Compound **1**: (Yellow solid, yield 56.1%, M.p.: 95 ℃), ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 7.95-7.90 (m, 4H), 7.10 (d, J = 8.4 Hz, 2H), 6.97 (d, J = 8.4 Hz, 2H), 6.79-6.74 (m, 10H), 4.78 (d, J = 2.4 Hz, 2H), 4.02 (t, J = 2.4 Hz, 2H), 3.91 (t, J = 6 Hz, 2H), 3.80 (s, 2H), 3.77 (s, 8H), 3.71-3.62 (m, 27H), 2.56 (t, J = 2.4 Hz, 2H), 1.99-1.88 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): 161.28, 159.45, 150.99, 150.94, 150.86, 150.81, 150.67, 150.00, 147.57, 146.90,128.50, 128.36, 128.34, 128.31, 128.23, 128.17, 124.51, 124.31, 115.19, 115.00, 114.71, 114.24, 114.13, 114.03, 113.99, 113.94, 78.20, 75.96, 68.04, 67.83, 56.03, 55.93, 55.89, 55.84, 55.77, 29.86, 29.75, 29.62, 29.58, 29.53, 26.29, 26.03. MALDI-TOF-MS: m/z $[M+H]^+$ 1043.7, $[M+Na]^+$ 1066.5, $[M+K]^+$ 1082.4. Elemental analysis for $C_{63}H_{66}N_2O_{12}$ (1043.20 g/mol): C: 72.53%, H: 6.38%, N: 2.69%, found: C: 72.56%, H: 6.44%, N: 2.63%.

Compound **2**: (White solid, yield 58.2%, M.p.: 117 ℃), ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 7.50-7.45 (m, 4H), 7.03 (d, J = 8.7 Hz, 2H), 6.94 (d, J = 8.7 Hz, 2H), 6.79-6.75 (m, 10H), 4.71 (d, J = 2.4 Hz, 2H), 4.01 (t, J = 6.0 Hz, 2H), 3.89, (t, J = 6.0 Hz, 2H), 3.80 (s, 2H), 3.77 (s, 8H), 3.69-3.63 (m, 27H), 2.53 (t, J = 2.4 Hz, 2H), 2.03-1.88 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): 158.30, 156.71, 150.97, 150.87, 150.84, 150.81, 150.71, 150.04, 134.43, 133.26, 128.36, 128.33, 128.31, 127.82, 127.76, 115.25, 114.94, 114.80, 114.27, 114.14, 114.09, 114.01, 113.98, 78.70, 75.64, 68.07, 67.64, 55.94, 55.90, 55.84, 55.81, 55.77, 29.81, 29.78, 29.73, 29.67, 29.55, 26.50, 26.29. MALDI-TOF-MS: m/z $[M]^+$ 1015.2, $[M+Na]^+$ 1038.0, $[M+K]^+$ 1054.4. Elemental analysis for $C_{63}H_{66}O_{12}$ (1015.19 g/mol): C: 74.54%, H: 6.55%, found: C:

74.47%, H: 6.63%.

Compound **5**: (White solid, yield 71.9%, M.p.: 45 ℃), ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 6.83 (s, 4H), 3.95 (t, J = 6.0 Hz, 2H), 3.77 (s, 3H), 3.49 (t, J = 6.0 Hz, 2H), 2.11-2.01 (m, 2H), 1.96-1.86 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): 153.85, 153.02, 115.41, 114.67, 67.47, 55.75, 33.56, 29.52, 28.02. Elemental analysis for $C_{11}H_{15}BrO_2$ (259.14 g/mol): C: 50.98%, H: 5.83%, found: C: 50.62, H: 5.79.

Compound **H_3**: (White solid, yield 21.2%, M.p.: 249 ℃), ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 6.75 (s, 10H), 3.78 (s, 10H), 3.64 (s, 30H). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): 150.86, 128.24, 114.16, 55.81, 29.73. MALDI-TOF-MS: m/z $[M]^+$ 751.5, $[M+Na]^+$ 774.6. Elemental analysis for $C_{45}H_{50}O_{10}$ (750.87 g/mol): C: 71.98%, H: 6.71%, found: C: 71.85, H: 6.63.

Compound **H_4**: (White solid, yield 21.1%, M.p.: 129 ℃), ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 6.79-6.70 (m, 10H), 3.83 (t, J = 6.0 Hz, 2H), 3.77 (s, 10H), 3.70-3.60 (m, 27H), 3.29 (t, J = 6.0 Hz, 2H), 1.92-1.87 (m, 2H), 1.83-1.76 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): 151.54, 151.47, 151.41, 151.37, 150.86, 150.82, 150.76, 150.66, 150.64, 149.92, 128.46, 128.40, 128.32, 128.30, 128.23, 128.21, 128.17, 128.08, 127.97, 127.63, 114.89. 114.25, 114.17, 114.13, 114.09, 114.06, 113.98, 113.89, 113.67, 67.40, 56.26, 56.20, 56.18, 56.11, 56.06, 56.01, 55.93, 55.80, 55.75, 30.34, 29.75, 29.70, 29.67, 29.61, 29.57, 29.34, 28.35. MALDI-TOF-MS: m/z $[M]^+$ 872.5, $[M+K]^+$ 911.5. Elemental analysis for $C_{48}H_{55}BrO_{10}$ (871.85 g/mol): C: 66.13%, H: 6.36%, found: C: 66.37%, H: 6.12%.

Compound ***β*-CD-OTs**: (White solid, yield 13.2%, M.p.: 179 ℃), ^{1}H NMR (300 MHz, DMSO-d_6, δ, ppm): 7.76 (d, J = 9.0 Hz, 2H), 7.44 (d, J = 9.0 Hz, 2H), 5.84-5.63 (m, 14H), 4.85-4.75 (m, 7H), 4.53-4.44 (m, 6H), 4.38-4.31 (m, 2H), 4.23-4.16 (m, 1H), 3.66-3.47 (m, 27H), 2.43 (s, 3H). ^{13}C NMR (75 MHz, DMSO-d_6, ppm): 145.21, 133.13, 130.35, 128.04, 102.39, 81.94, 81.90, 73.53, 72.83, 72.49, 70.07, 69.32, 60.37, 21.66. MALDI-TOF-MS: m/z $[M+Na]^+$ 1313.4. Elemental analysis for $C_{49}H_{76}O_{37}S$ (1289.17 g/mol): C: 45.65%, H: 5.94%, S: 2.49%, found: C: 45.12%, H: 6.01%, S: 2.45%.

Compound ***β*-CD-N_3**: (White solid, yield 97.8%, M.p.: 210 ℃), ^{1}H NMR (300 MHz,

DMSO-d_6, δ, ppm): 5.76-5.64 (m, 14H), 4.88-4.83 (m, 7H), 4.55-4.47 (m, 6H), 3.80-3.77 (m, 2H), 3.76-3.43 (m, 40H). ^{13}C NMR (75 MHz, DMSO-d_6, ppm): 102.73, 102.40, 102.06, 83.43, 82.33, 82.01, 81.86, 73.52, 72.85, 72.67, 72.49, 70.65, 60.38, 51.56. Elemental analysis for $C_{42}H_{69}N_3O_{34}$ (1160.00 g/mol): C: 43.49%, H: 6.00%, N: 3.62%, found: C: 43.02, H: 6.25, N: 3.59.

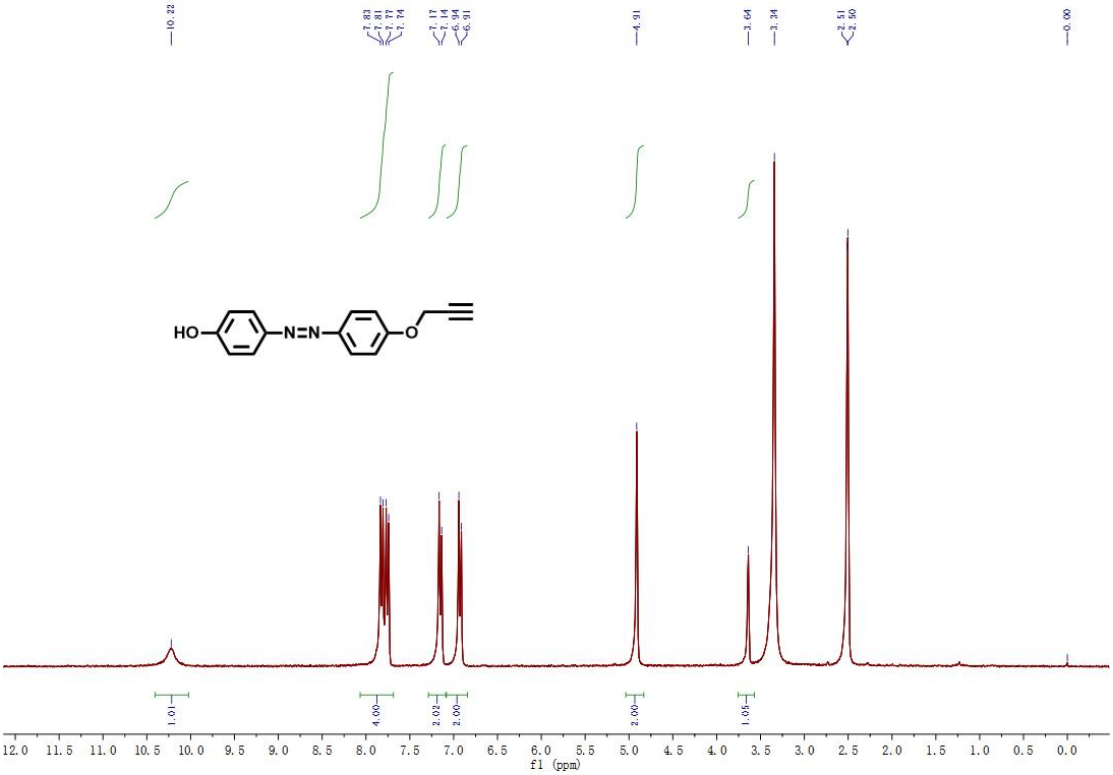


Figure S1 ^{1}H-NMR spectrum of molecule **3** in DMSO-d_6.

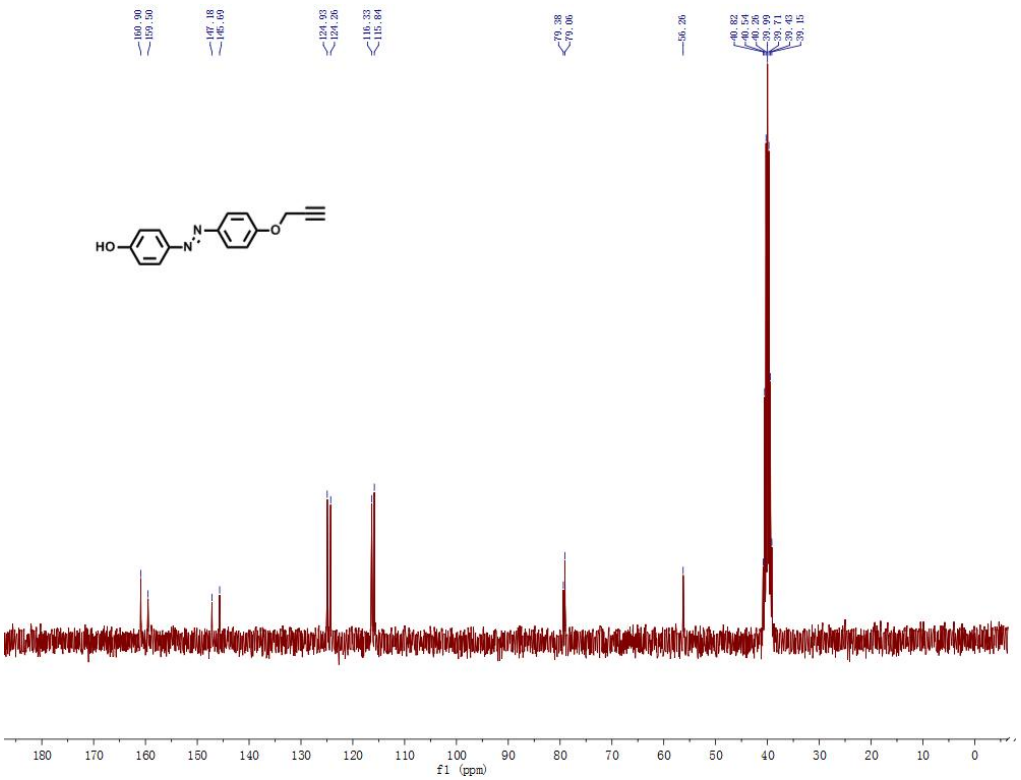


Figure S2 ^{13}C-NMR spectrum of molecule **3** in DMSO-d_6.

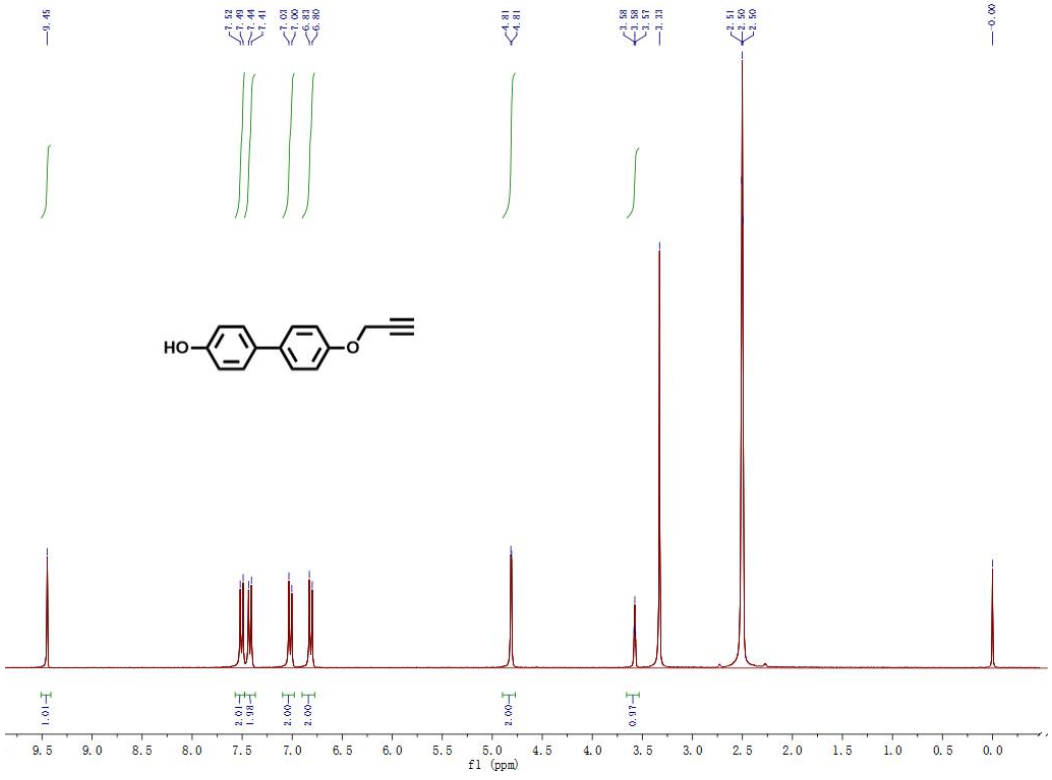


Figure S3 ^{1}H-NMR spectrum of molecule **4** in DMSO-d_6.

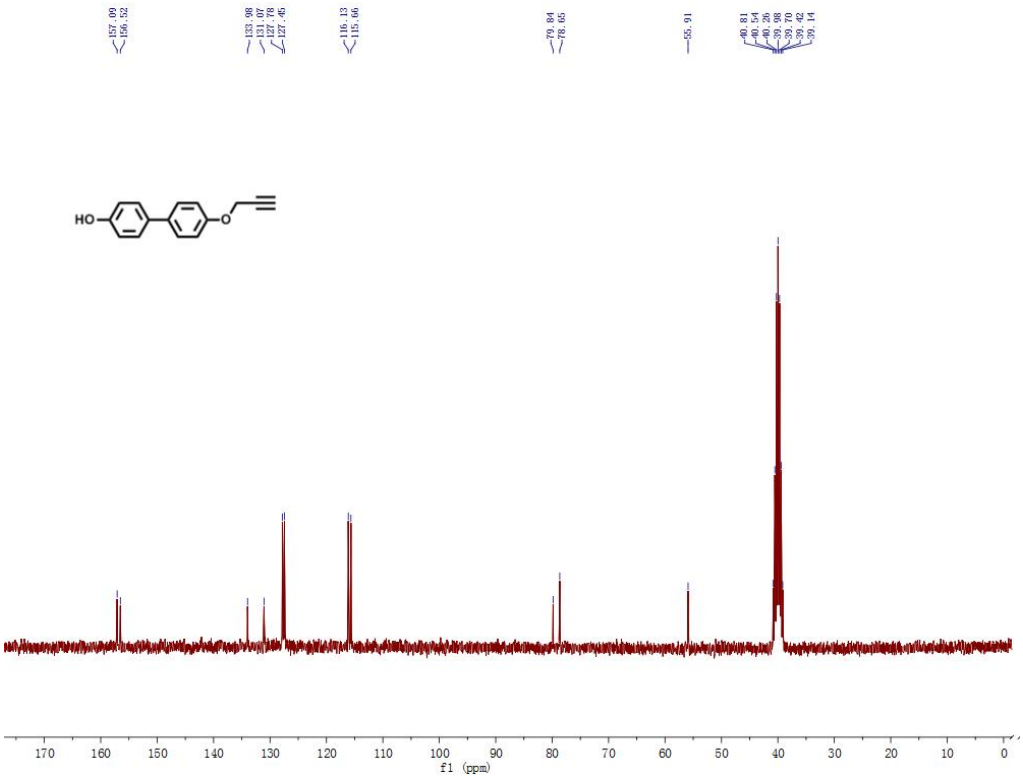


Figure S4 ^{13}C-NMR spectrum of molecule **4** in DMSO-d_6.

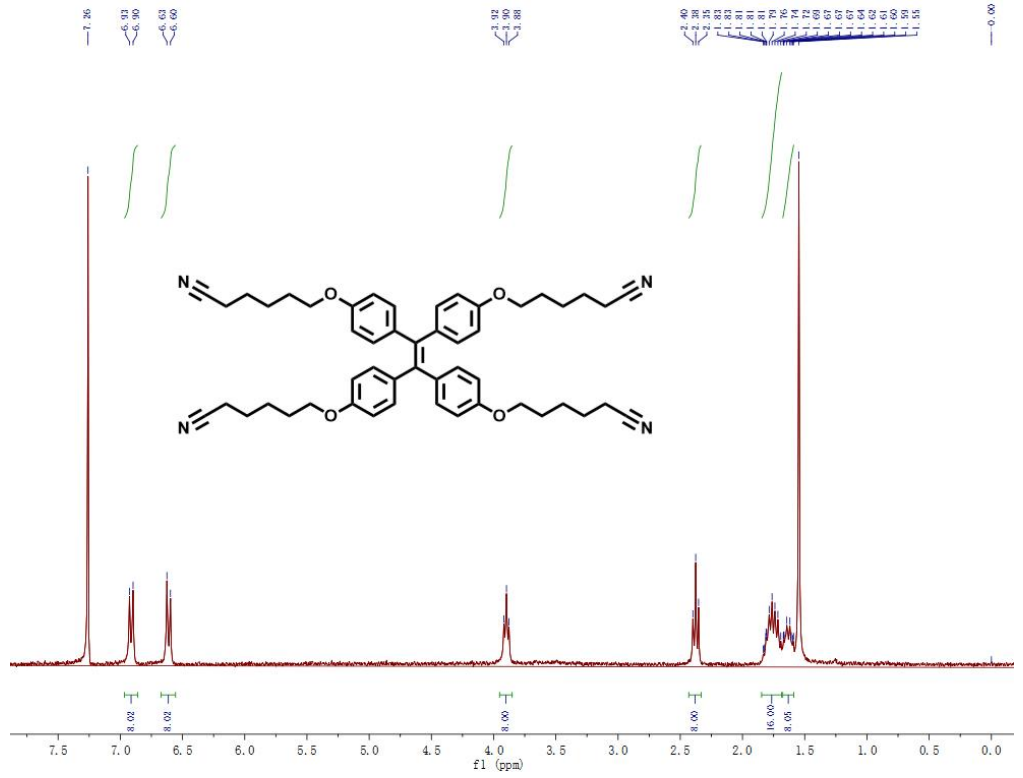


Figure S5 ^{1}H-NMR spectrum of molecule **G** in $CDCl_3$.

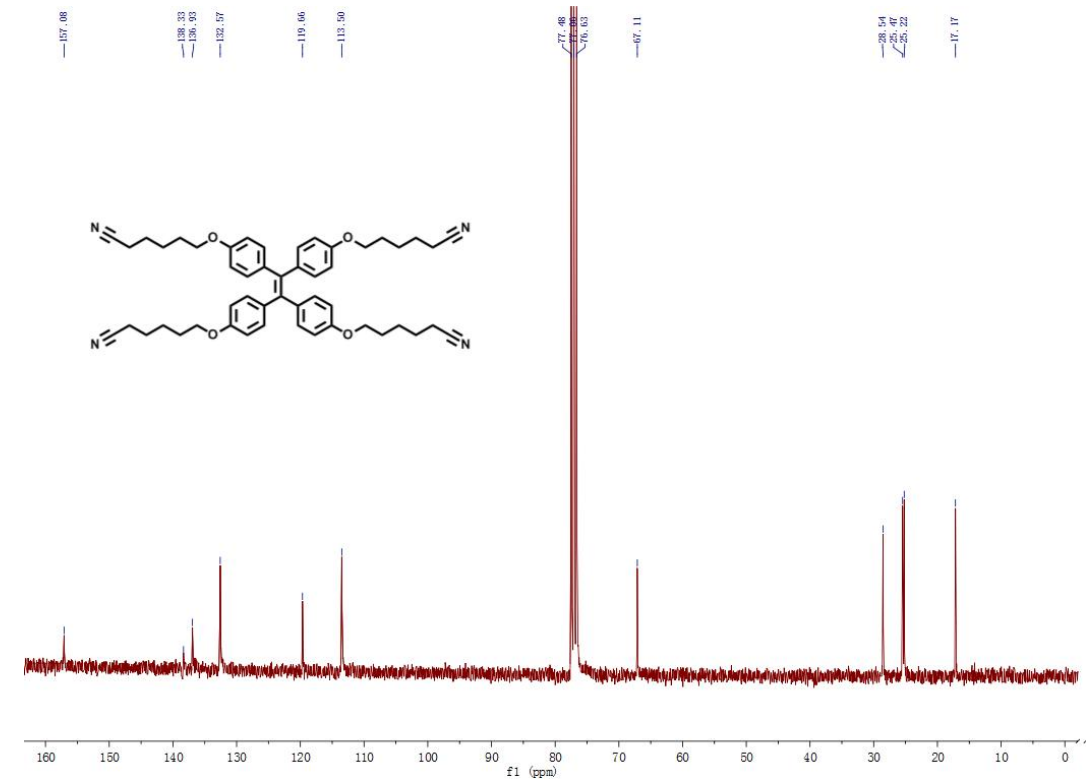


Figure S6 ^{13}C-NMR spectrum of molecule **G** in $CDCl_3$.

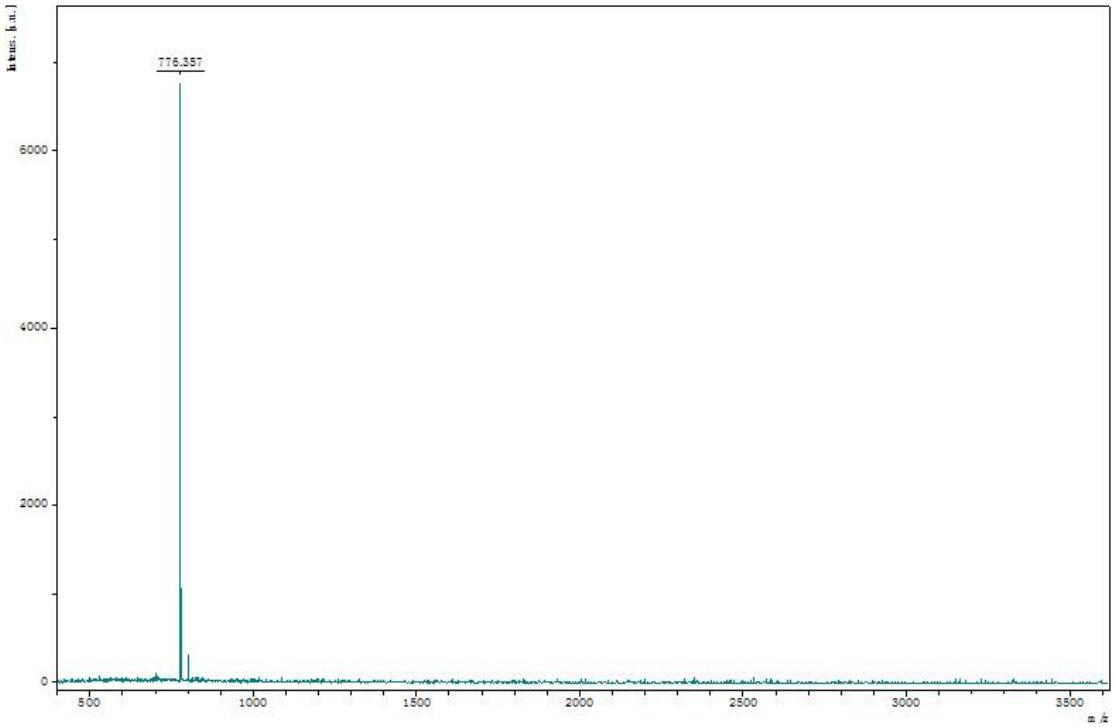


Figure S7 MALDI-TOF-Mass spectra of molecule **G**.

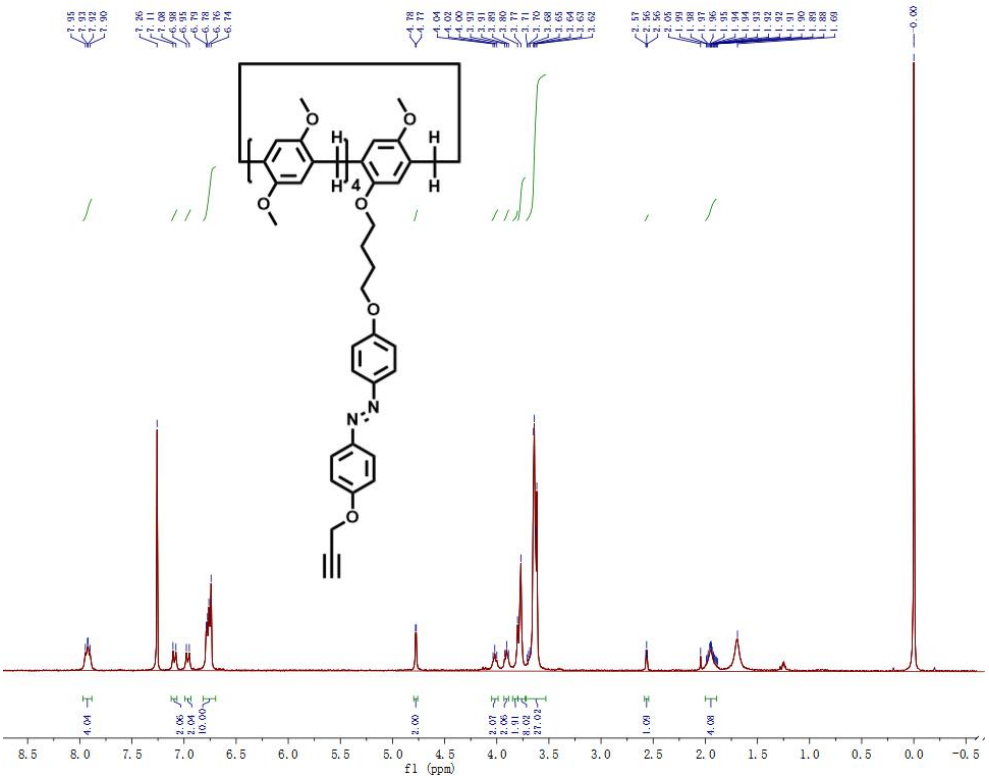


Figure S8 ^{1}H-NMR spectrum of molecule **1** in $CDCl_3$.

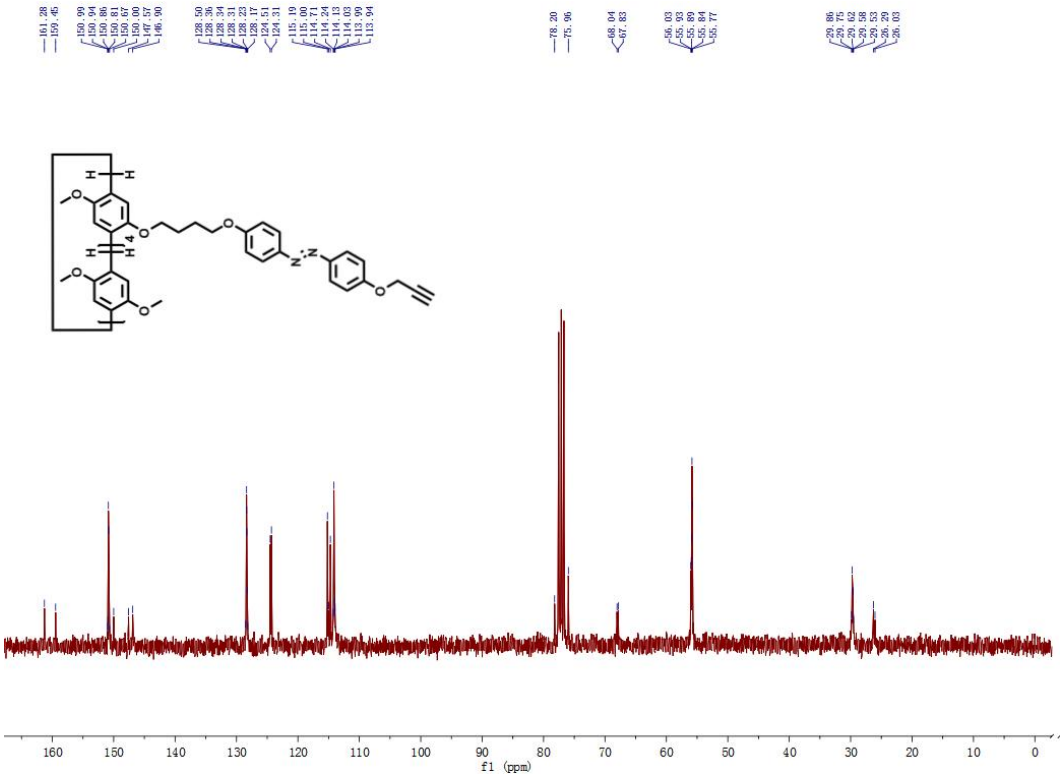


Figure S9 ^{13}C-NMR spectrum of molecule **1** in $CDCl_3$.

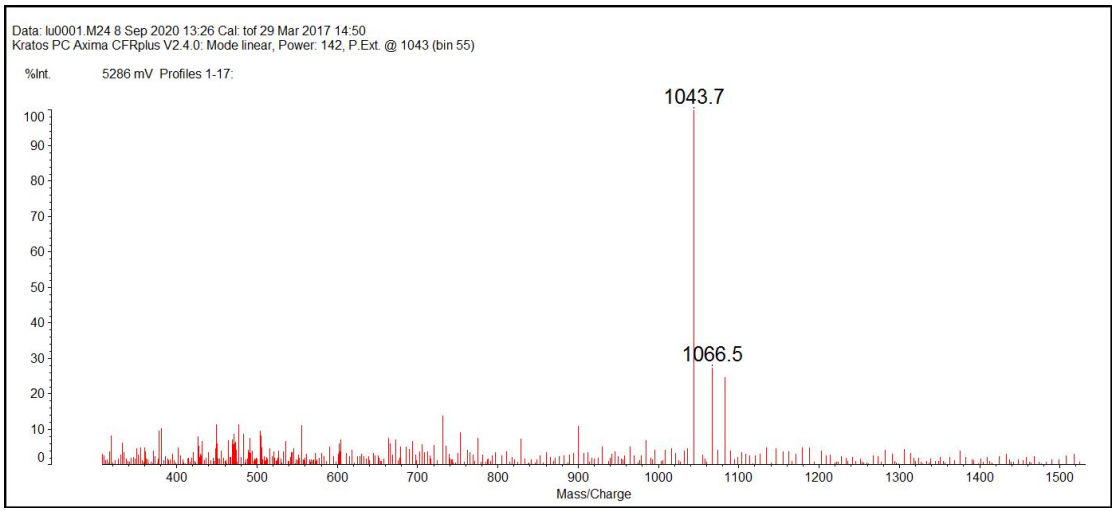


Figure S10 MALDI-TOF-Mass spectra of molecule **1**.

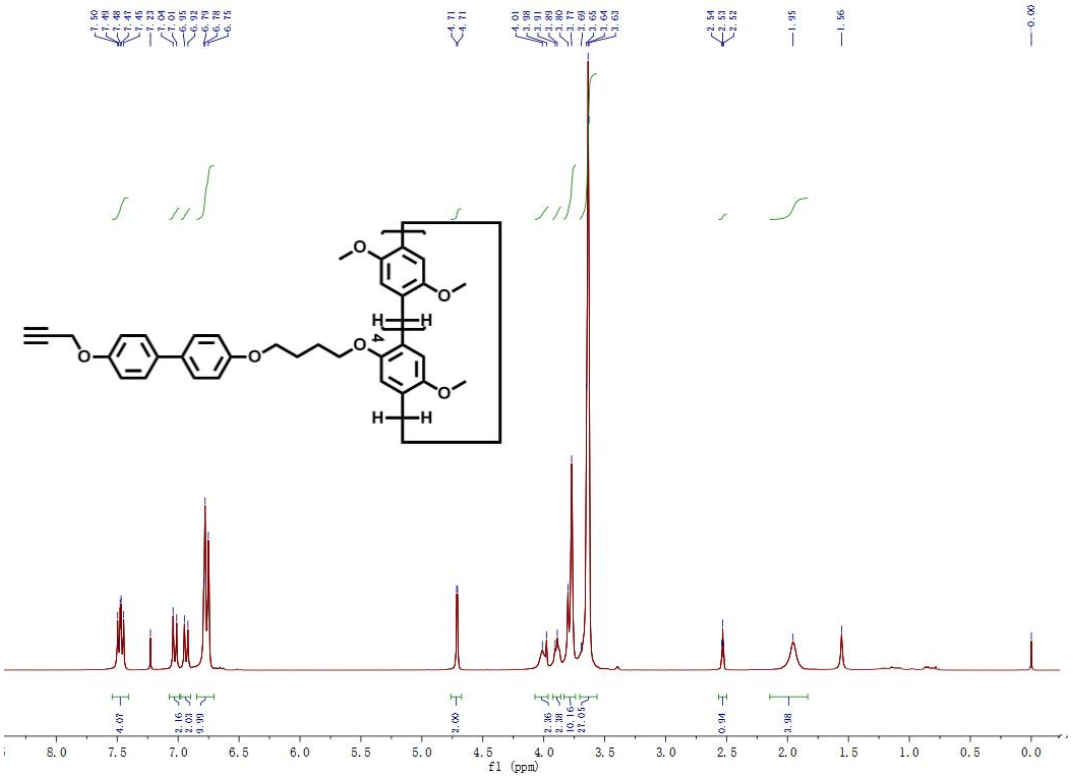


Figure S11 ^{1}H-NMR spectrum of molecule **2** in $CDCl_3$.

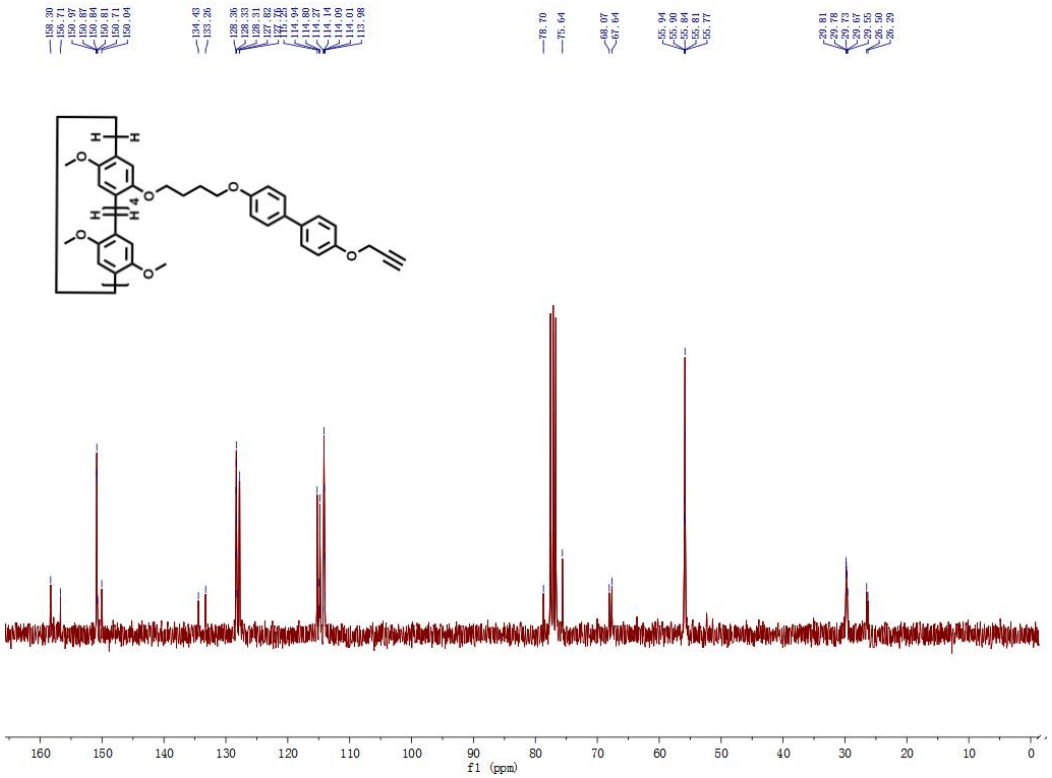


Figure S12 ^{13}C-NMR spectrum of molecule **2** in $CDCl_3$.

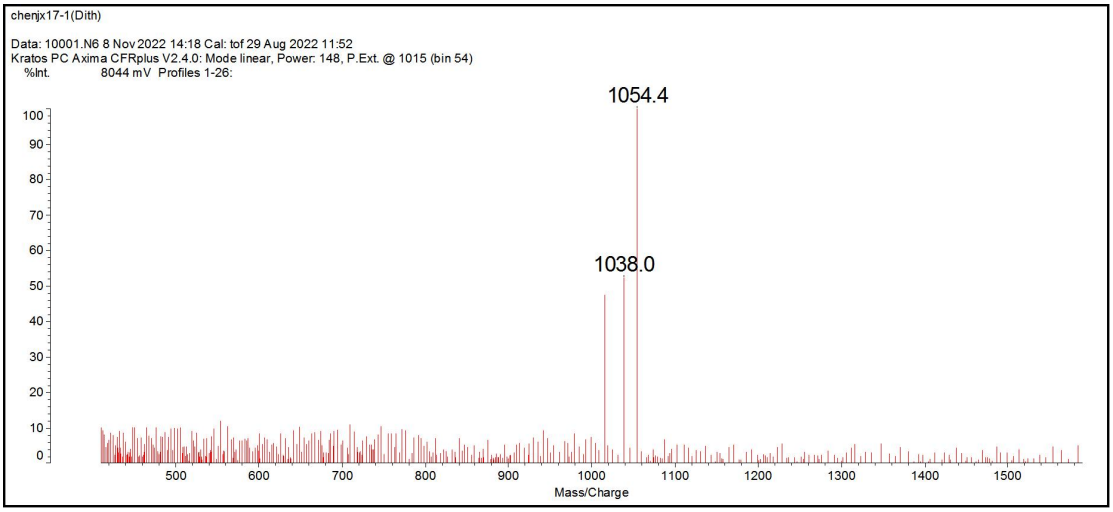


Figure S13 MALDI-TOF-Mass spectra of molecule **2**.

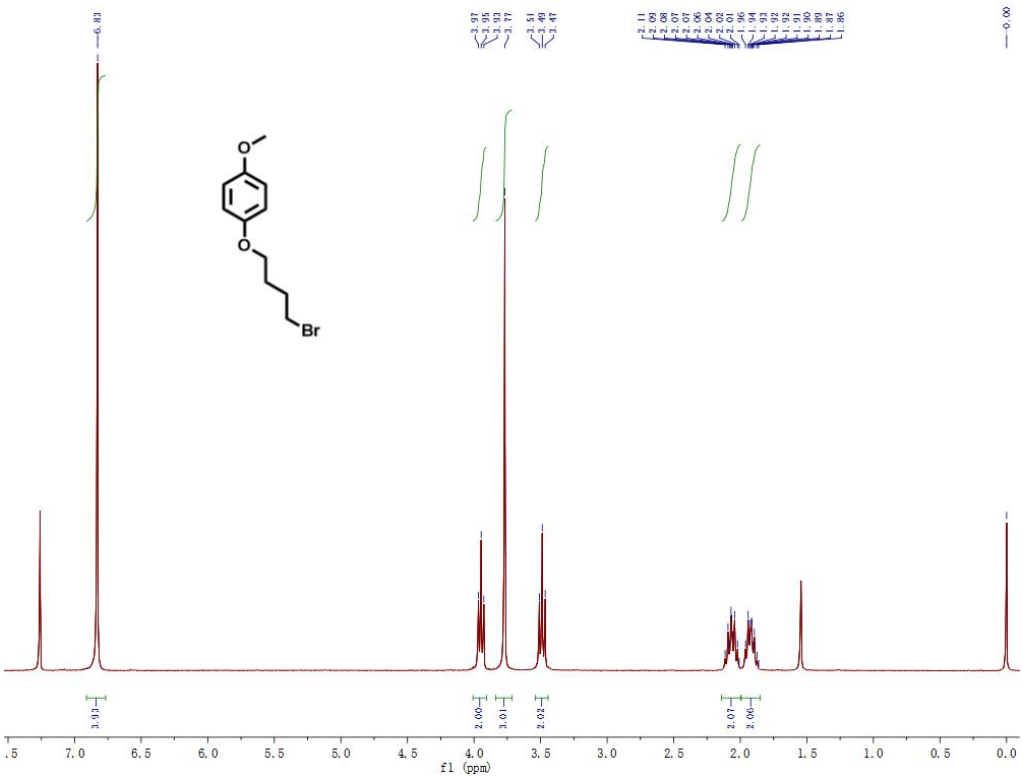


Figure S14 ^{1}H-NMR spectrum of molecule **5** in $CDCl_3$.

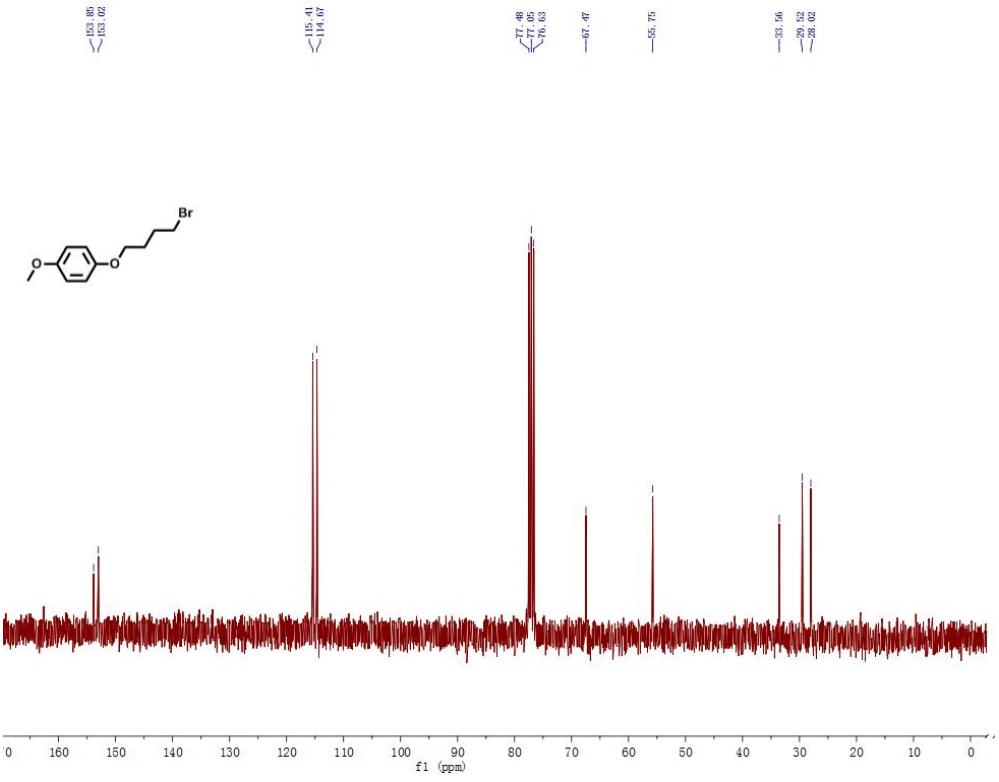


Figure S15 ^{13}C-NMR spectrum of molecule **5** in $CDCl_3$.

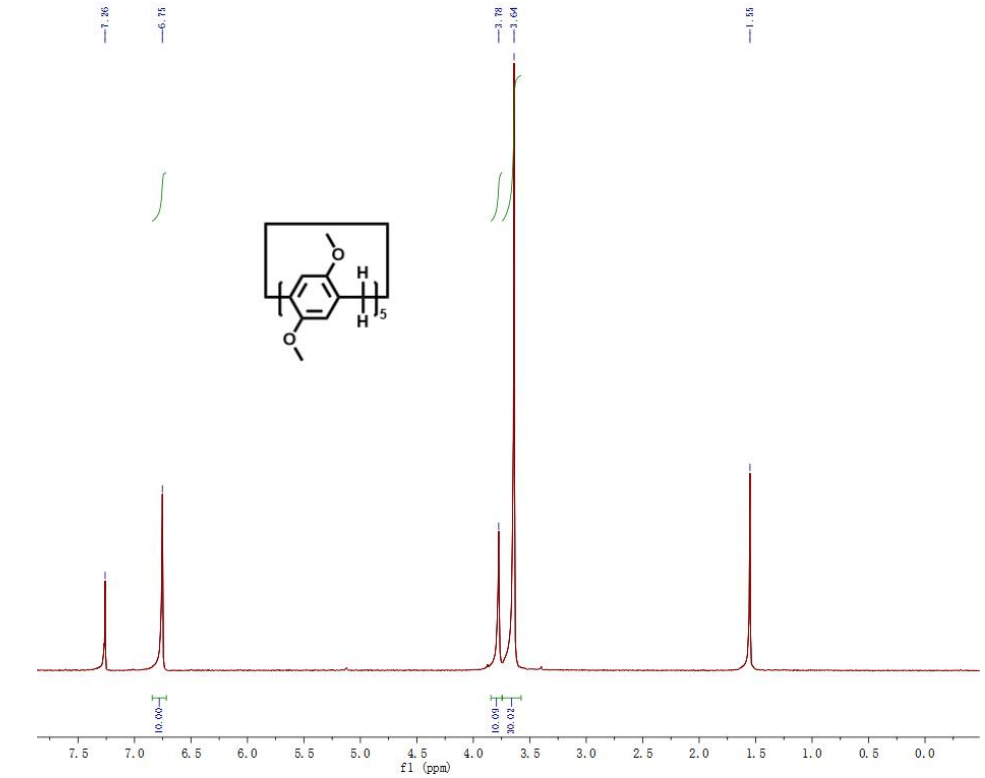


Figure S16 ^{1}H-NMR spectrum of molecule **H$_3$** in $CDCl_3$.

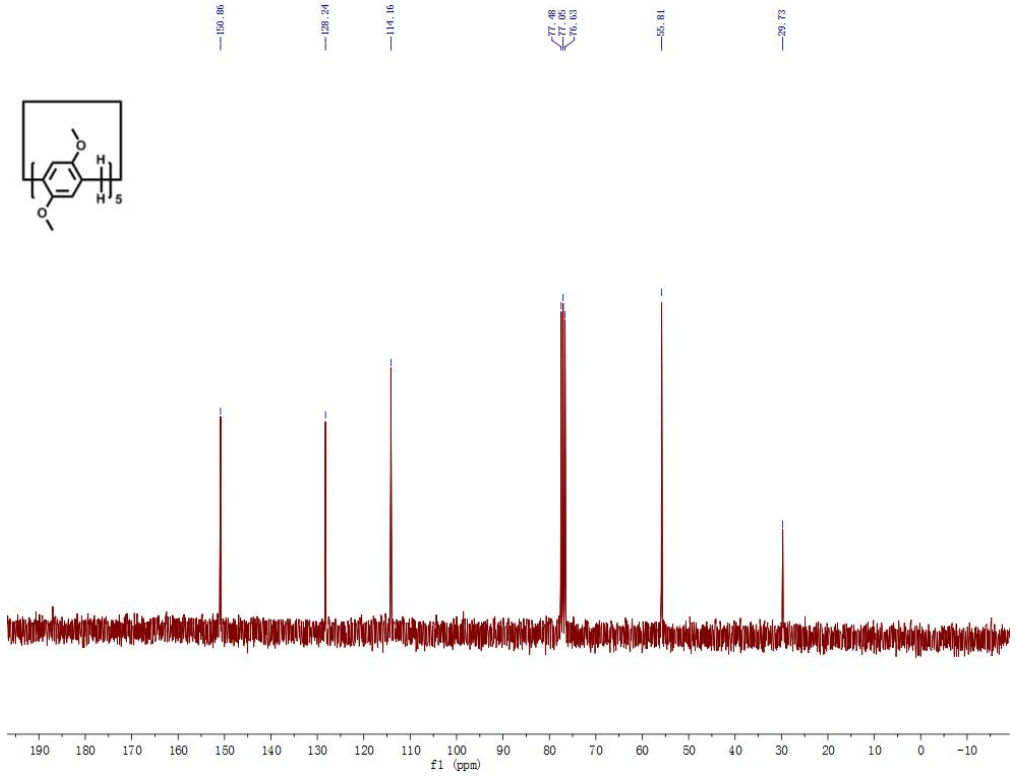


Figure S17 ^{13}C-NMR spectrum of molecule **H$_3$** in $CDCl_3$.

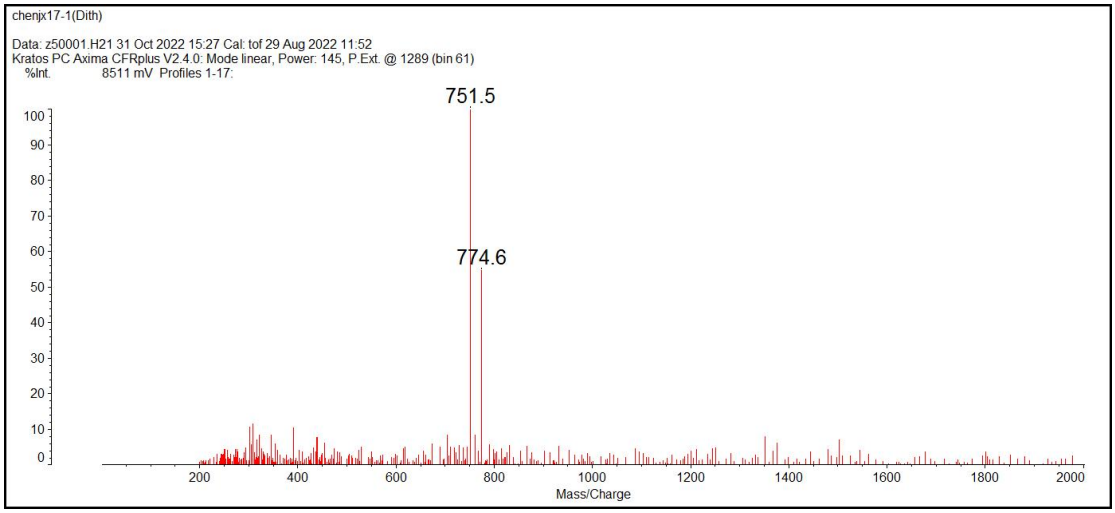


Figure S18 MALDI-TOF-Mass spectra of molecule **H_3**.

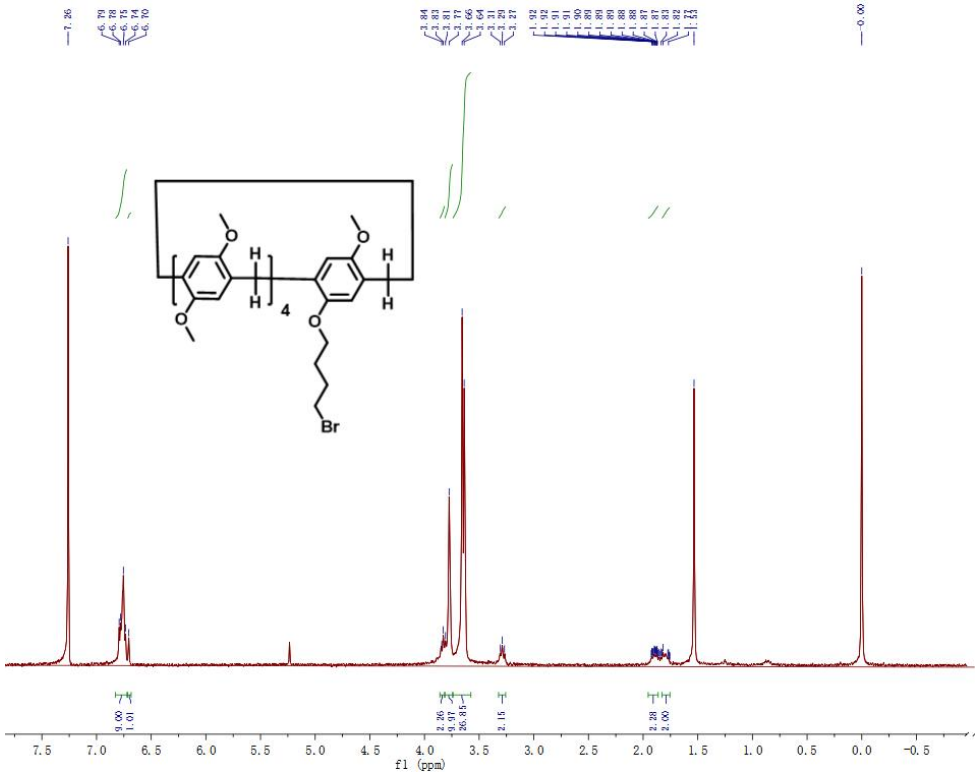


Figure S19 ^{1}H-NMR spectrum of molecule **H_4** in $CDCl_3$.

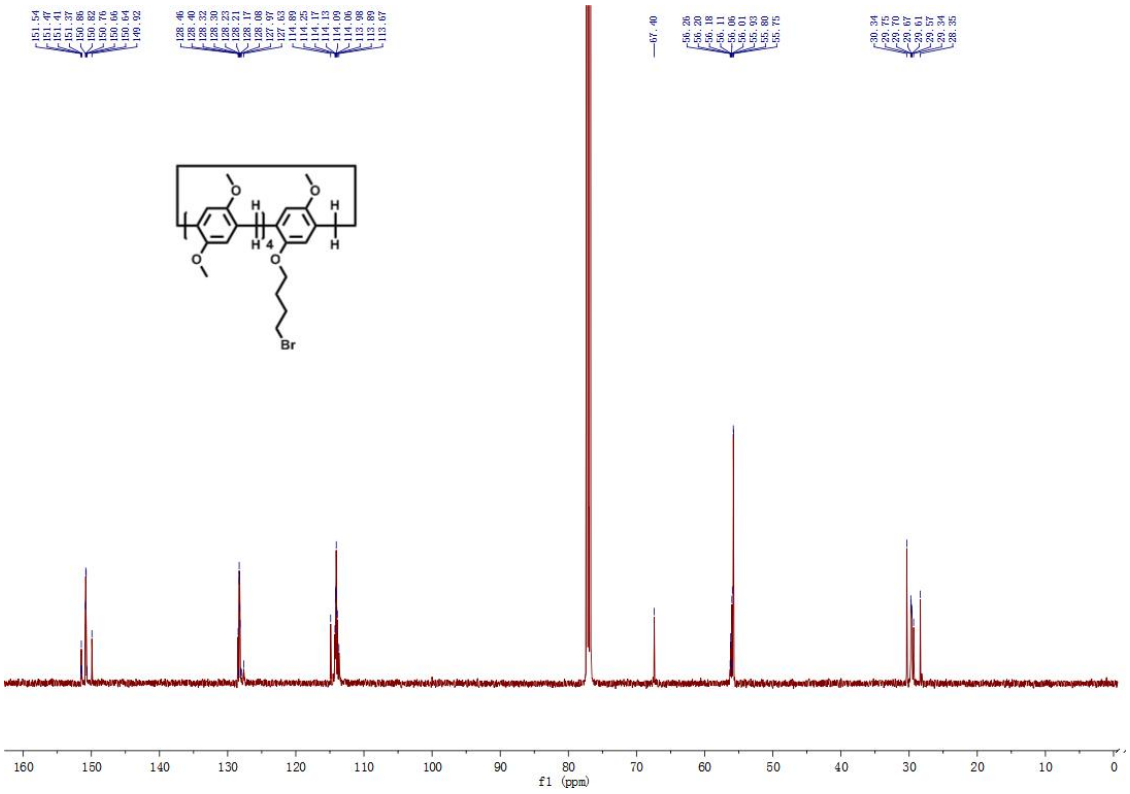


Figure S20 ^{13}C-NMR spectrum of molecule **H4** in $CDCl_3$.

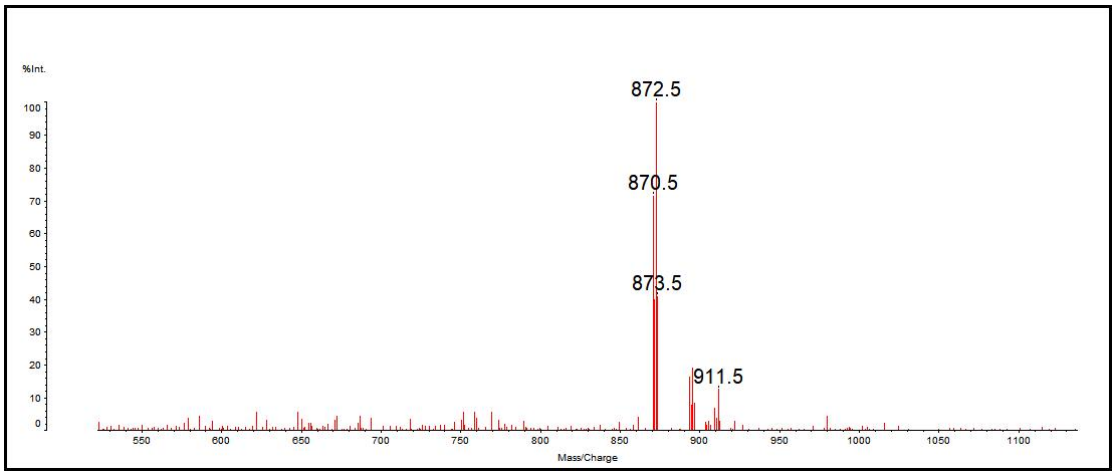


Figure S21 MALDI-TOF-Mass spectra of molecule **H4**.

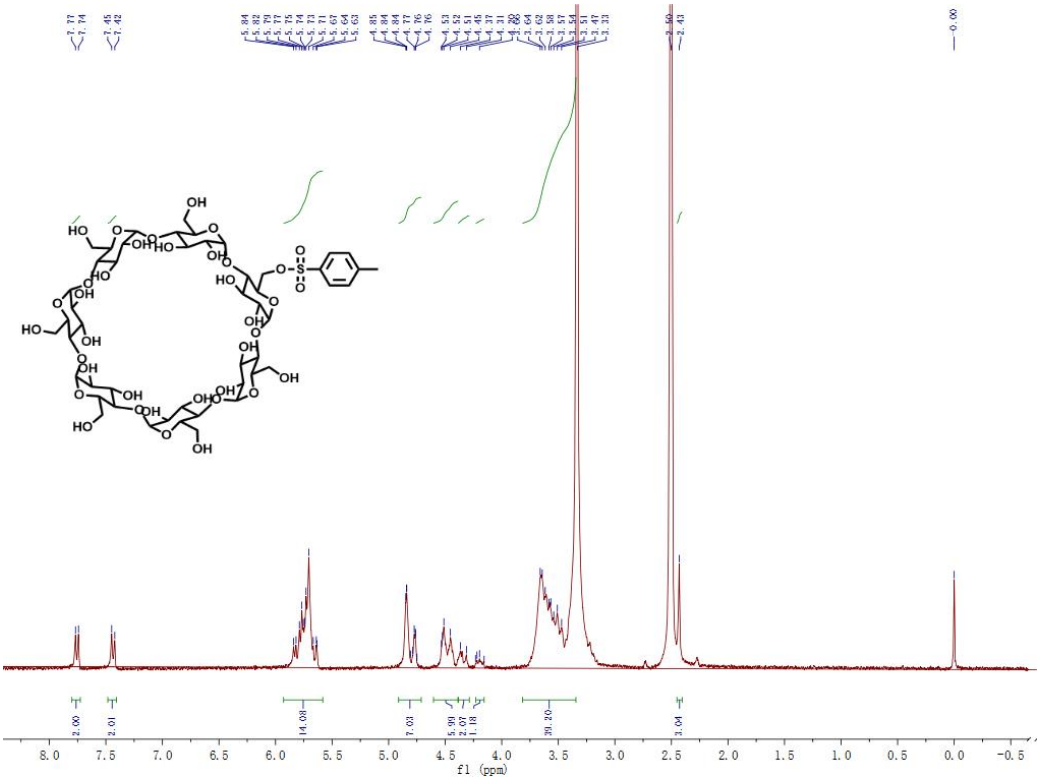


Figure S22 ^{1}H-NMR spectrum of molecule **β-CD-OTs** in DMSO-*d*$_6$.

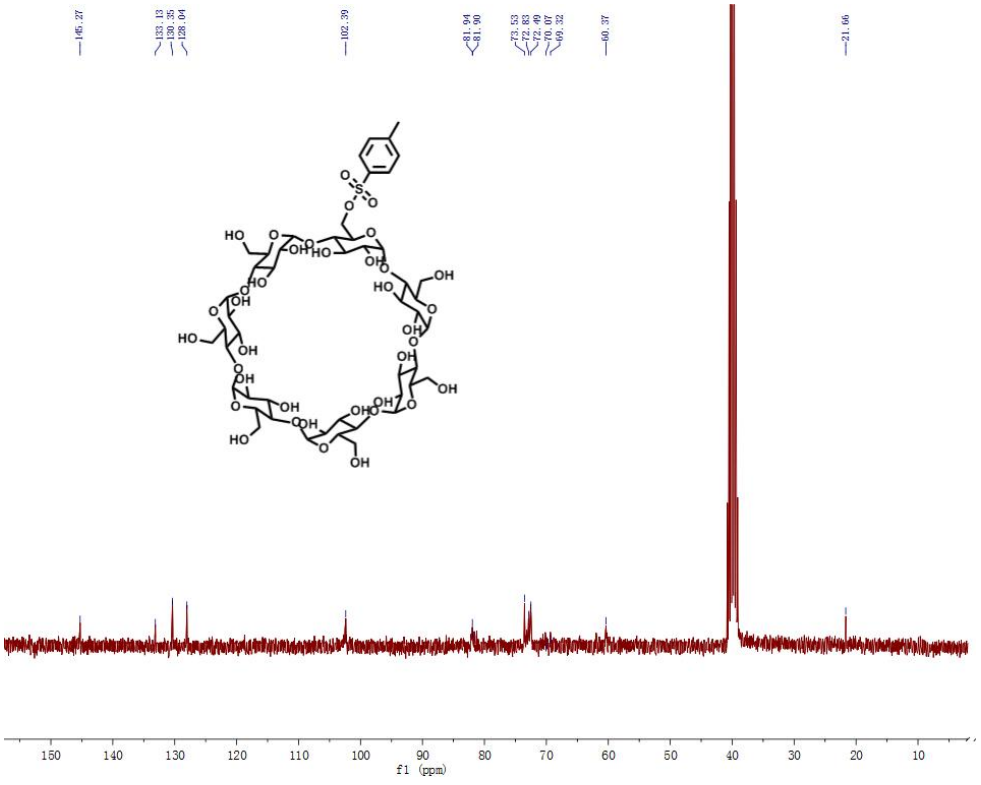


Figure S23 ^{13}C-NMR spectrum of molecule **β-CD-OTs** in DMSO-*d*$_6$.

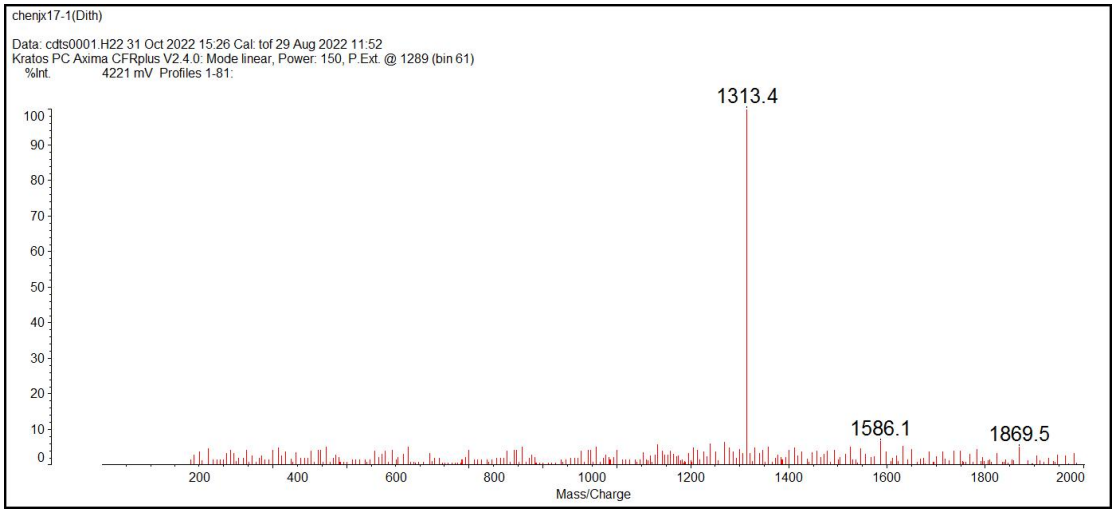


Figure S24 MALDI-TOF-Mass spectra of molecule **β-CD-OTs**.

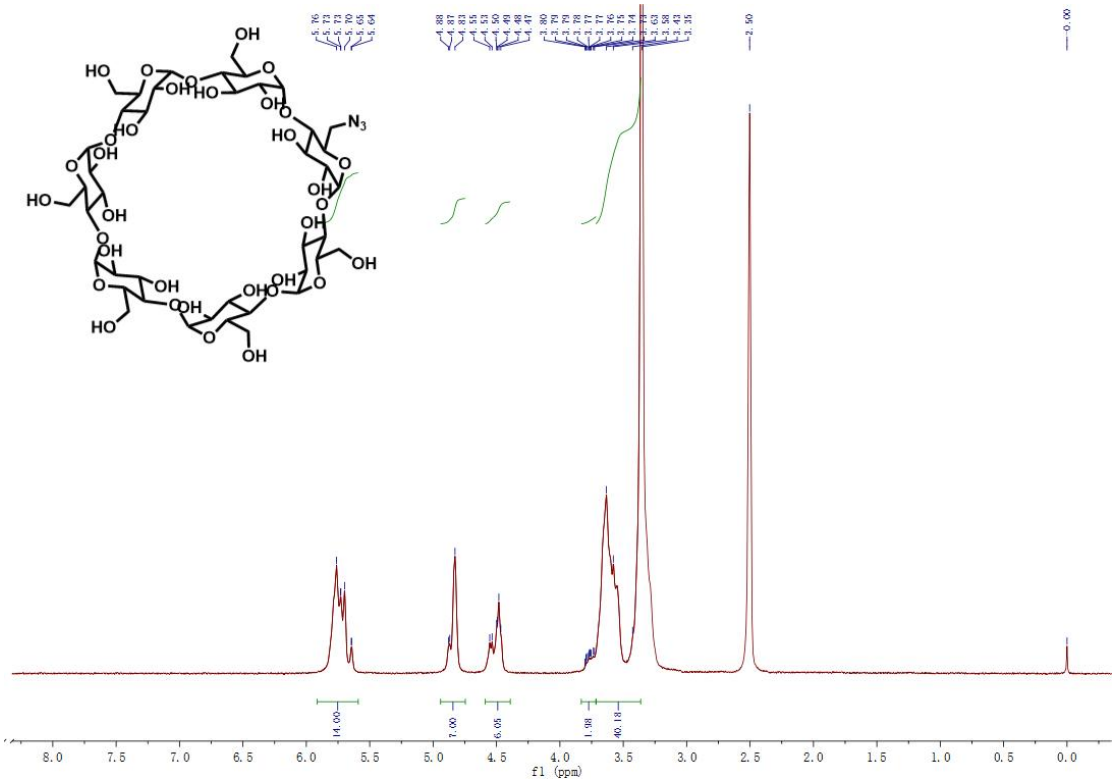


Figure S25 ^{1}H-NMR spectrum of molecule **β-CD-N$_3$** in DMSO-*d*$_6$.

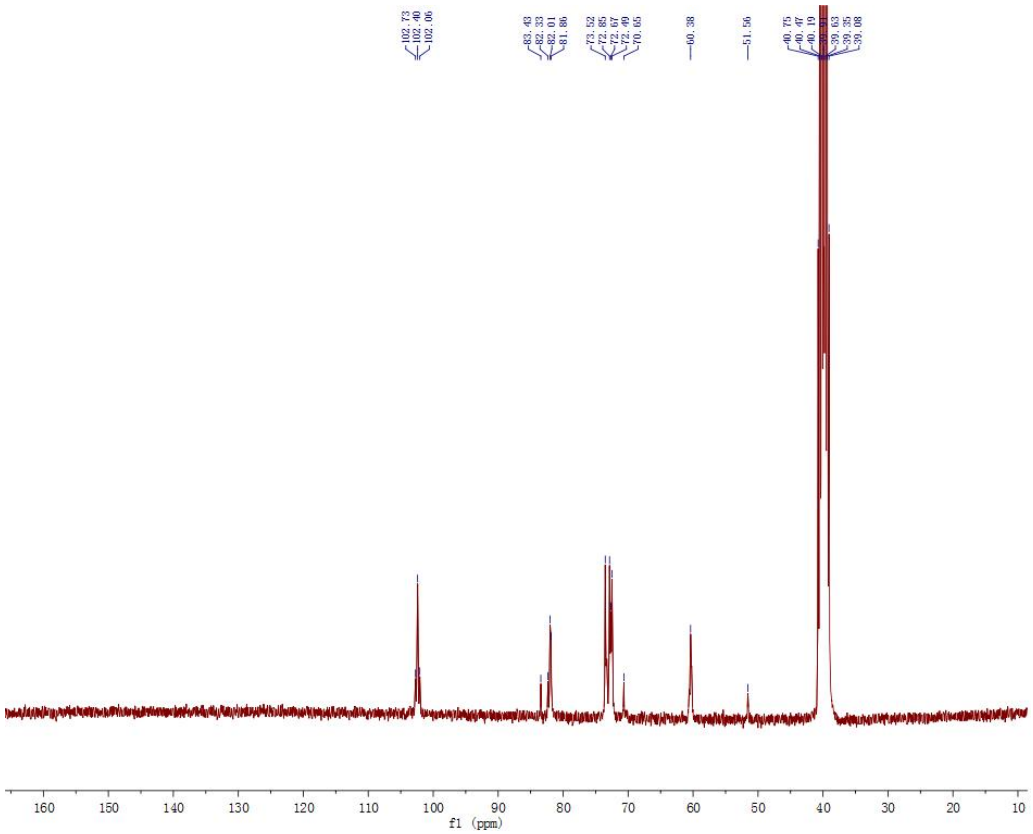


Figure S26 ^{13}C-NMR spectrum of molecule **β-CD-N$_3$** in DMSO-*d*$_6$.

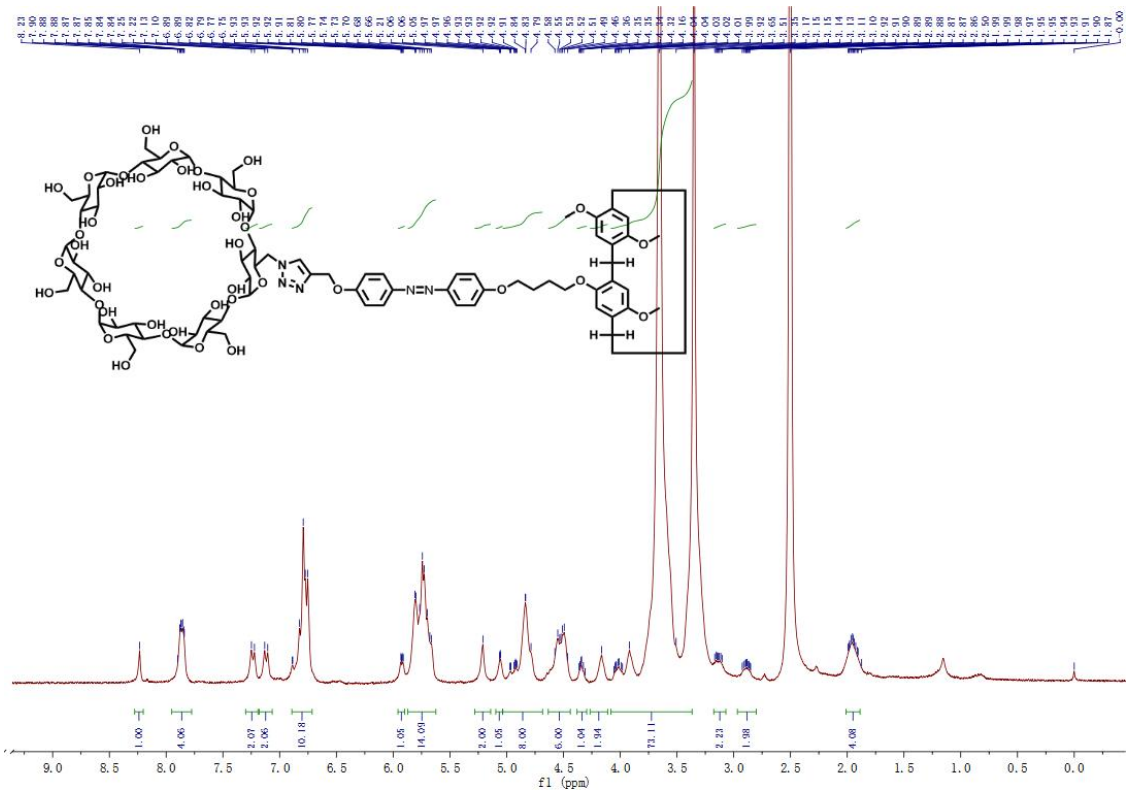


Figure S27 ^{1}H-NMR spectrum of molecule **H$_1$** in DMSO-*d*$_6$.

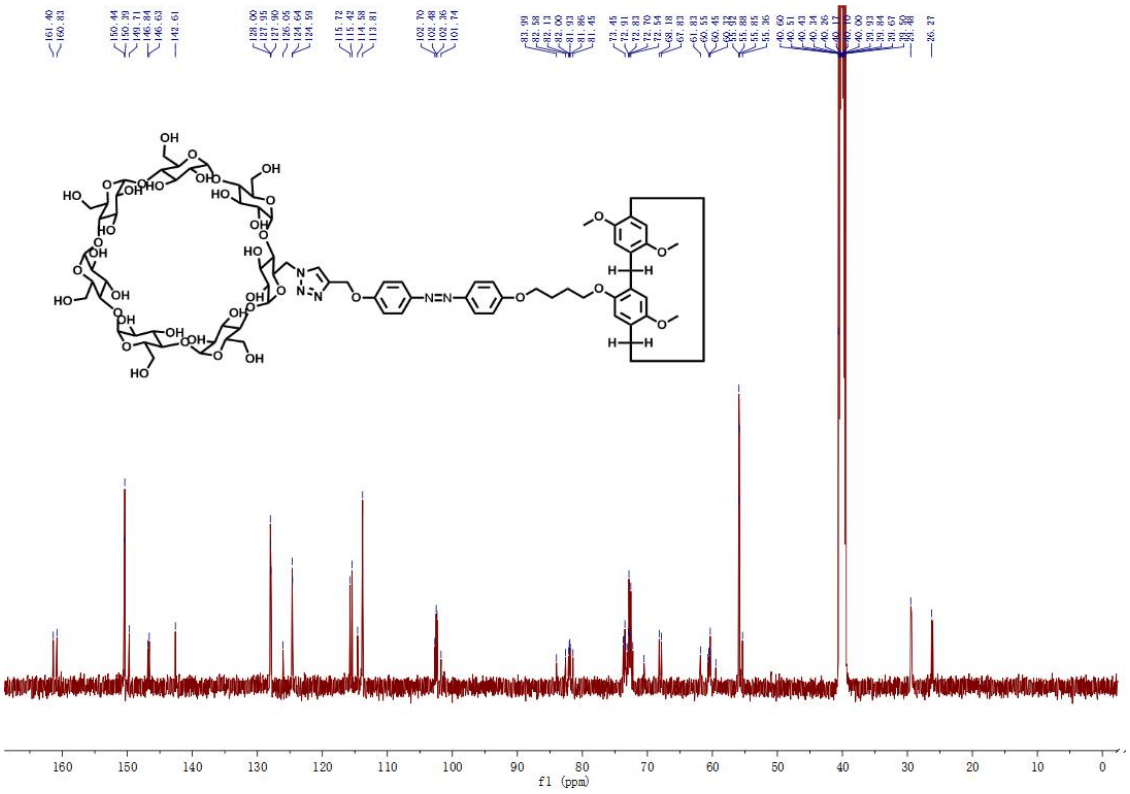


Figure S28 ^{13}C-NMR spectrum of molecule $\mathbf{H_1}$ in DMSO-d_6.

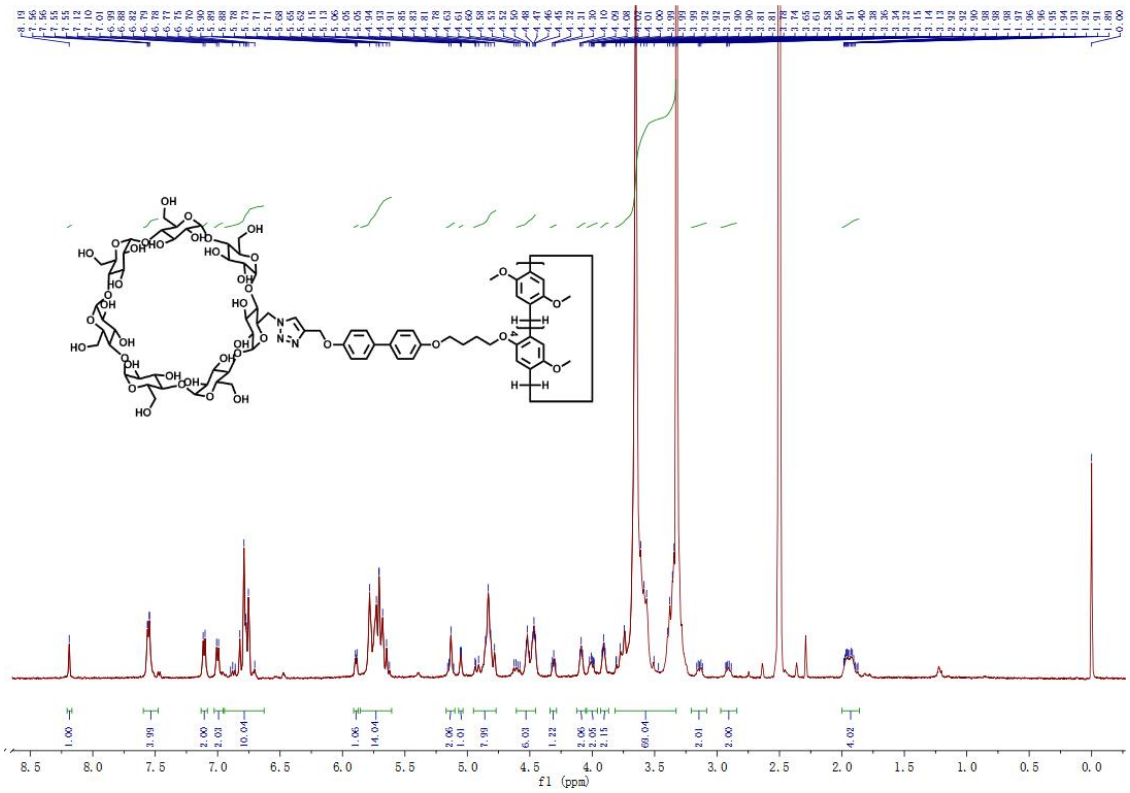


Figure S29 ^{1}H-NMR spectrum of molecule $\mathbf{H_2}$ in DMSO-d_6.

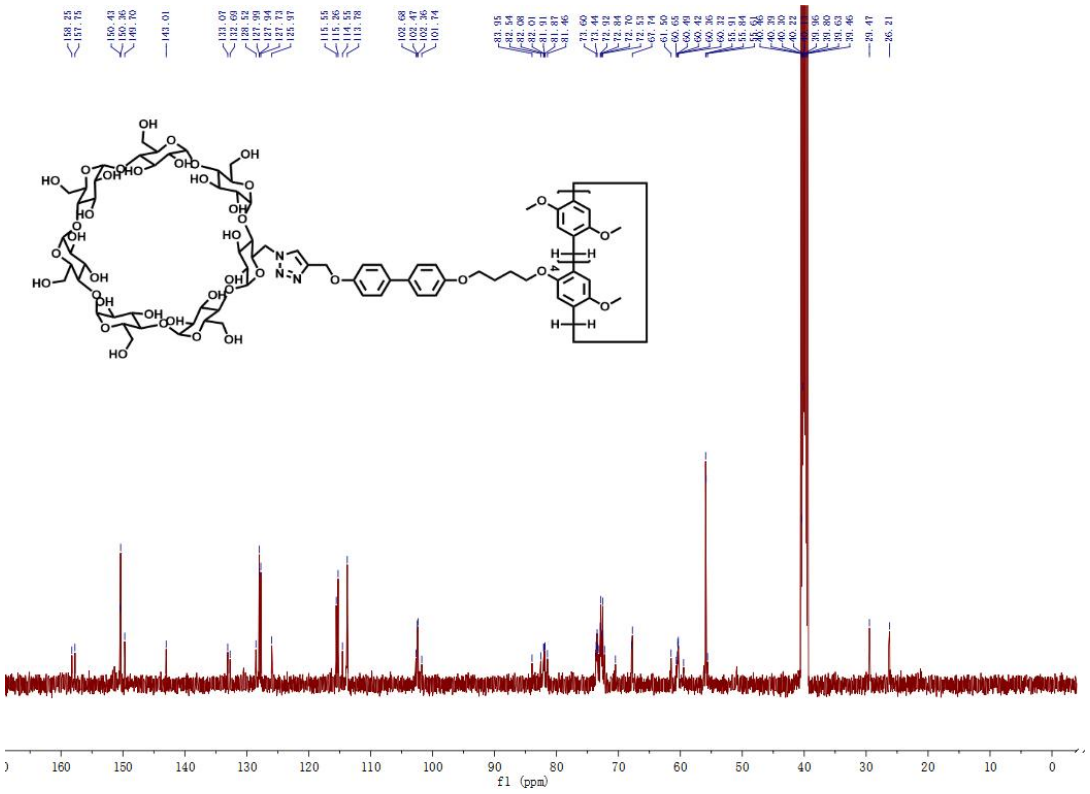


Figure S30 ^{13}C-NMR spectrum of molecule $\mathbf{H_2}$ in DMSO-d_6.

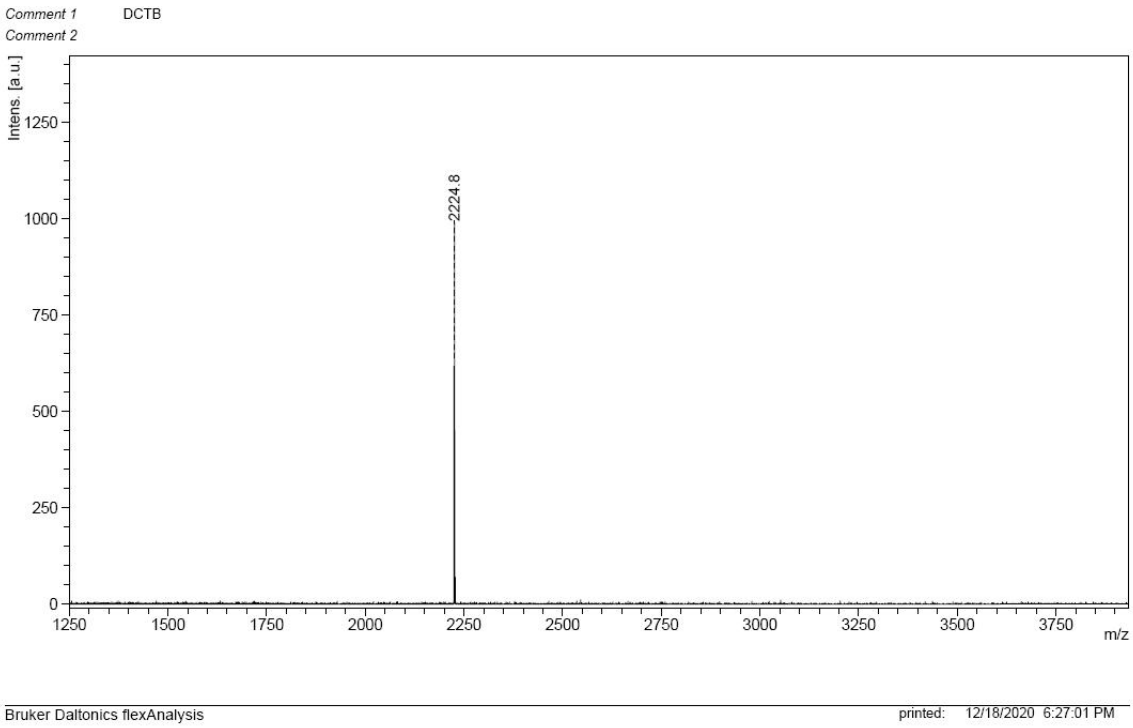


Figure S31 MALDI-TOF-Mass spectra of molecule $\mathbf{H_1}$.

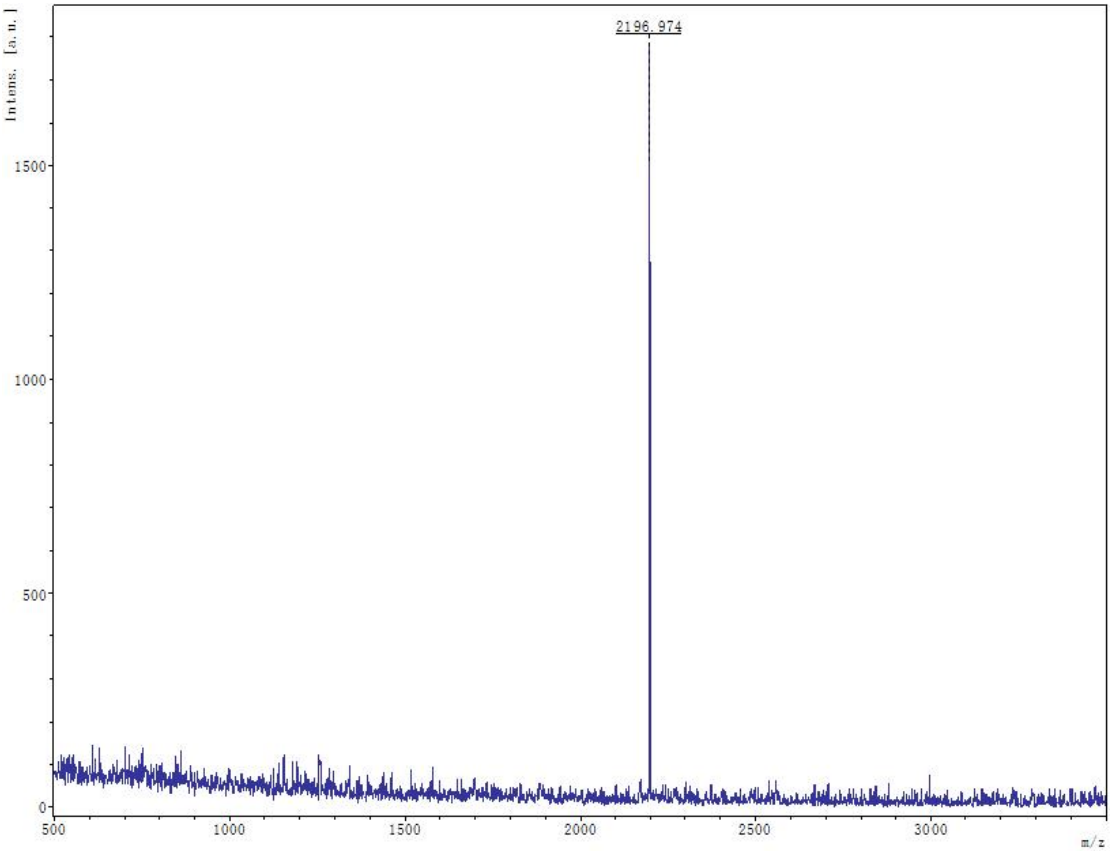


Figure S32 MALDI-TOF-Mass spectra of molecule $\mathbf{H_2}$.

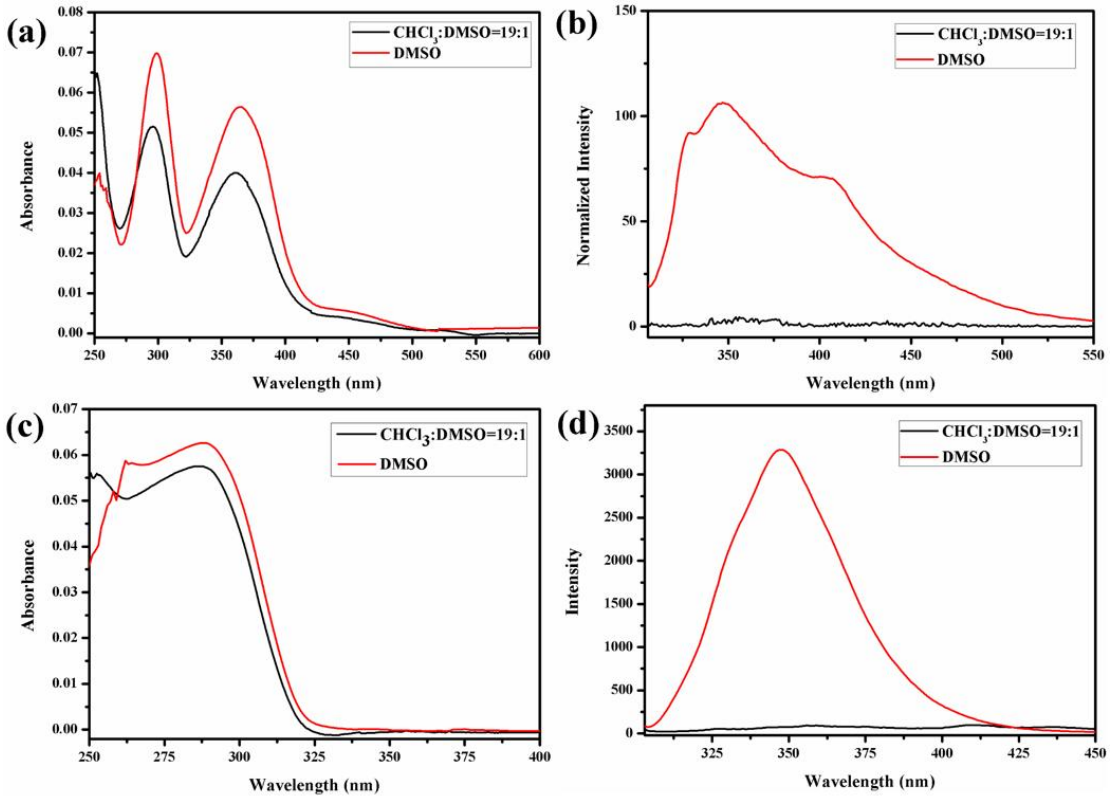


Figure S33 Absorption spectra of (a) $\mathbf{H_1}$ and (c) $\mathbf{H_2}$ and emission (excited at 298 nm,

Ex bandwidth: 2.5 nm; Em bandwidth: 5 nm) spectra of (b) **H₁** and (d) **H₂** in DMSO and $CHCl_3$/DMSO (v/v = 19:1) solutions (3.03×10^{-6} mol/L).

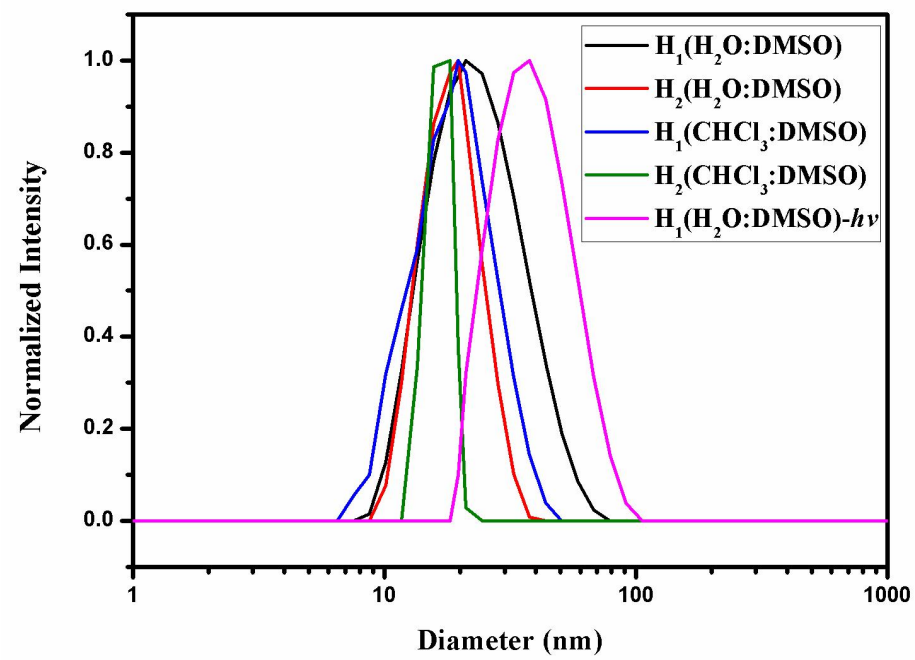


Figure S34 Size distribution graphs of H_2O/DMSO (v/v = 19:1) and $CHCl_3$/DMSO (v/v = 19:1) solutions of **H₁** and **H₂** (3.03×10^{-6} mol/L) from DLS measurements.

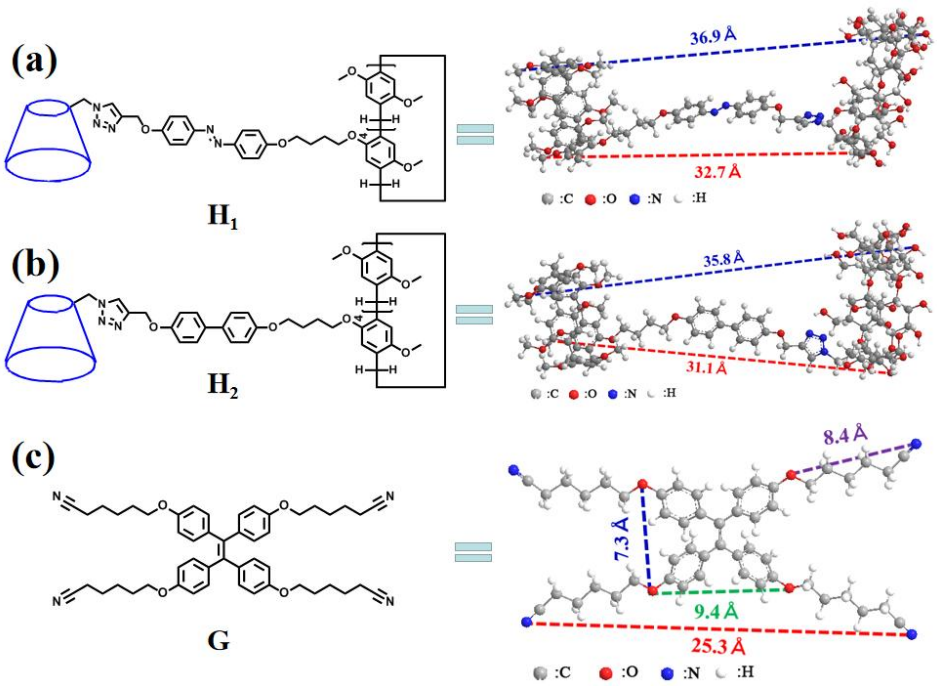


Figure S35 The molecular lengths of compounds **H₁-₂** and **G** simulated by CPK at the lowest energy

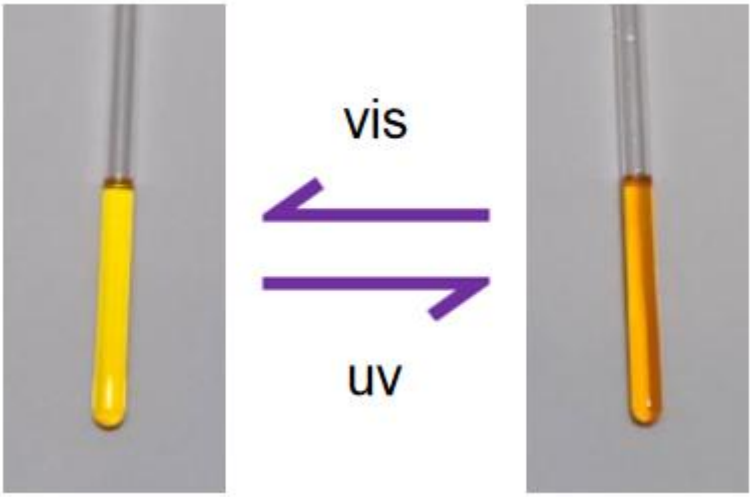


Figure S36 Photographs of H_2O/DMSO (v/v = 19:1) solutions of $\mathbf{H_1}$ (left, c = 2.72×10^{-3} mol/L) and after irradiation with 365nm UV light for 20 minutes (right, c = 2.72×10^{-3} mol/L).

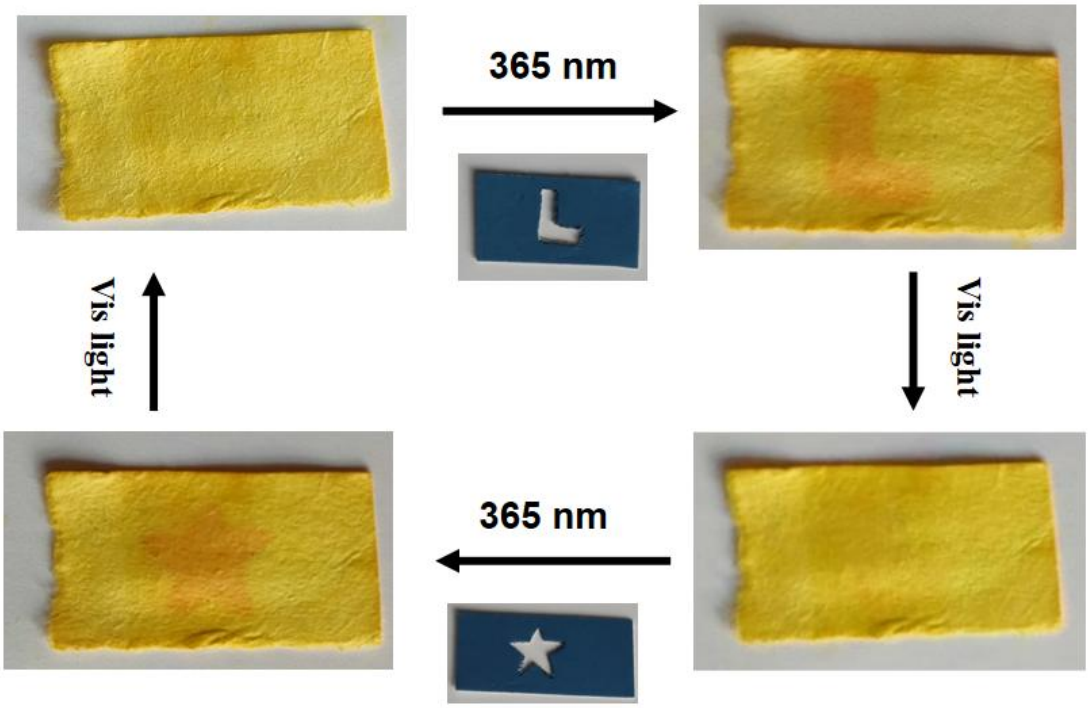


Figure S37 The rewritable process of patterned $\mathbf{H_1}$ via the irradiation of 365 nm and visible light.

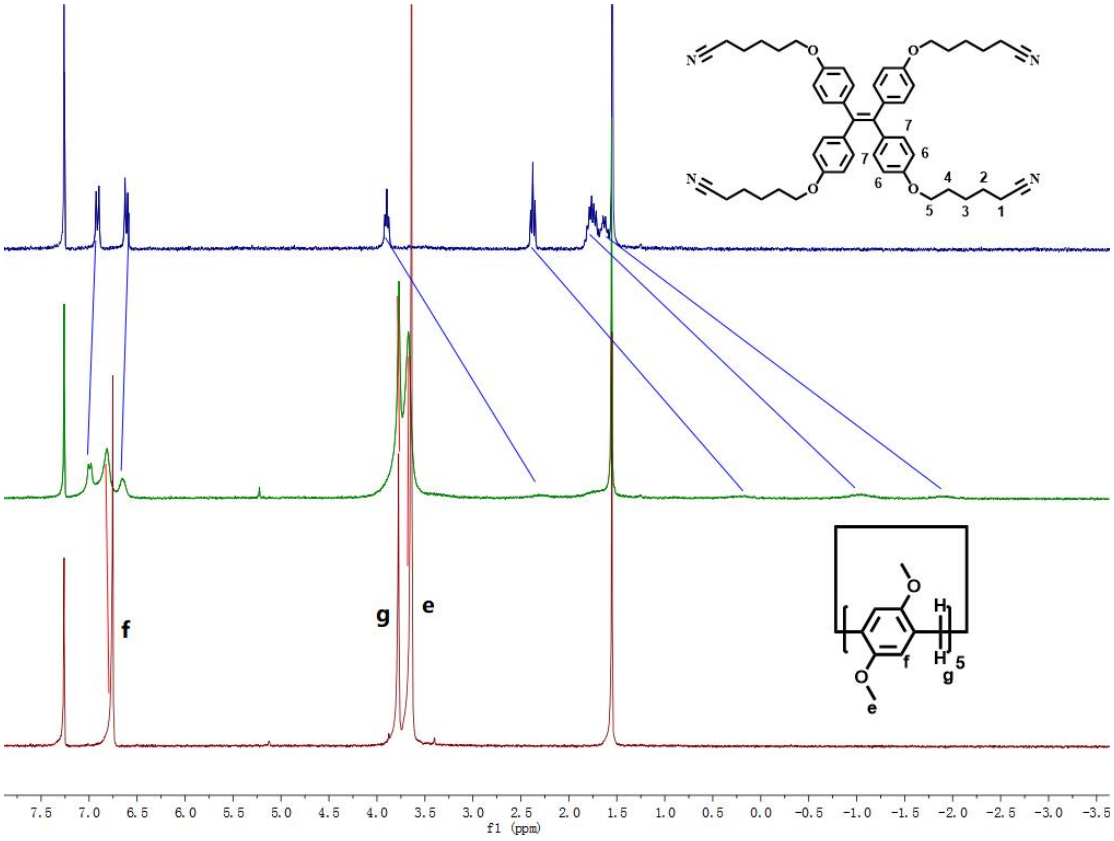


Figure S38 ^{1}H NMR spectra of **G** (blue line), **H$_3$+G** (green line) and **H$_3$** (red line) in $CDCl_3$ at 25 ℃.

Association constant determination for H$_3$⊃G in $CDCl_3$

In order to further determine the association constant and stoichiometry of **H$_3$⊃G**, FL titration and continuous Job's variation method was done[3].

Stoichiometry (n) and apparent binding constant (K) were calculated according to Benesi – Hildebrand equation, $1/\Delta X = 1/\alpha + 1/\alpha K[Host]^n$ with the plot of $1/\Delta X$ vs $1/[Host]^n$ determined by fluorescent.

Where ΔX is the changes of fluorescent emission intensity (ΔI), As shown in Figure S39, the plot of $1/\Delta I$ vs $1/[Host]^4$ has a good linear least-squares fit with a better correlation coefficient than that of the plot of $1/\Delta I$ vs $1/[Host]^n$ (n=1,2,3), indicating that the stoichiometry of the inclusion complex between **H$_3$** and the compound **G** is 4 : 1. The stoichiometry was also confirmed by the continuous Job's variation method (Job's plot) as shown in Figure S40.

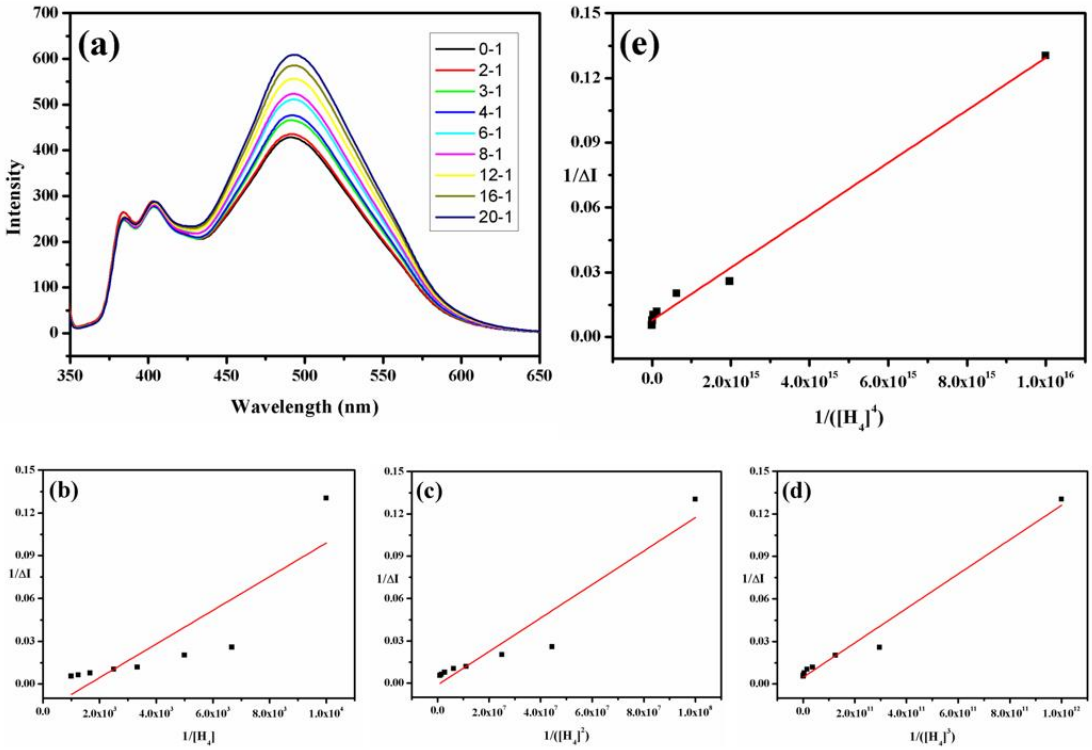


Figure S39 (a) Fluorescent spectra of the complex of $\mathbf{H_3}$ and **G** (curves from top to bottom, molar ratios = 0 : 1, 2 : 1, 3 : 1, 4 : 1, 6 : 1, 8 : 1, 12 : 1, 16 : 1, 20:1) in $CDCl_3$ solution (~ 5.0×10^{-5} mol L^{-1}), excited at 343 nm. (b) The plot of $1 / \Delta I$ vs $1 / [\boldsymbol{H_3}]$ detected by fluorescent intensity at 500 nm. $K = 1.18\times10^{5}$ M^{-1}, $R = 0.7280$. (c) The plot of $1 / \Delta I$ vs $1 / [\boldsymbol{H_3}]^2$ detected by fluorescent intensity at 500 nm. $K = 1.19\times10^{9}$ M^{-2}, $R = 0.9060$. (d) The plot of $1 / \Delta I$ vs $1 / [\boldsymbol{H_3}]^3$ detected by fluorescent intensity at 500 nm. $K = 1.21\times10^{13}$ M^{-3}, $R = 0.9749$. (e) The plot of $1 / \Delta I$ vs $1 / [\boldsymbol{H_3}]^4$ detected by fluorescent intensity at 500 nm. $K = 1.22\times10^{17}$ M^{-4}, $R = 0.9926$.

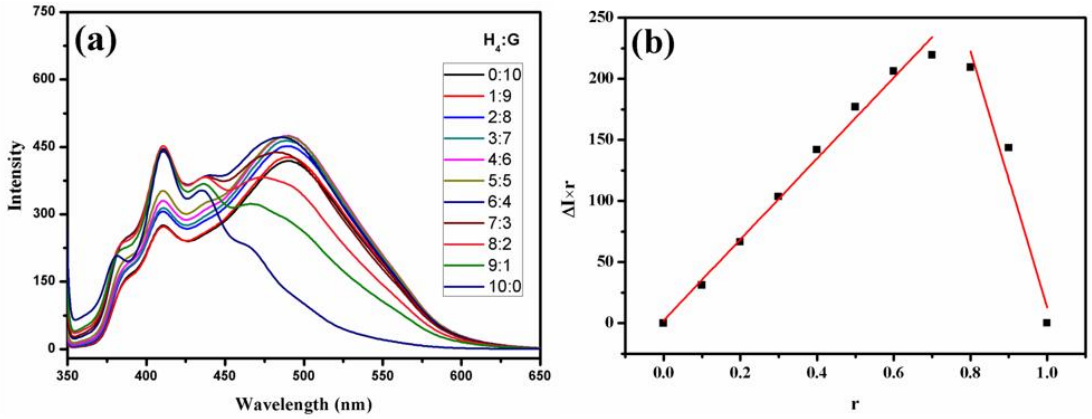


Figure S40 Fluorescent spectra of the complex of **H_3** and **G** (curves from top to bottom, molar ratios from 0 : 10 to 10 : 0) in $CDCl_3$ solution (0.01 ~ 0.1 mM), excited at 343 nm. (b) Job's plot of $\Delta I \times r$ vs r detected by fluorescent intensity at 500 nm.

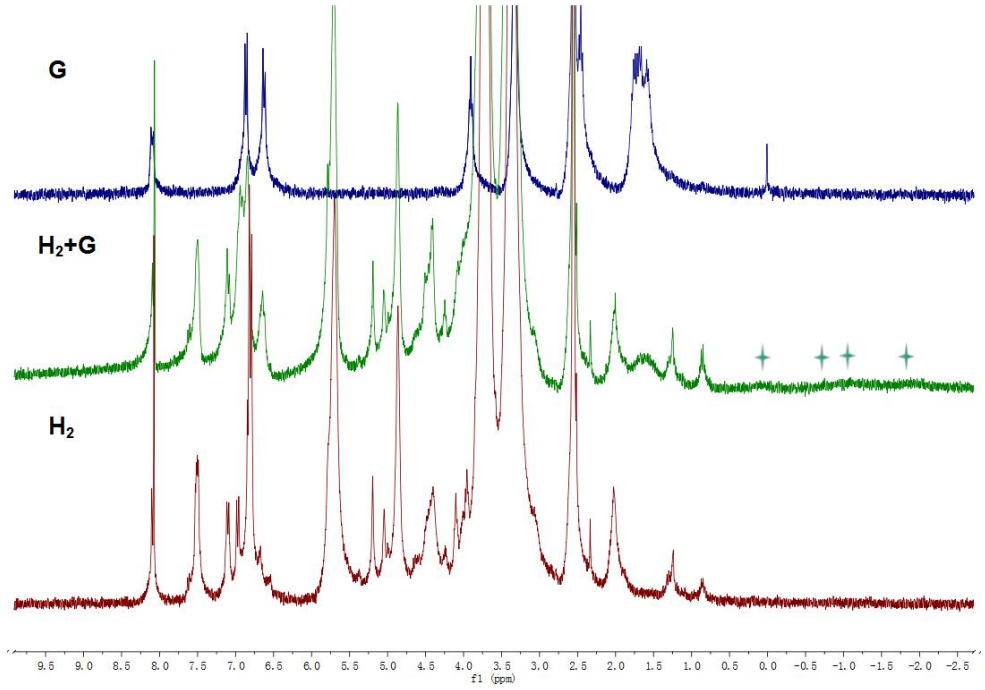


Figure S41 ^{1}H NMR spectra of **G** (blue line), **H_2+G** (green line) and **H_2** (red line) in $CDCl_3$:DMSO-d_6 (v/v = 1:1) at 25 ℃.

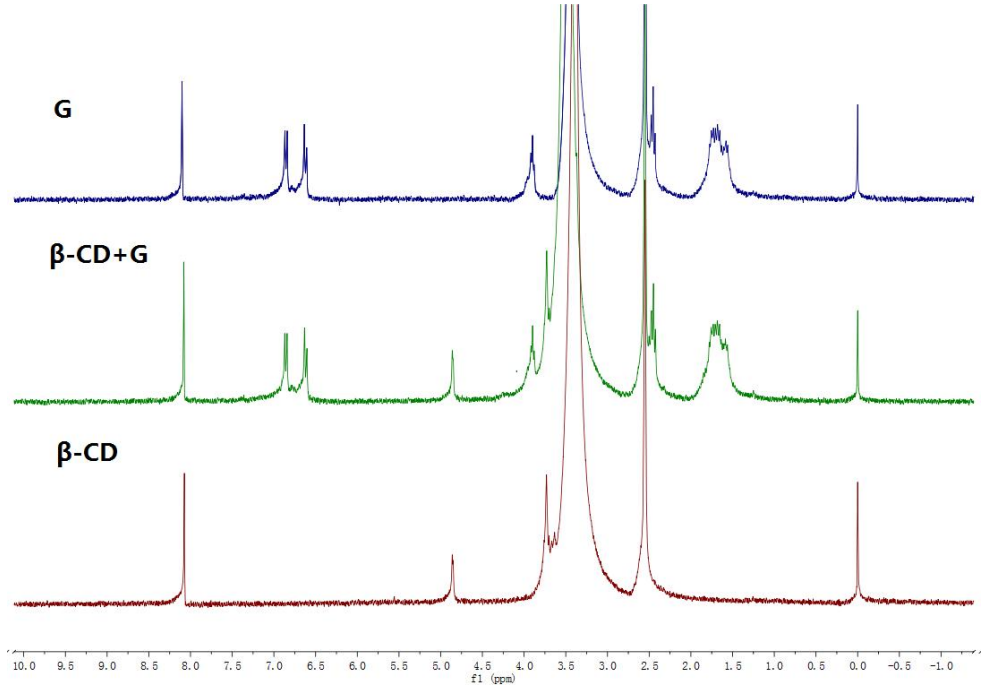


Figure S42 ^{1}H NMR spectra of **G** (blue line), **β-CD+G** (green line) and **β-CD** (red line) in $CDCl_3$:DMSO-d_6 (v/v = 1:1) at 25 ℃.

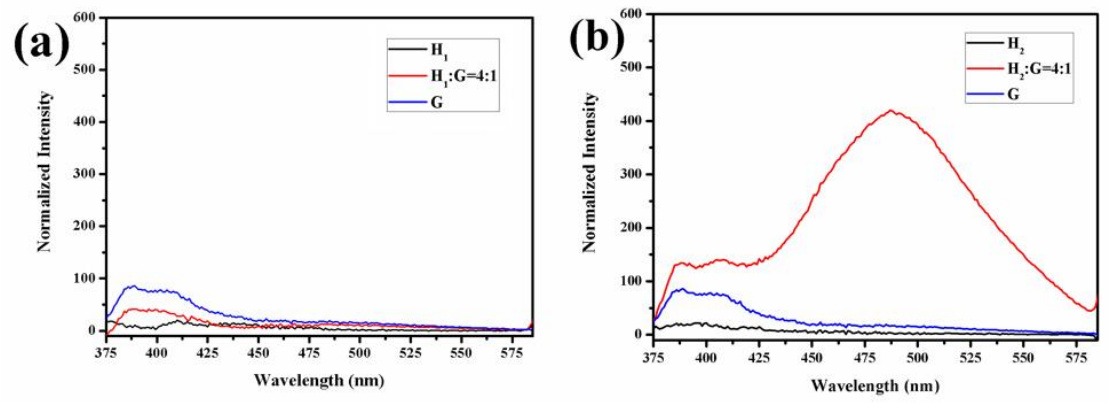


Figure S43 (a) Fluorescence spectra (excited at 298 nm, Ex bandwidth: 5 nm; Em bandwidth: 5 nm) of $\mathbf{H_1}$ (3.03×10^{-6} mol/L), $\mathbf{H_1}$:**G** (c/c = 4:1) and **G** (7.58×10^{-7} mol/L) in $CHCl_3$/DMSO (v/v = 19:1) solution at 25℃; (b) Fluorescence spectra (excited at 298 nm, Ex bandwidth: 5 nm; Em bandwidth: 5 nm) of $\mathbf{H_2}$ (3.03×10^{-6} mol/L), $\mathbf{H_2}$:**G** (c/c = 4:1) and **G** (7.58×10^{-7} mol/L) in $CHCl_3$/DMSO (v/v = 19:1) solution at 25℃.

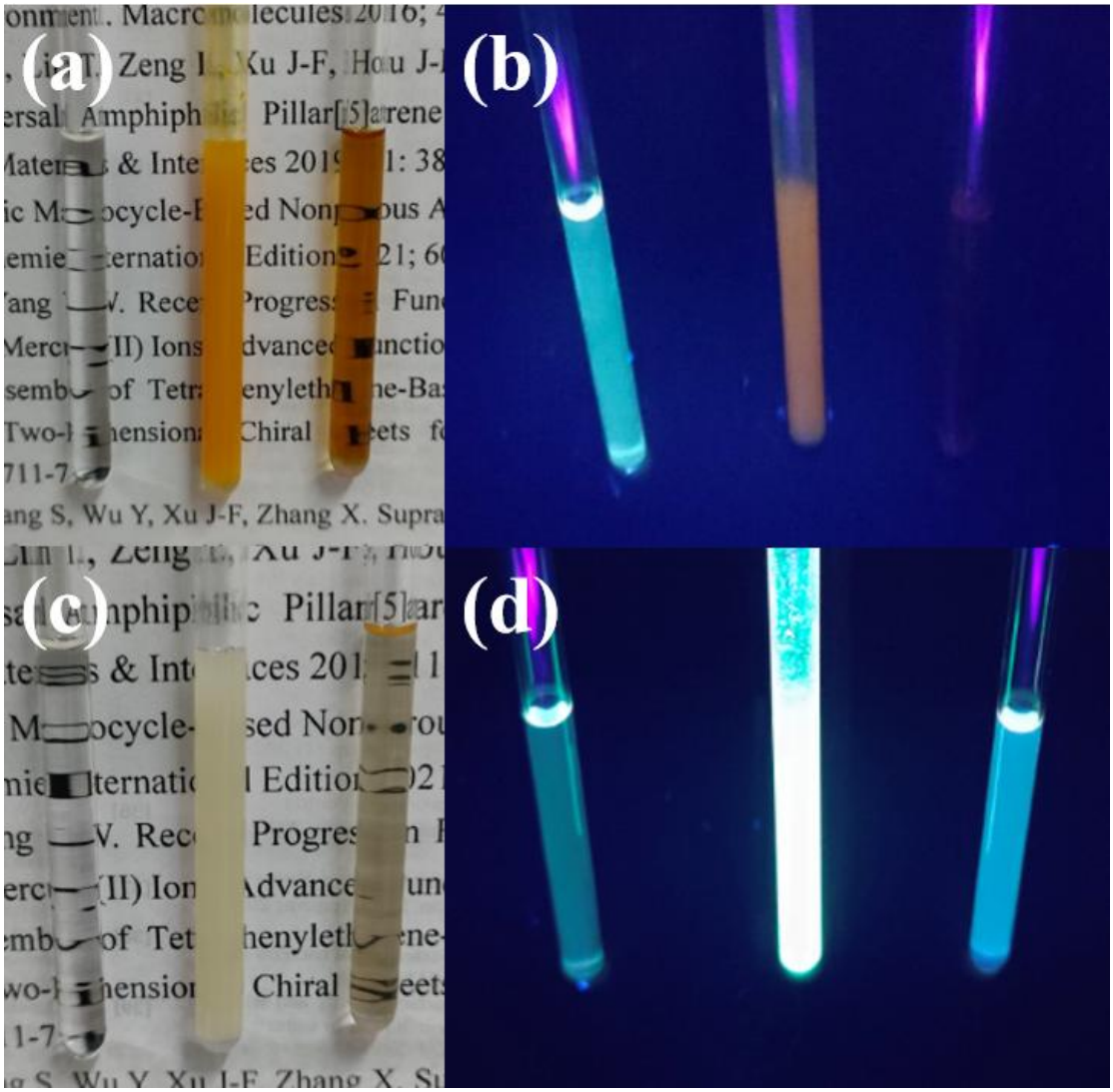


Figure S44 Photographs of (a) or (b) **G** (left, c = 2.15×10^{-3} mol/L), **H$_1$** + **G** (middle, c/c = 4:1), **H$_1$** (right, c = 8.58×10^{-3} mol/L) and (c) or (d) **G** (left, c = 2.15×10^{-3} mol/L), **H$_2$** + **G** (middle, c/c = 4:1), **H$_2$** (right, c = 8.58×10^{-3} mol/L) in $CDCl_3$/DMSO-*d$_6$* (v/v = 5:1) solution at 25℃: (a) and (c) under visible light; (b) and (d) under 365 nm UV lamp.

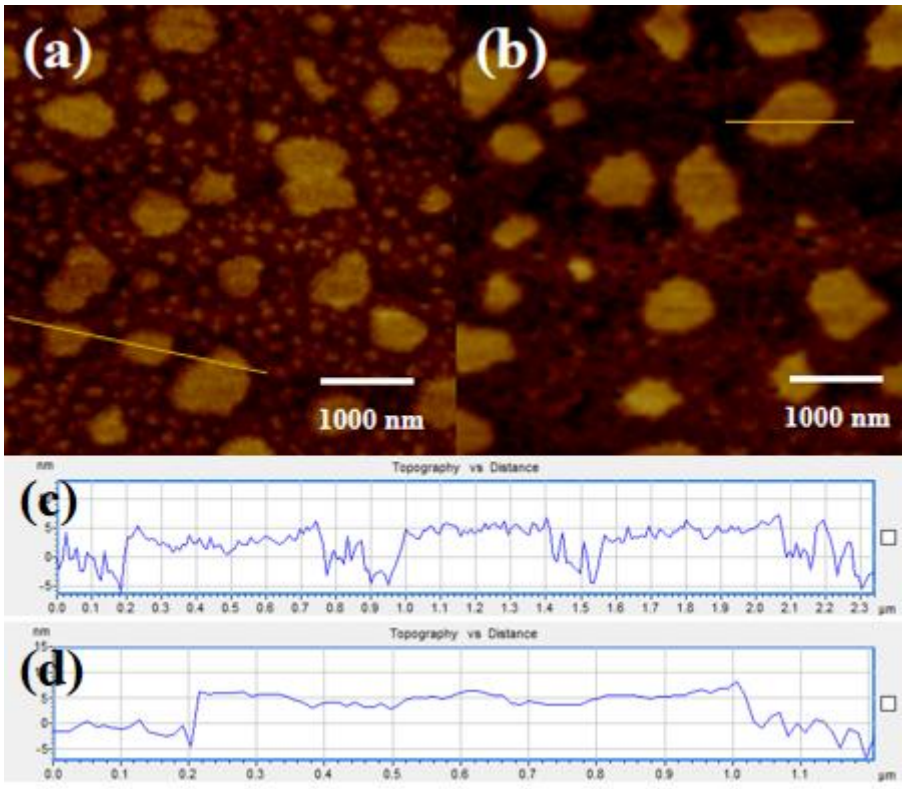


Figure S45 AFM images of molecules **H$_1$⊂G** (c/c = 4:1) obtained from $CHCl_3$/DMSO (v/v = 19:1) solutions (a) 24 h, (c) the corresponding height profile analysis; AFM images of molecules **H$_2$⊂G** (c/c = 4:1) obtained from $CHCl_3$/DMSO (v/v = 19:1) solutions (b) 24 h, (d) the corresponding height profile analysis.

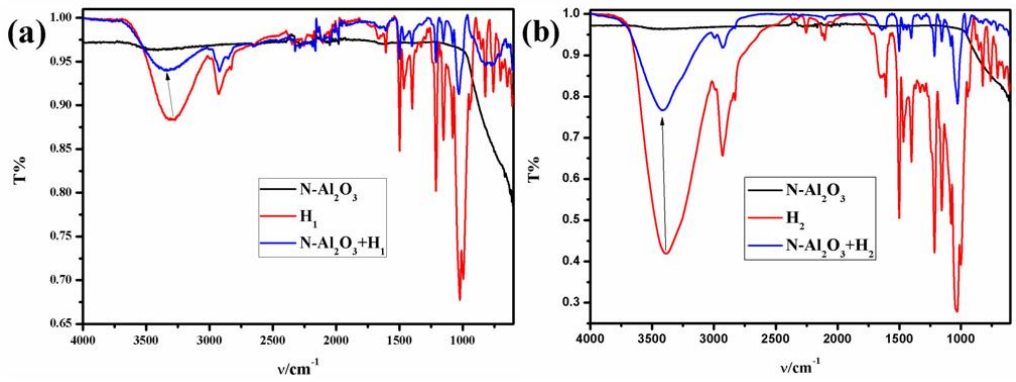


Figure S46 ATR-FTIR spectra of the stationary phase after separation of (a) Neutral

alumina + $\mathbf{H_1}$ and (b) Neutral alumina + $\mathbf{H_2}$.

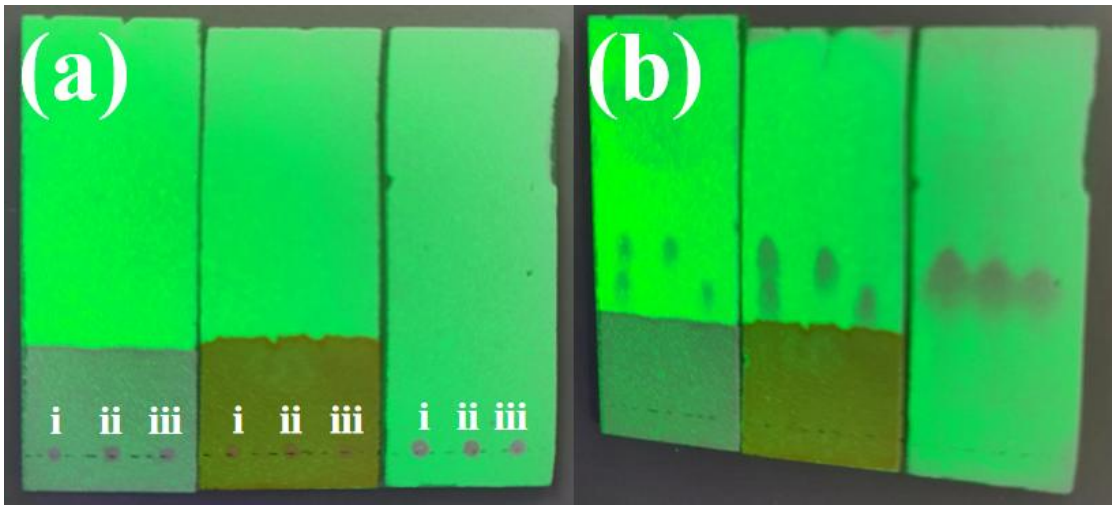


Figure S47 Thin layer chromatography (a) or (b) Neutral alumina thin laminate + $\mathbf{H_1}$ (left), Neutral alumina thin laminate + $\mathbf{H_2}$ (middle), Neutral alumina thin laminate (right). (i: $\mathbf{H_3}$ + $\mathbf{H_4}$; ii: $\mathbf{H_3}$; iii: $\mathbf{H_4}$)

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1. G. Zhang, B. Li, Y. Zhou, X. Chen, B. Li, Z.-Y. Lu and L. Wu, *Nature Communications,* 2020, **11**, 425.

2. B. Gao, G. Wang, B. Li and L. Wu, *Acs Omega,* 2020, **5**, 8127-8136.

3. H. Zhang, N. Kim Truc, X. Ma, H. Yan, J. Guo, L. Zhu and Y. Zhao, *Organic & Biomolecular Chemistry,* 2013, **11**, 2070-2074.