ChemComm

Electronic Supplementary Information (ESI)

for

Stimuli-Responsive Blue Fluorescent Supramolecular Polymers Based on a Pillar[5]arene Tetramer

*Nan Song, Dai-Xiong Chen, Yu-Chen Qiu, Xiao-Yue Yang, Bin Xu, Wenjing Tian, Ying-Wei Yang**

State Key Laboratory of Supramolecular Structure and Materials, College of Chemistry,

Jilin University, 2699 Qianjin Street, Changchun, 130012, P. R. China.

**Corresponding Author, E-mail: ywyang@jlu.edu.cn*

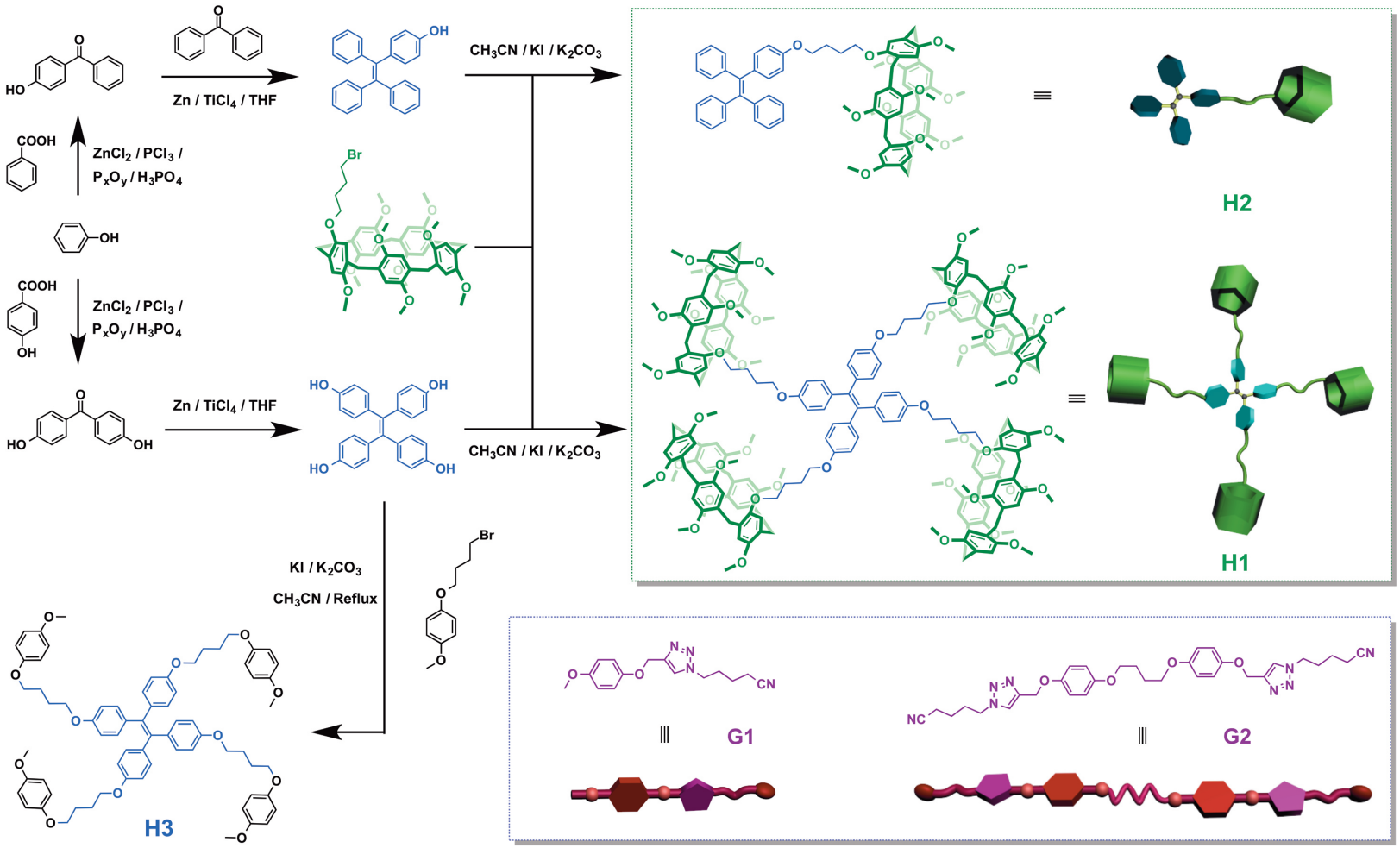
Table of Contents

1. Materials and Methods

Materials: 5-Bromopentanenitrile, p-hydroxyl anisole, paraformaldehyde $(CH_2O)_n$, zinc, titanium tetrachloride ($TiCl_4$), phosphorus trichloride (PCl_3), phosphoric acid (H_3PO_4), polyphosphoric acid (P_xO_y), propargyl bromide, sodium ascorbate, NaN_3, 1,4-dibromobutane and zinc chloride were reagent grade and purchased from Aladdin Reagents or Sigma-Alrich. Potassium carbonate (K_2CO_3) and potassium iodide (KI) was obtained from J&K Co. Ltd. Solvents used in the study were reagent grade, purchased from commercial sources, and used without further purification unless otherwise noted.

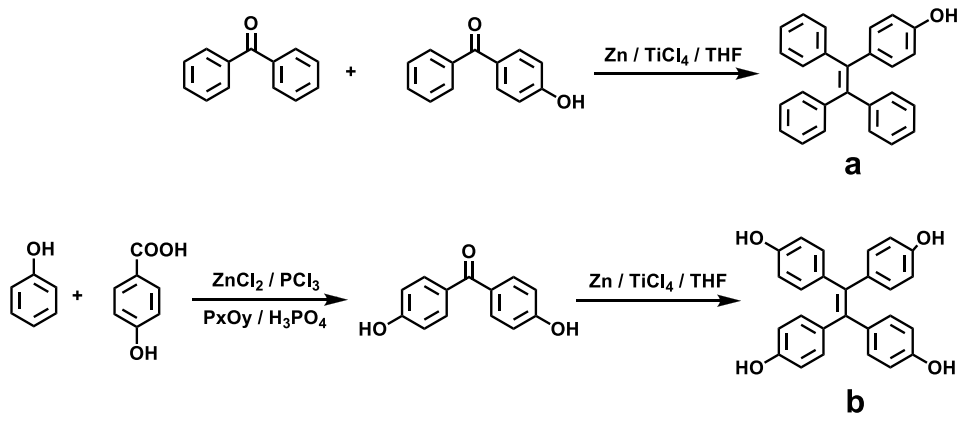
Methods: ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker 300 MHz NMR spectrometer. MALDI-TOF MS spectra were obtained from an autoflex TOF/TOF (Bruker, Germany) mass spectrometer, equipped with a nitrogen laser (337 nm, 3 ns pulse). ITC experiments were carried out on a thermostated and fully computer-operated ITC (Microcal ITC200) instrument, purchased from General Electric Company. SEM images were collected on a JEOL JSM 6700F instrument with an accelerating voltage of 3 kV. TGA was carried out on a TA Q500 instrument with a heating program consisting of a heating rate of 10 °C/min from 25 °C to 900 °C. DSC measurements were performed on a Netzsch DSC 204 with a scanning rate of 5 °C /min from 263 K to 543 K. All the samples were sealed in aluminum capsules in air, and the atmosphere of holder was sustained under dry nitrogen. The fluorescence microscopy images were obtained on an Olympus BX51 fluorescence microscopy and CLSM was conducted on a FV 1000 instrument. Fluorescence spectra were obtained on a Shimadzu RF-5301PC spectrofluorometer.

2. Syntheses and Characterization



Scheme S1. Synthetic routes of **H1**, **H2**, **H3**

2.1. Synthesis of hydroxy-substituted tetraphenylethene derivatives a and b



Monohydroxyl tetraphenylethene (**a**) was obtained by the reaction of diphenyl ketone and *p*-hydroxyl diphenyl ketone in THF, in the presence of $TiCl_4$ and Zn as the catalyst according to a modified literature procedure.[S1] Under a nitrogen atmosphere, Zn powder (1.7 g, 25 mmol) was dispersed in THF (40 mL), the mixture was cooled to 0 °C, and $TiCl_4$ (1.7 mL, 15 mmol) was slowly added while maintaining the temperature under 10 °C. The mixture was warmed to room temperature for 0.5 h. Then, the mixture was cooled to 0 °C again, the solution of two carbonyl compounds, *i.e.*, diphenyl ketone (0.455 g, 2.5 mmol) and *p*-hydroxyl diphenyl ketone (0.495 g, 2.5 mmol), in THF (15 mL) was added slowly. After addition, the reaction mixture was heated at reflux until the carbonyl compounds were consumed. The reaction was quenched with 10% K_2CO_3 aqueous solution and extracted with CH_2Cl_2. The organic layer was collected and concentrated. The crude material was purified by flash chromatography (silica gel, n-hexane : CH_2Cl_2 : acetone = 20 : 5 : 1) to give the desired products. ^{1}H NMR (300 MHz, d_6-DMSO, 25 °C) δ (ppm): 8.26 (s, 1H), 7.10 (m, 15H), 6.86 (d, J = 9Hz, 2H) 6.61 (d, J = 9Hz, 2H).

Tetrahydroxyl tetraphenylethene (**b**)[S1] was obtain through the reaction of two bis(4-hydroxyphenyl)methanones *via* the same method as the synthesis of monohydroxyl tetraphenylethene described above. ^{1}H NMR (300 MHz, d_6-DMSO, 25 °C) δ (ppm): 9.21 (s, 4H), 6.70 (d, J = 6Hz, 8H), 6.47 (d, J = 6Hz, 8H).

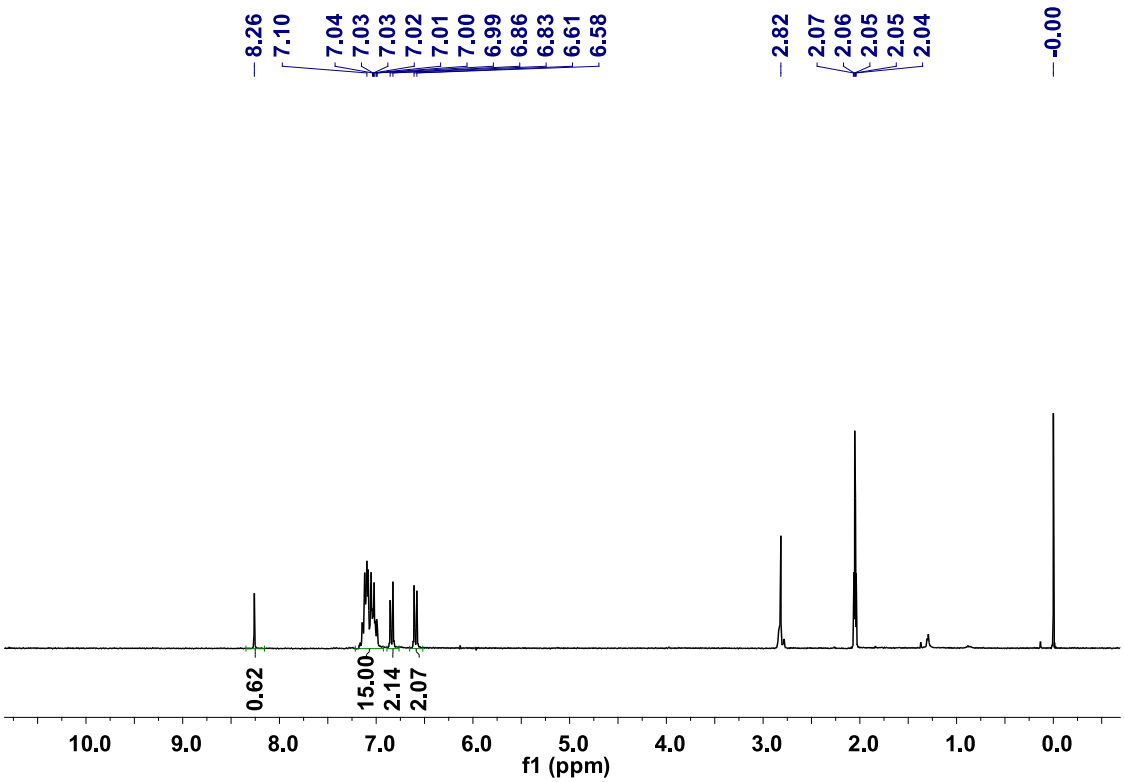


Figure S1. ^{1}H NMR spectrum of compound **a**.

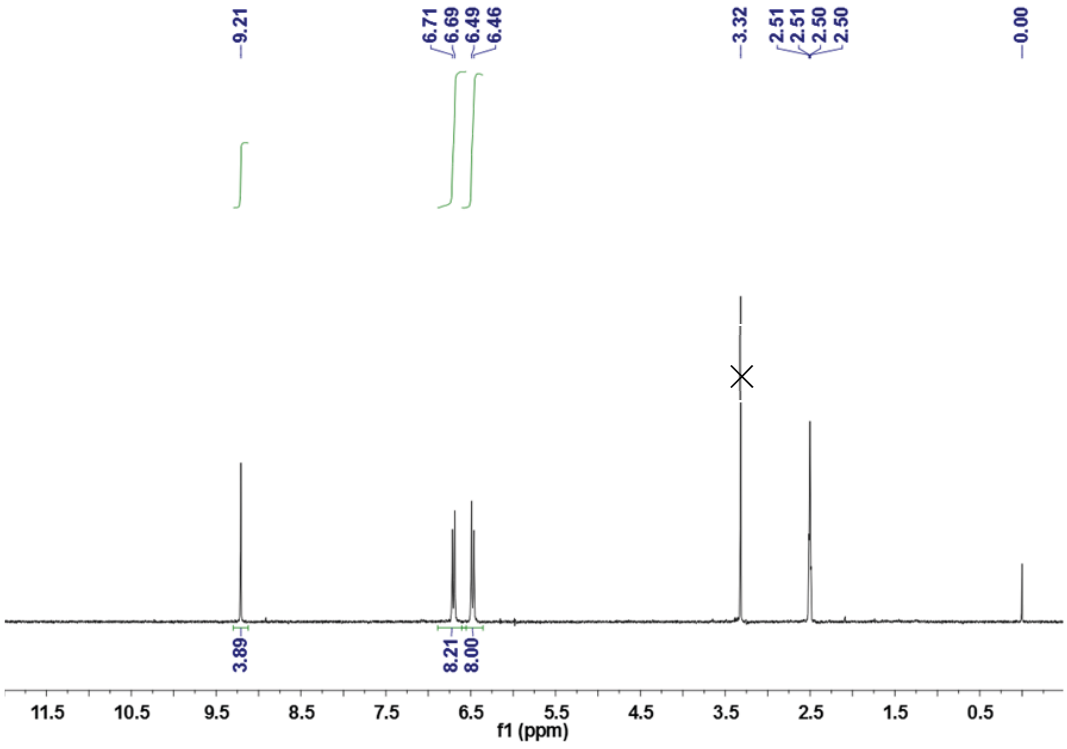
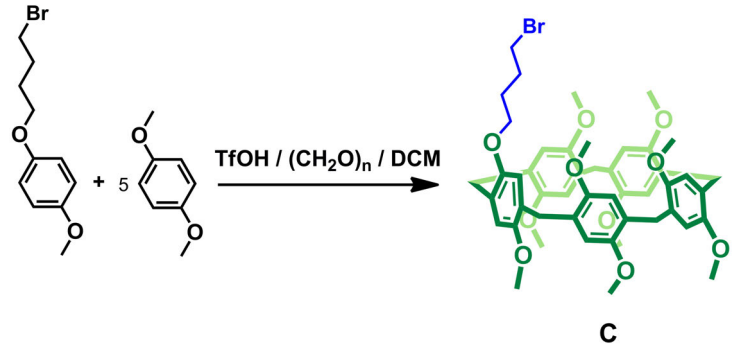


Figure S2. ^{1}H NMR spectrum of compound **b**.

2.2. Synthesis and characterizations of H1, H2 and H3

2.2.1. Synthesis of copillar[5]arene (**c**)



Monofunctionalized pillar[5]arene (**CoP[5]A**) was prepared by the reaction of 1,4-dimethoxybenzene, 4-bromobutyl-anisole and paraformaldehyde in dichloromethane, in the presence of 5% mmol of trifluoromethanesulfonate (TfOH) as catalyst, according to our published procedure.[S2] ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ (ppm): 6.76 (m, 10 H), 3.84 (t, 2 H), 3.77 (s, 10H), 3.68 (m, 27H), 3.28 (t, 2H), 1.83 (m, 4H).

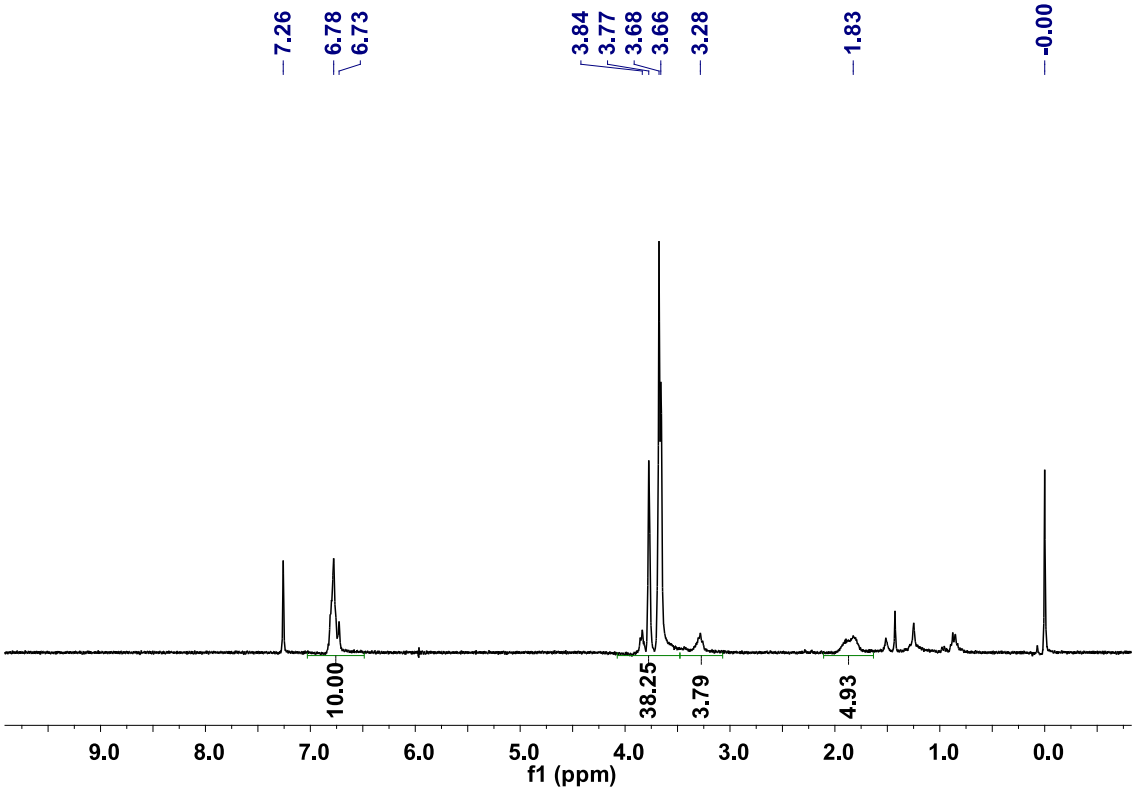


Figure S3. ^{1}H NMR spectrum of compound **c**.

2.2.2. Synthesis and characterization **of H1**.

Tetrahydroxyl tetraphenylethene (100 mg, 0.25 mmol) was dispersed in MeCN (60 mL) and K_2CO_3 (2 g) was added. The mixture was stirred for 30 min at room temperature. Then, a small amount of KI and excess **CoP[5]A** (1.2 g, 1.4 mmol) were added. The mixture was heated under reflux for 40 h under a nitrogen atmosphere. Then, the mixture was filtered and washed with chloroform. The filtrate was collected and concentrated, and the residue was subjected to column chromatography (silica gel, n-hexane: EtOAc = 4:1), a light yellow product was obtained. Yield: 0.1 g, 11%. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ (ppm): 6.94 (d, J = 9 Hz, 8H), 6.77 (m, 40H), 6.64 (d, J = 9 Hz, 8H), 3.94 (t, 8H), 3.87 (t, 8H), 3.77 (s, 40H), 363-3.53 (m, 108H), 1.93 (m, 16H). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ (ppm): 157.3, 150.7, 149.9, 138.4, 136.9, 132.6, 128.3, 114.7, 113.9, 113.6, 68.0, 67.4, 55.7, 29.6 26.5, 26.4. MALDI-TOF: Calcd for $C_{218}H_{236}O_{44}$ [M]: 3557.6229, Found: 3557.6329.

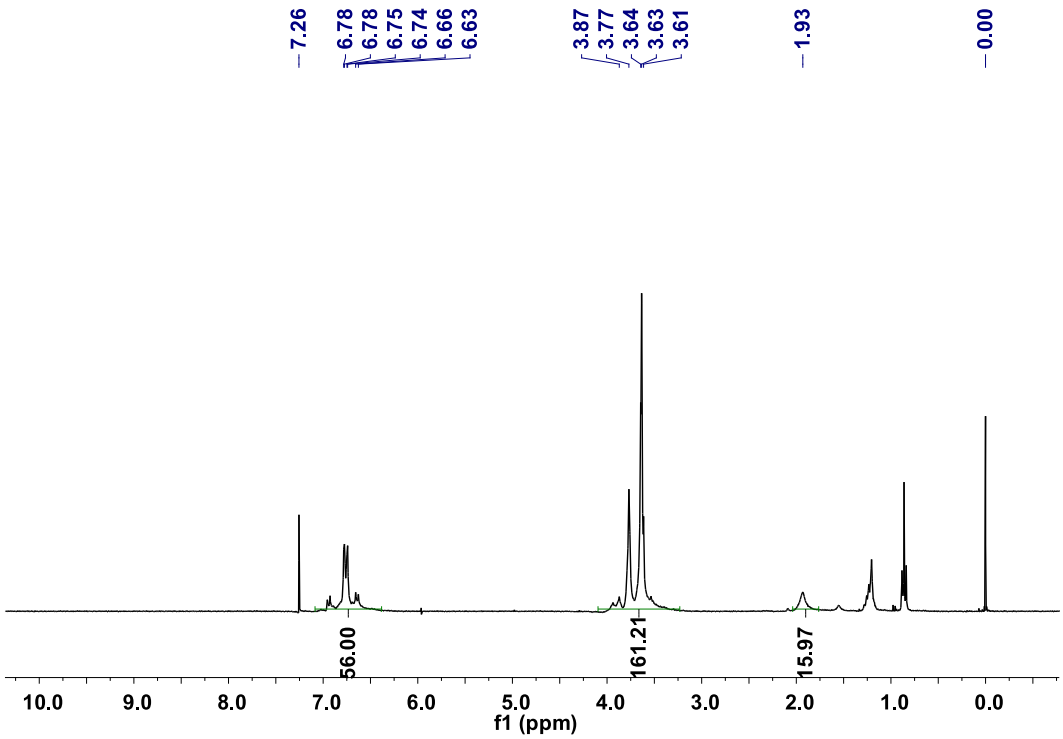


Figure S4. ^{1}H NMR spectrum of compound **H1**.

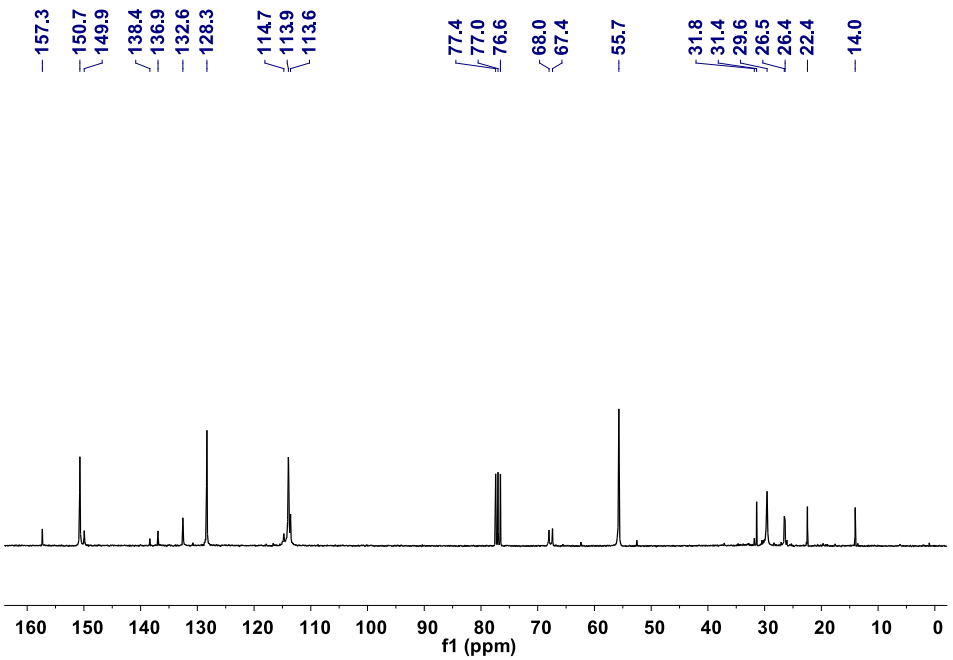


Figure S5. ^{13}C NMR spectrum of compound **H1**.

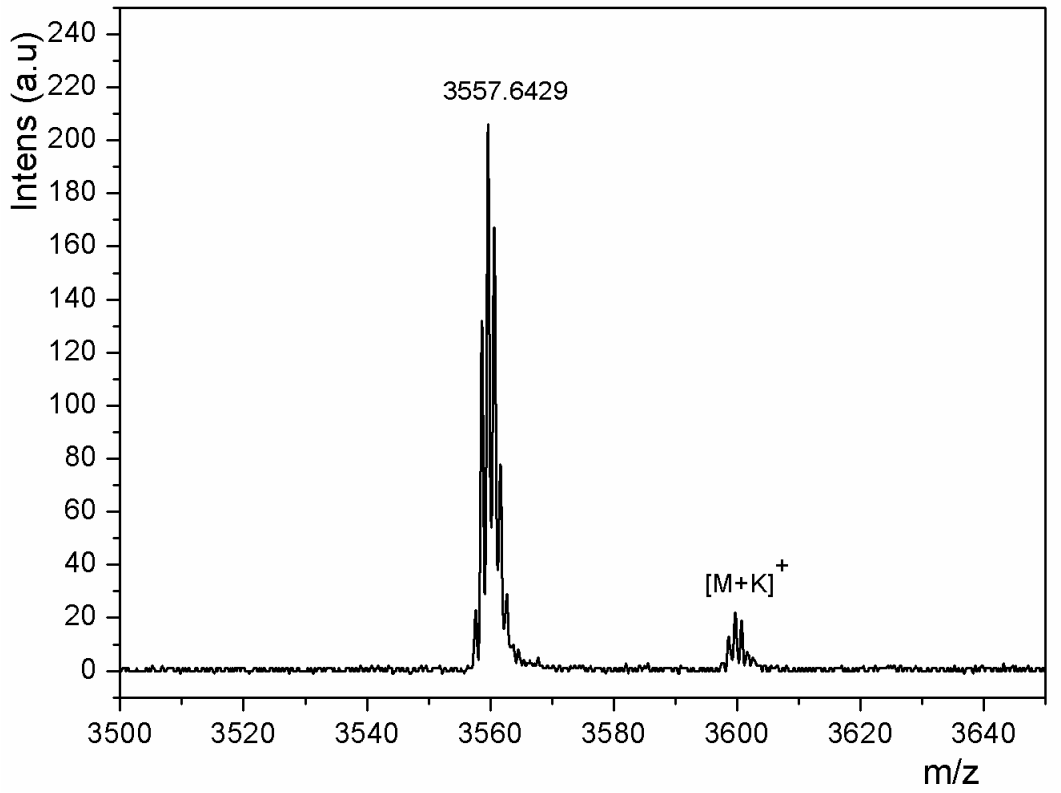


Figure S6. MOLDI-TOF MS spectrum of **H1**.

2.2.3. Synthesis and characterization of **H2**.

Monohydroxyl tetraphenylethene (80 mg, 0.2 mmol) was dispersed in MeCN (60 mL) and K_2CO_3 (0.5 g) was added. The mixture was stirred for 30 min at room temperature, then a small amount of KI and **CoP[5]A** (180 mg, 0.2 mmol) were added. The mixture was heated under reflux for 40 h under a nitrogen atmosphere, and then filtered and washed with chloroform after cooling down. The filtrate was concentrated, and the residue was subjected to column chromatography (silica gel, EtOAc : n-hexane = 1:20, 1:10, 1:5 in gradient), a white product was obtained. Yield: 110 mg, 50%. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ (ppm): 7.09 (m, 15H), 6.92 (d, *J* =15 Hz, 2H), 6.75 (m, 10H), 6.62 (d, *J* = 15 Hz, 2H), 3.98 (t, 2H), 3.86 (t, 2H), 3.62 (m, 27H), 1.92 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ (ppm): 157.4, 149.9, 132.5, 128.1, 127.5, 126.2, 114.7, 114.0, 113.4, 67.9, 67.2, 55.7, 29.6, 26.4, 26.2. MALDI-TOF: Calcd for $C_{74}H_{74}O_{11}$ [M]: 1138.5231, $[M+K]^+$: 1177.4862, Found: [M]: 1138.4221, $[M+K]^+$: 1177.4615.

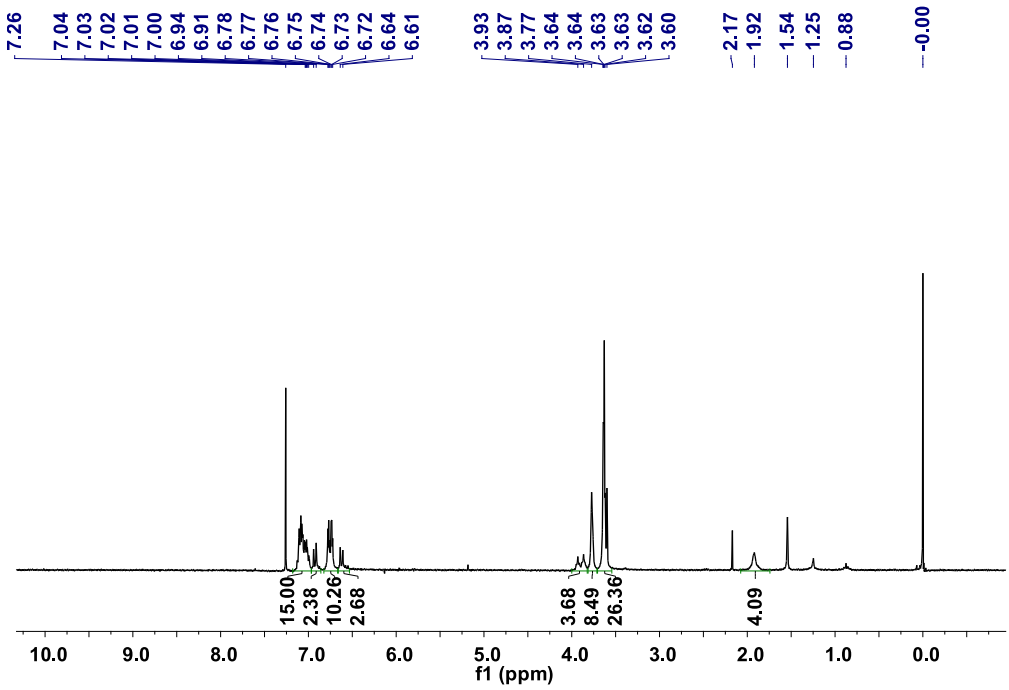


Figure S7. ^{1}H NMR spectrum of compound **H2**.

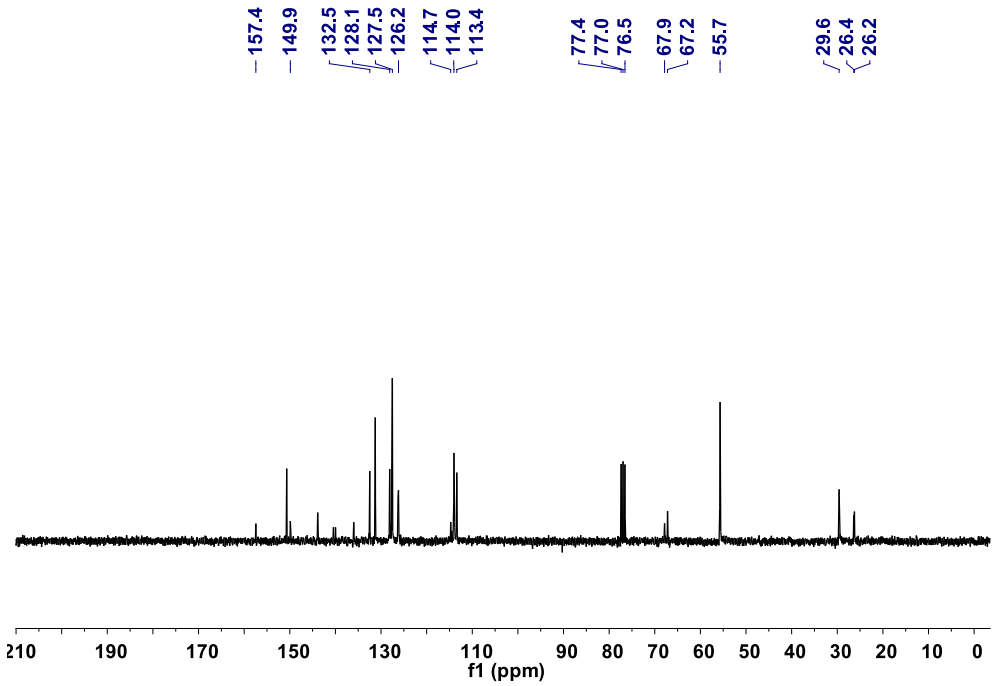


Figure S8. ^{1}C NMR spectrum of compound **H2**.

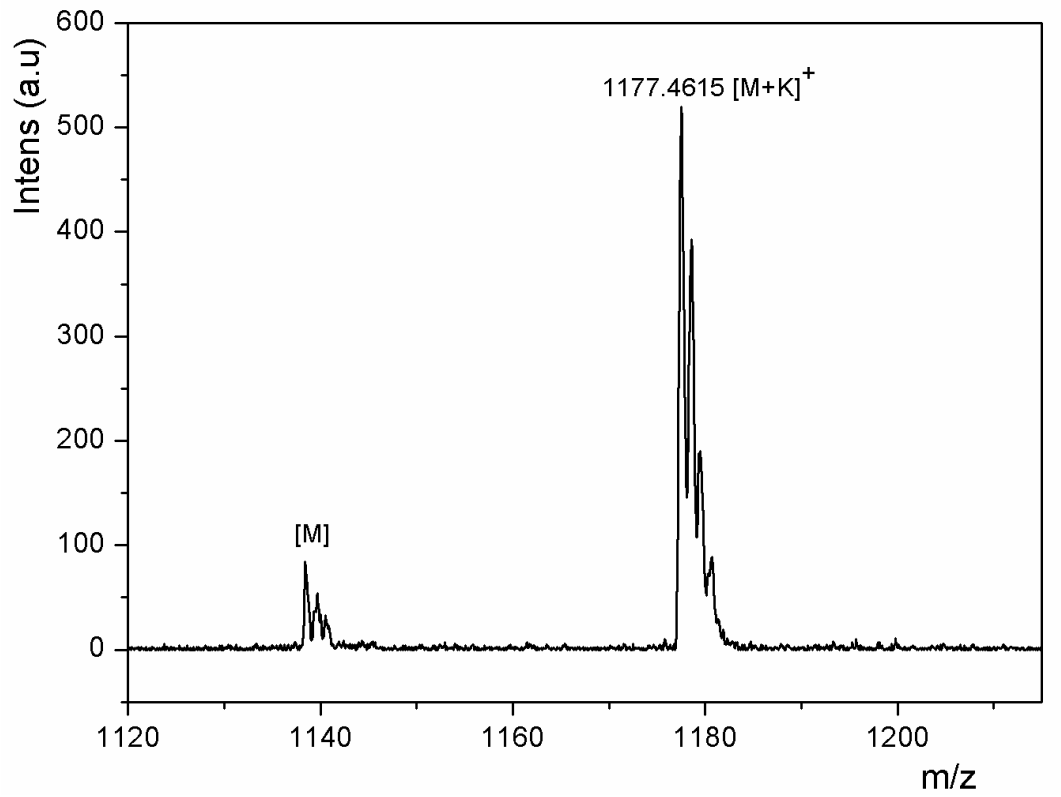


Figure S9. MOLDI-TOF MS spectrum of **H2**.

2.2.4. Synthesis and characterization of **H3**.

Tetrahydroxyl tetraphenylethene (40 mg, 0.1 mmol) was dispersed in MeCN (60 mL) and K_2CO_3 (2 g) was added. The mixture was stirred for 30 min at room temperature. Then, a small amount of KI and excess 4-(4-bromobutanyl)-anisole (0.256 g, 1 mmol) were added. The mixture was heated under reflux for 40 h under a nitrogen atmosphere. The mixture was filtered and washed with chloroform after cooling down. The filtrate was collected and concentrated, the residue was subjected to column chromatography (silica gel, CH_2Cl_2 : n-hexane = 3:2), the white product **H3** was obtained. Yield: 72 mg, Yield: 65%. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) δ (ppm): 6.91 (d, J = 5 Hz, 8H), 6.82 (s, 16H), 6.63 (d, J = 5 Hz, 8H), 3.96 (t, J = 5 Hz, 16H), 3.76 (s, 12H), 1.92 (m, 16H). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ (ppm): 157.2, 153.8, 153.2, 138.4, 136.9, 132.5, 115.5, 114.7, 113.6, 68.2, 67.3, 55.7, 29.6, 26.1, 26.0. MALDI-MS: Calcd for $C_{70}H_{76}O_{12}$ [M]: 1108.5336, Found: 1108.5259.

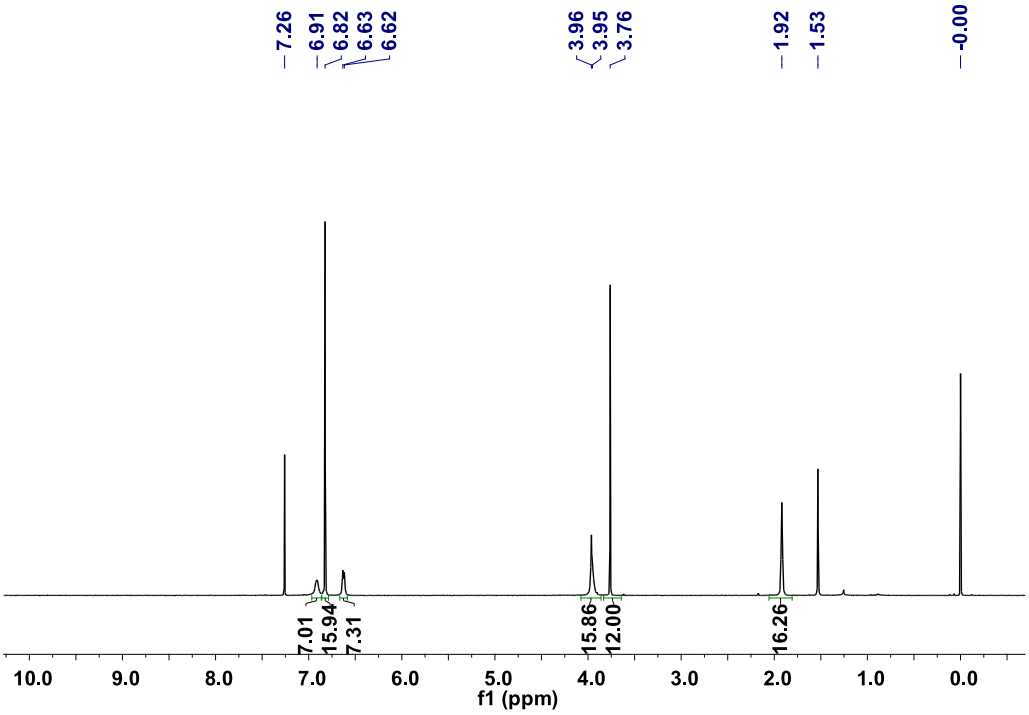


Figure S10. ^{1}H NMR spectrum of compound **H3**.

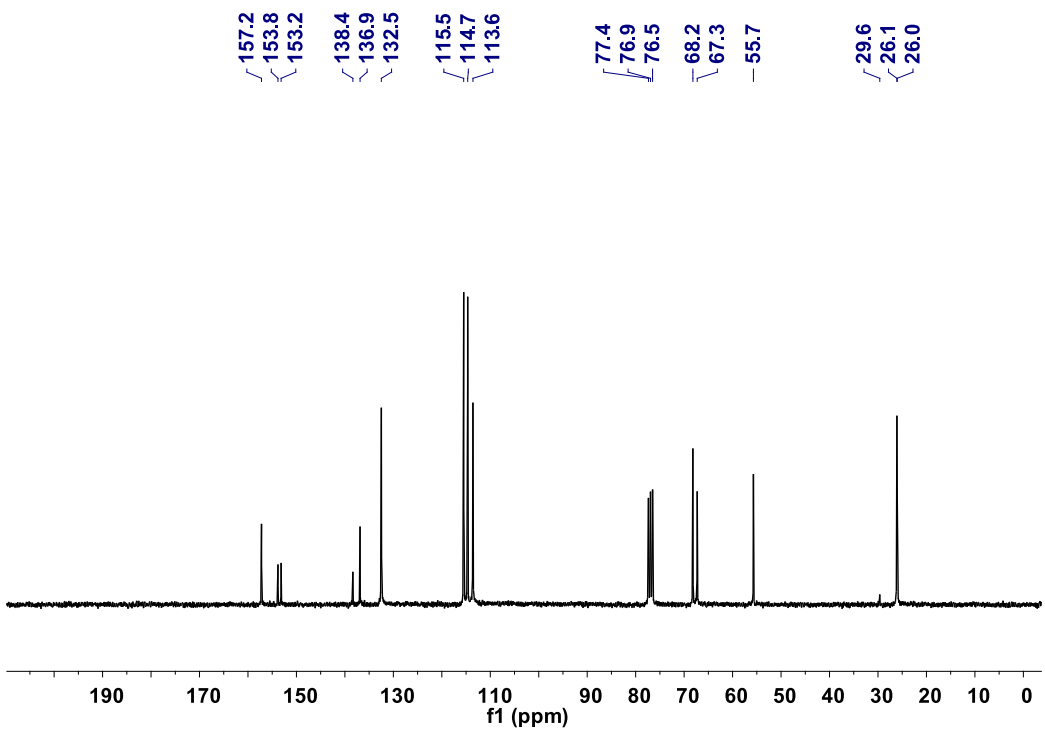


Figure S11. ^{13}C NMR spectrum of compound **H3**.

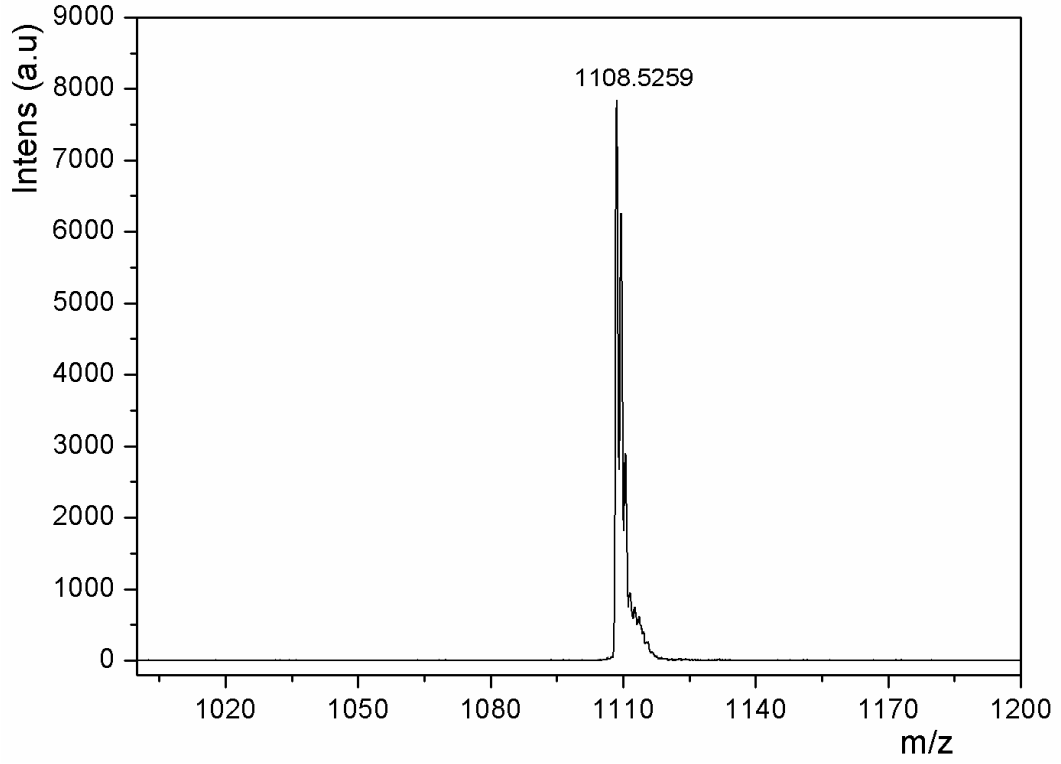
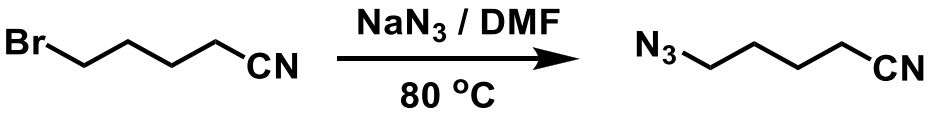


Figure S12. MOLDI-TOF MS spectrum of **H3**.

2.3. Synthesis and characterization of neutral guest molecules

2.3.1. Synthesis of 5-azidepentanenitrile



A mixture of 5-bromopentanenitrile (1 g, 6.25 mmol) and excess sodium azide (0.5 g, 7.69 mmol) in DMF (10 mL), the mixture was stirred at 90 °C for 14 h. After cooling to room temperature, the mixture was added to diethyl ether (30 mL). The solution was washed with H_2O (2 × 30 mL) and brine (2 × 30 mL), the organic phase was collected and dried overnight with anhydrous Na_2SO_4. The mixture was filtered and the filtrate was concentrated under vacuum to give 5-azidepentanenitrile. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ (ppm): 3.36 (t, *J* = 6 Hz, 2H), 2.40 (t, *J* = 6 Hz, 2H), 1.77 (m, 4H).

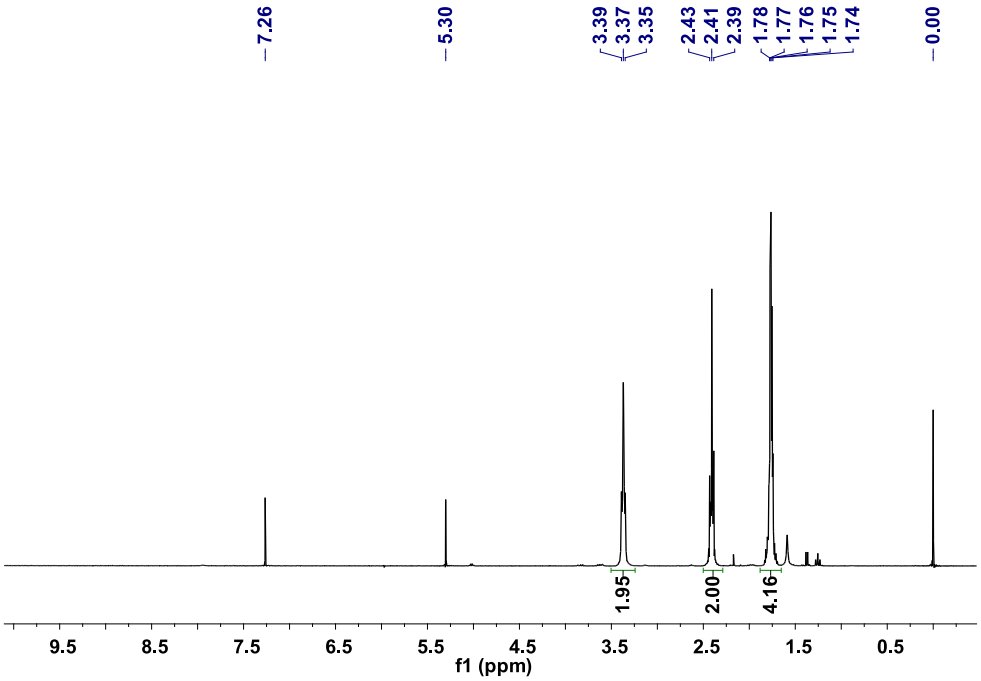
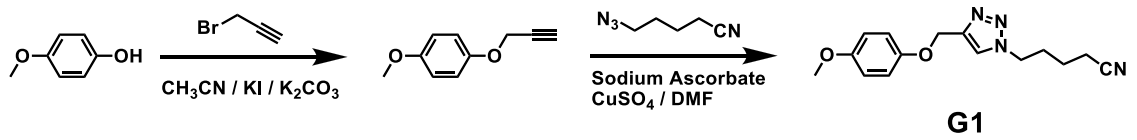


Figure S13. ^{1}H NMR spectrum of 5-azidepenpanenitrile.

2.3.2. Synthesis and characterization of neutral guest **G1**



G1

Methoxy-4-(prop-2-ynyloxy)benzene (0.38 g, 2.3 mmol) and 5-azidepenpanenitrile (0.31 g, 2.34 mmol) were dissolved in DMF (10 mL), then sodium ascorbate (0.20 g) and $CuSO_4$ (0.16 g) were added. The mixture was stirred at 90 °C for 14 h. Then, the mixture was poured into brine (30 mL) and extracted with CH_2Cl_2 (2 × 30 mL), the organic phase was dried overnight with anhydrous Na_2SO_4. The organic phase was concentrated under vacuum and subjected to silica gel chromatography (silica gel, EtOAc : n-hexane = 10:1) to give the light yellow product **G1**. 0.41 g Yield: 58 %. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ (ppm): 7.60 (s, 1H), 6.92 (d, *J* = 9 Hz, 2H), 6.83 (d, *J* = 9 Hz, 2H), 5.17 (s, 2H), 4.42 (t, *J* = 7.5 Hz, 2H), 3.77 (s, 3H), 2.40 (t, *J* = 6 Hz, 2H), 2.05 (m, 2H), 1.68 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ (ppm): 148.5, 146.6, 138.8, 117.0, 113.3, 110.1, 109.0, 56.9, 50.0, 43.5, 23.3, 16.6, 10.9.. MS-ESI: Calcd for $C_{15}H_{18}N_4O_2$ $[M+H]^+$: 287.1502, Found: 287.1508.

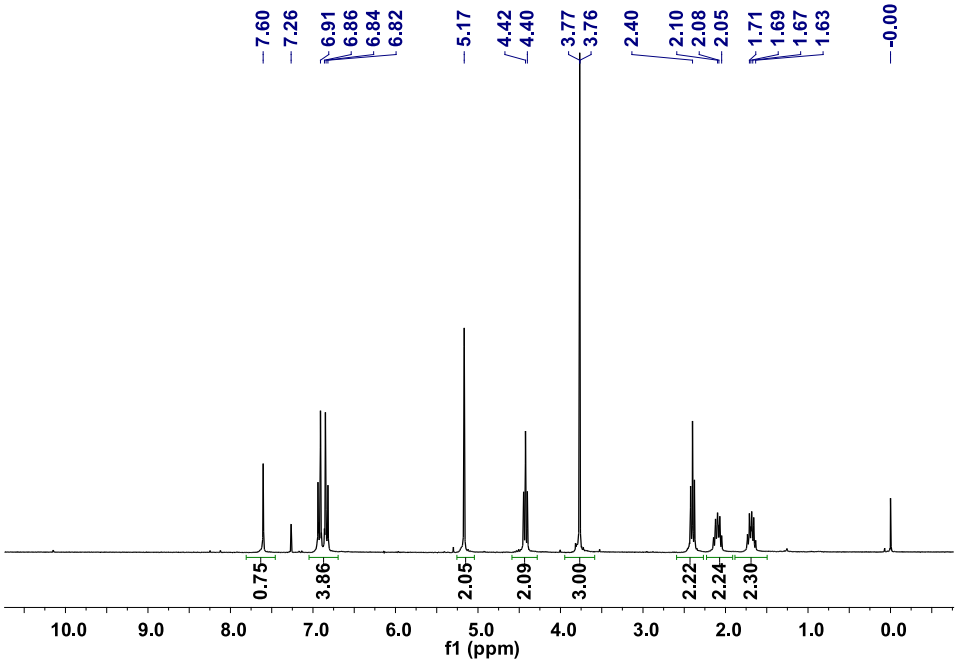


Figure S14. ^{1}H NMR spectrum of **G1**.

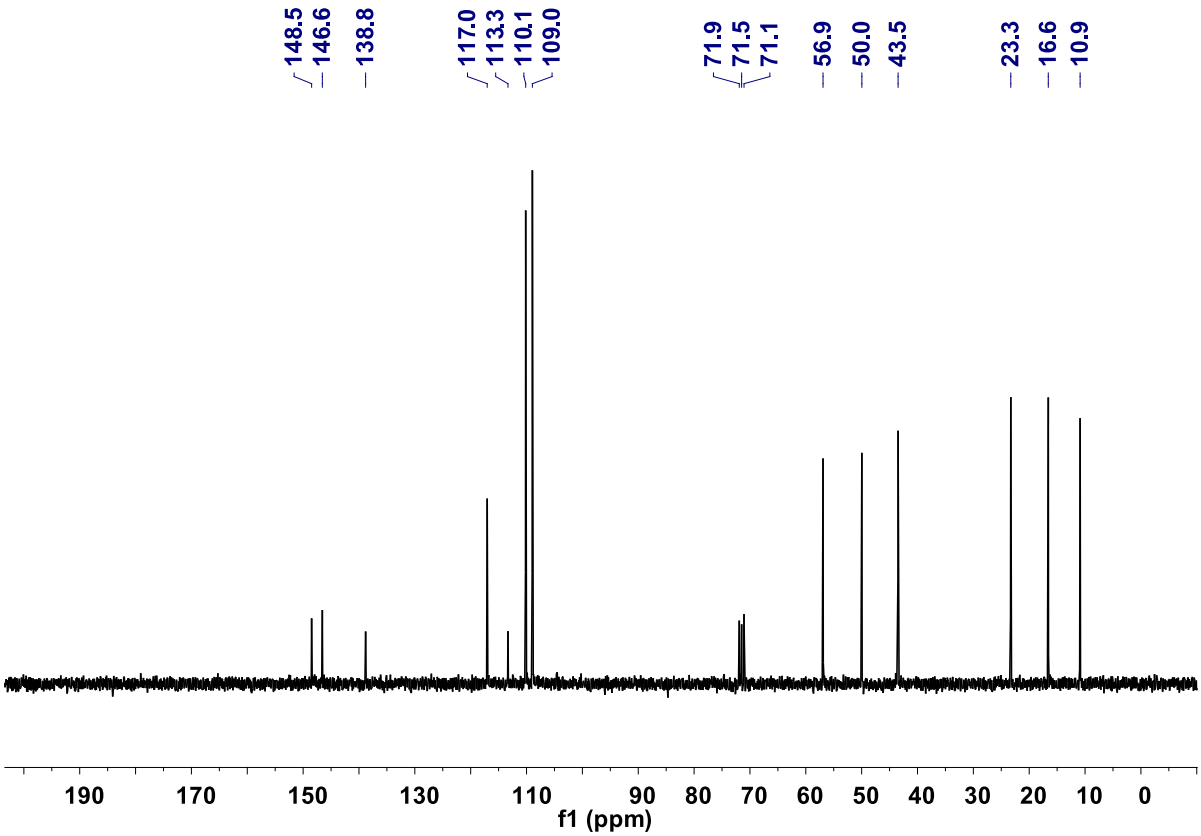


Figure S15. ^{13}C NMR spectrum of **G1**.

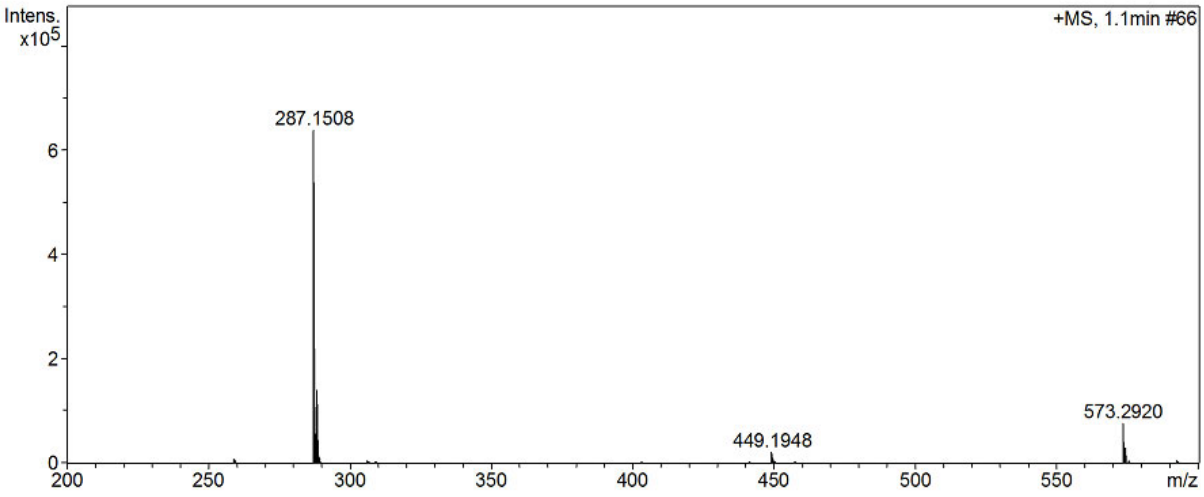
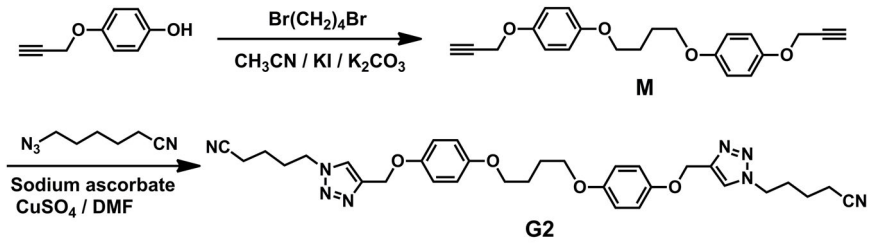


Figure S16. ESI-MS spectrum of Synthesis of **G1**.

2.3.3. Synthesis and characterization of neutral guest **G2**



Methoxy-4-(prop-2-ynyloxy)-benzene (1.1 g, 7 mmol) were dissolved in MeCN, and K_2CO_3 (1 g, 7.4 mmol) was added. The mixture was stirred for 0.5 h at room temperature, then a small amount of KI and 1,4-dibromobutane (0.3 mL, 2.5 mmol) were added. The mixture was stirred for 14 h at 90 °C. Then, the mixture was filtered and washed with CH_2Cl_2, the filtrate was concentrated and subjected to silica gel chromatography (EtOAc : n-hexane: = 1:5) to give the intermediate **M** as a white solid. 0.8 g, Yield: 68%. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ (ppm): 6.92 (d, *J* = 9 Hz, 4H), 6.83 (d, *J* = 9 Hz, 4H), 4.64 (d, *J* = 3Hz, 4H), 3.98 (t, *J* = 6 Hz, 4H), 2.50 (t, *J* = 3Hz, 2H), 1.94 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ (ppm): 153.8, 151.6, 116.1, 115.3, 78.9, 75.3, 68.0, 56.6, 26.0. Intermediate **M** (0.35 g, 1 mmol) and 5-azidepenpanenitrile (0.31 g, 2.34 mmol) were dissolved in DMF (8 mL), then sodium ascorbate (0.2 g) and $CuSO_4$ (0.12 g) were added. The mixture was stirred at 90 °C for 14 h. Then, the mixture was poured into brine (30 mL) and extracted with CH_2Cl_2 (2 × 30 mL), the organic phase was dried overnight with anhydrous Na_2SO_4. The organic phase was concentrated under vacuum and subjected to silica gel chromatography (EtOAc : n-hexane = 10:1) to give a light yellow product **G2**. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ (ppm): 7.61 (s, 2H), 6.91 (d, *J* = 9 Hz, 4H), 6.82 (d, *J* = 9 Hz, 4H), 5.18 (s, 4H), 4.45 (t, *J* = 6Hz, 4H), 3.98 (t, *J* = 6 Hz, 4H), 2.41 (t, *J* = 6Hz, 4H), 2.11 (m, 4H), 1.94 (m, 4H), 1.69 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ (ppm): 153.7, 152.4, 144.5, 122.3, 118.6, 116.0, 115.6, 68.2, 62.9, 49.1, 29.6, 28.9, 26.0, 22.3, 16.5. MALDI-MS: Calcd for $C_{32}H_{38}N_8O_4$, $[M+K]^+$: 621.2908, Found: $[M+K]^+$: 621.3095.

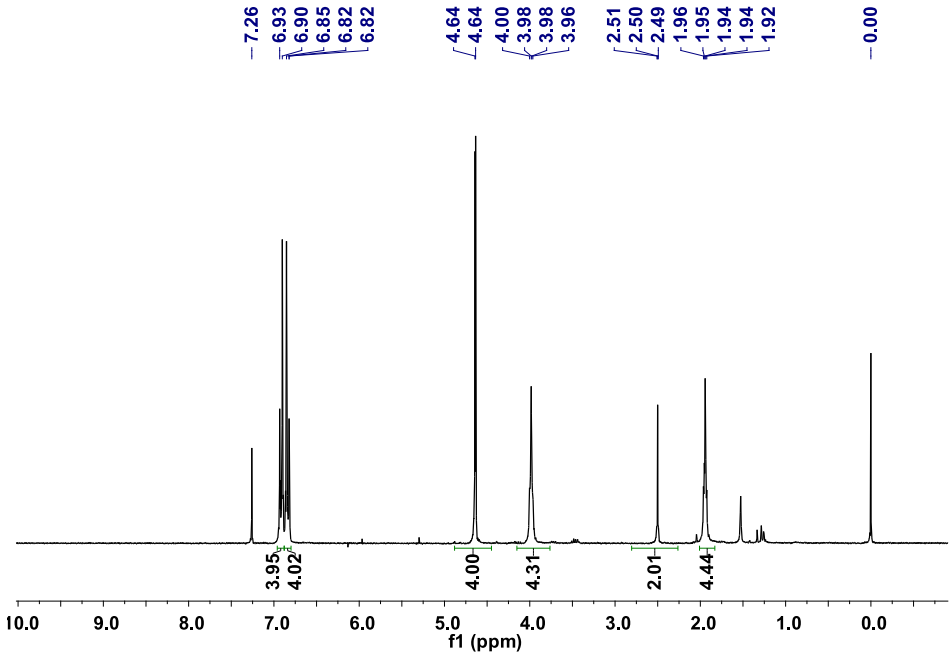


Figure S17. ^{1}H NMR spectrum of **M**.

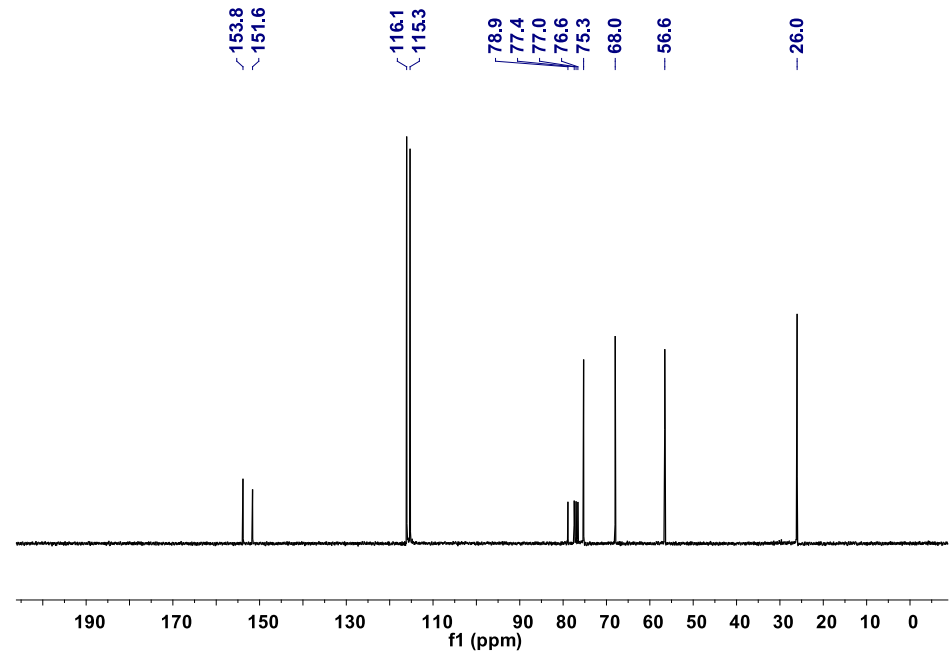


Figure S18. ^{13}C NMR spectrum of **M**.

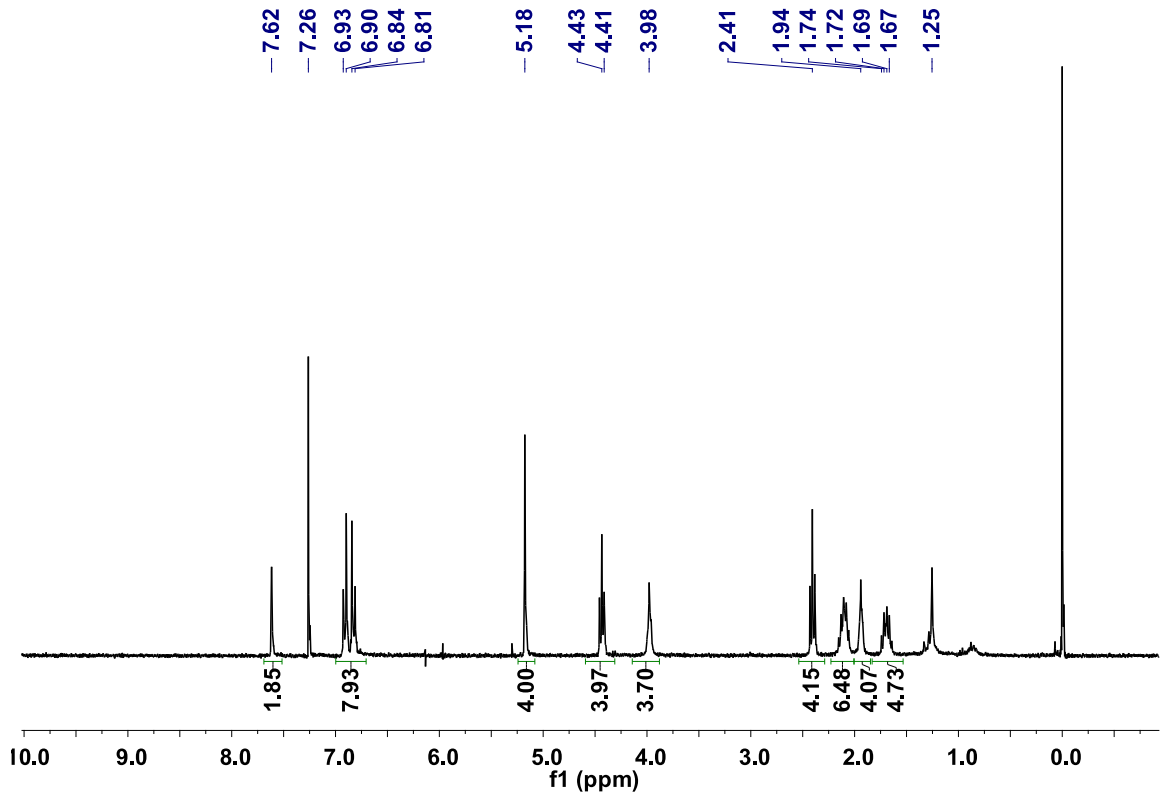


Figure S19. ^{1}H NMR spectrum of **G2**.

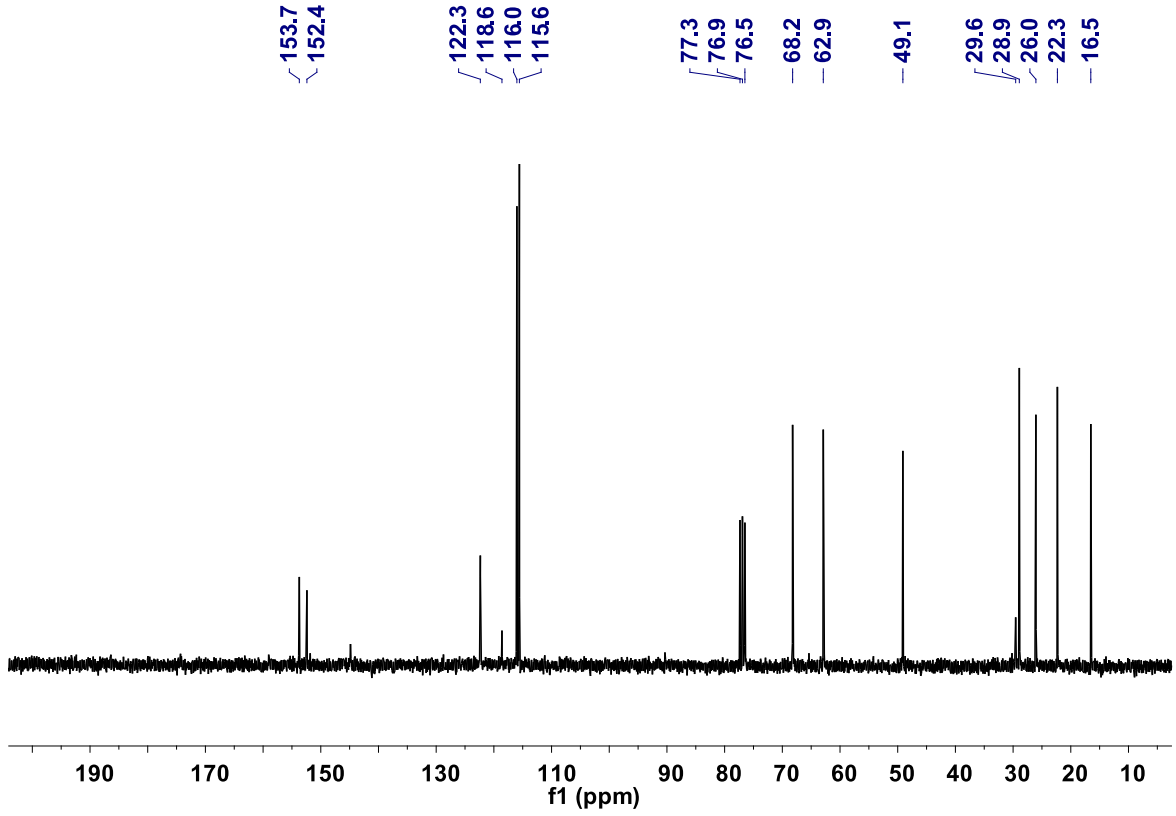


Figure S20. ^{13}C NMR spectrum of **G2**.

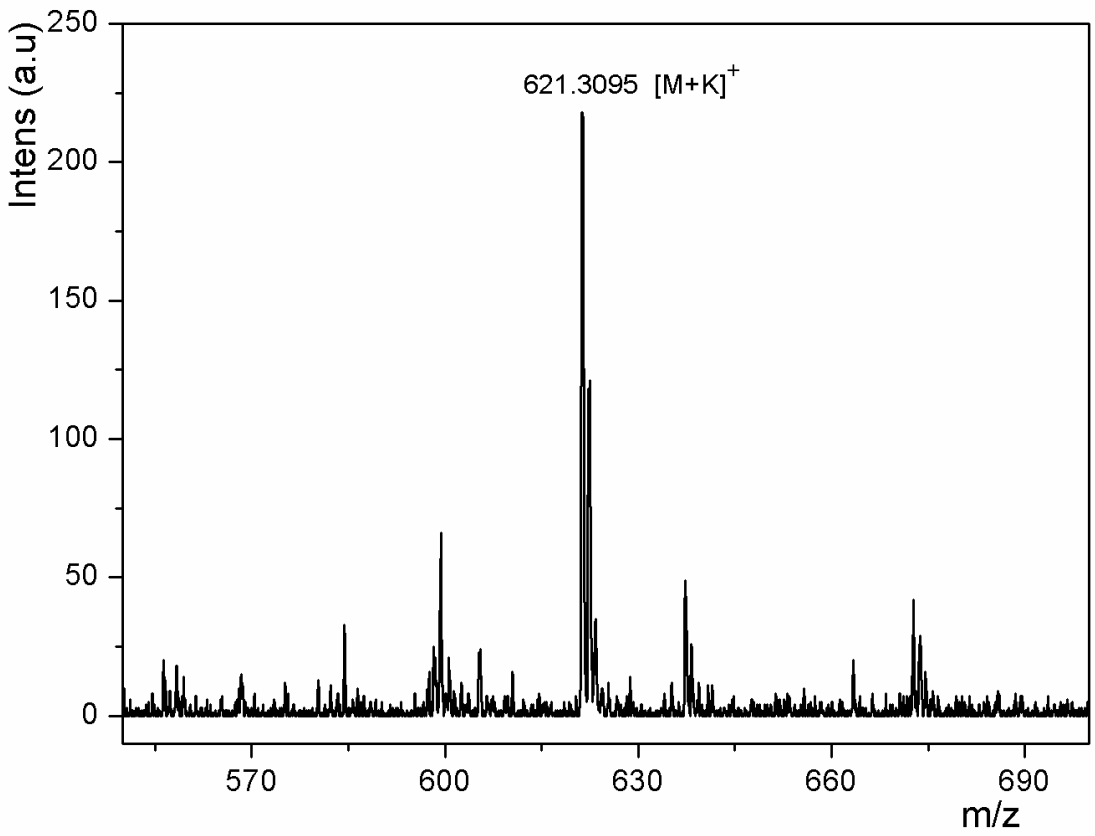


Figure S21. ESI-MS spectrum of **G2**.

3. AIE Properties of H1, H2 and H3 in THF/H_2O

We added different amounts of H_2O, a poor solvent of this luminogen, to the pure THF solutions and monitored the photoluminescence (PL) intensity changes by fluorescence spectroscopy. **H1** exhibits no fluorescence when it is completely dissolved in THF, and the PL intensity of **H1** increases slowly when the volume fraction of H_2O is low than 40%. However, a dramatic PL increase was observed with the addition of more H_2O to the **H1** solution, and reached the highest level when the volume fraction of H_2O is 95%. **H1** in the mixed solvents of H_2O/THF emits intense blue light with the PL emission peak centered at 488 nm. These results indicate that **H1** possesses a good AIE property. On the other hand, the control compound, non-fluorescent **H2** in pure THF also exhibited an AIE property *via* the addition of H_2O into its THF solution.

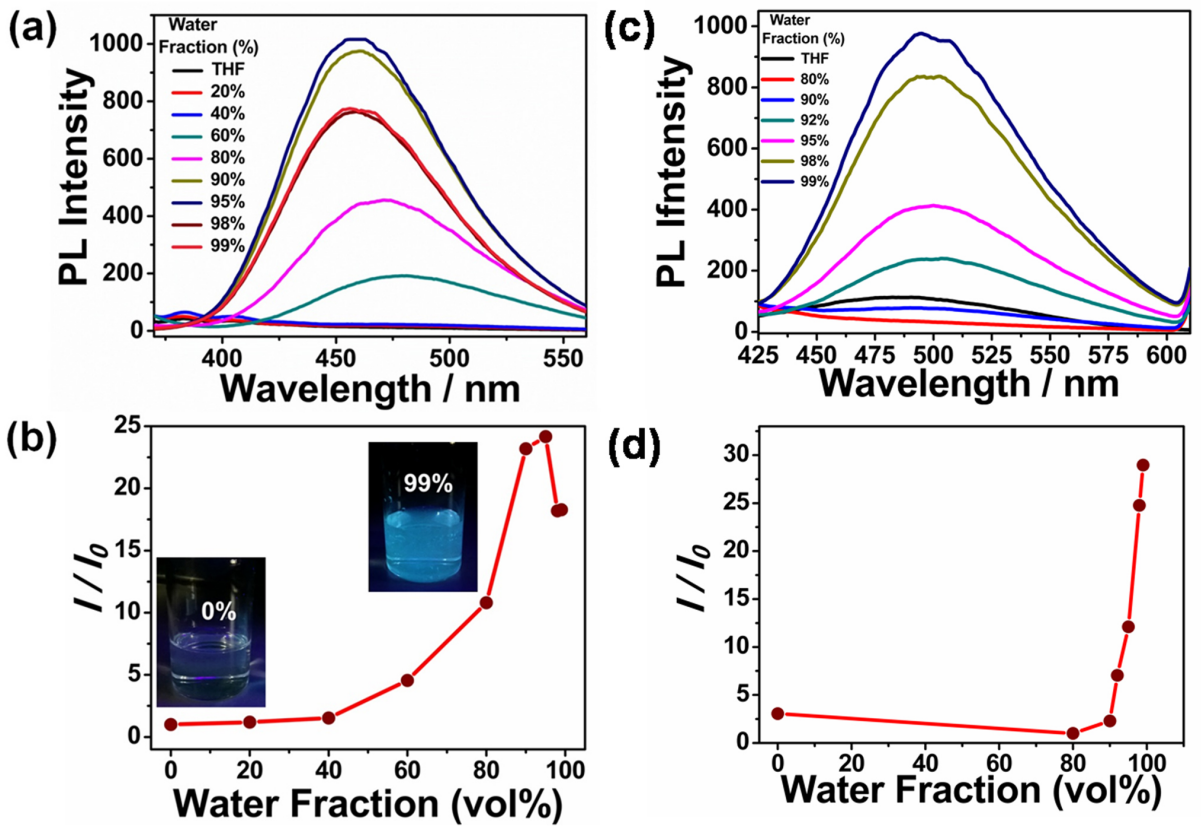


Figure S22. Fluorescence emission spectra of (a) **H1** (1 μM; λ_{ex} = 352 nm; λ_{em} = 456 nm; slit widths: Ex. 10 nm, Em. 10 nm; 25 °C) and (c) **H2** (1 μM; λ_{ex} = 300 nm; λ_{em} = 465 nm; slit widths: Ex. 10 nm, Em. 10 nm; 25 °C) in THF/H_2O mixtures with the volume fractions of water varying in the range of 0–99%. (b) Plot of the relative PL intensity (I/I_0) of **H1** at 456 nm *vs* the composition of the THF/water mixture (f_w). I_0 represents the PL intensity of **H1** in THF solution. (Inset) optical photographs recorded under 365 nm UV irradiation for **H1** in THF/H_2O mixtures for 0% and 99%. (d) Plot of the relative PL intensity (I/I_0) of **H2** at 465 nm *vs* the composition of the THF/water mixture (f_w). I_0 represents the PL intensity of **H2** in THF solution.

4. Fluorescence Properties of H1, H2 and H3 in Chloroform and THF

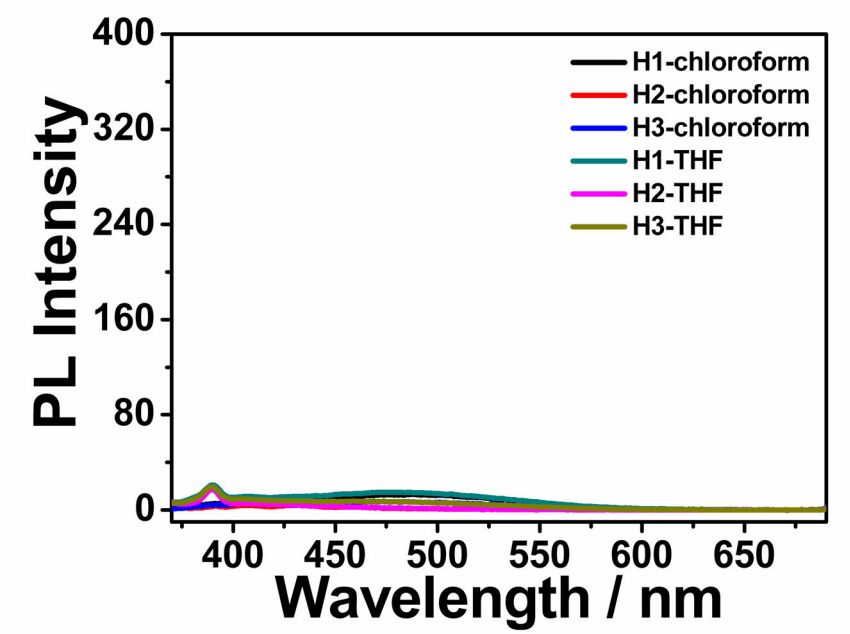


Figure S23. Fluorescence emission spectra of **H1**, **H2**, **H3** in THF and chloroform, respectively. (λ_{ex} = 350 nm; slit widths: Ex. 5 nm, Em. 5 nm; 25 °C, concentration: [**H1**] = 1.0 μM, [**H2**] = 1.0 μM, [**H3**] = 1.0 μM).

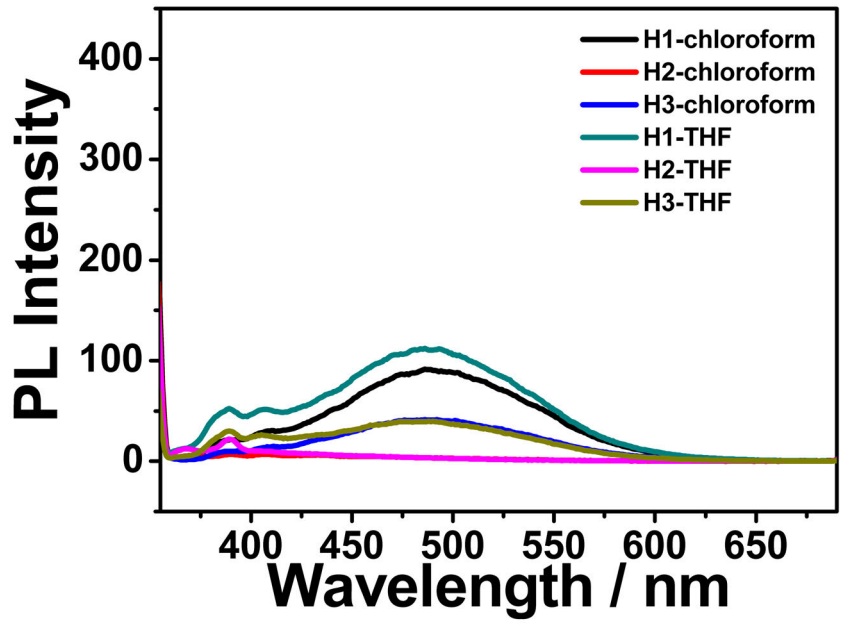


Figure S24. Fluorescence emission spectra of **H1**, **H2**, **H3** in THF and chloroform, respectively. (λ_{ex} = 350 nm; slit widths: Ex. 5 nm, Em. 5 nm; 25 °C, concentration: [**H1**] = 10 μM, [**H2**] = 10 μM, [**H3**] = 10 μM).

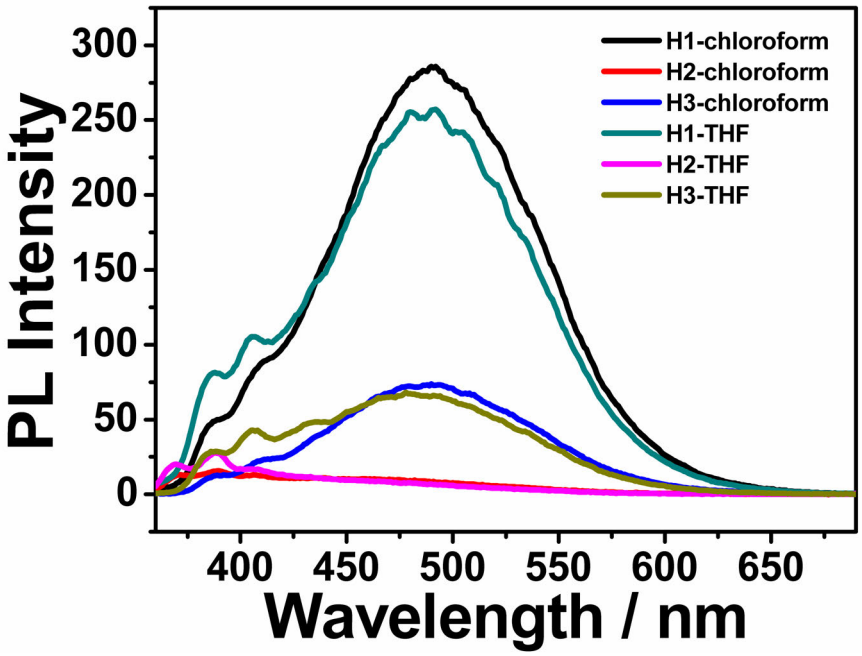
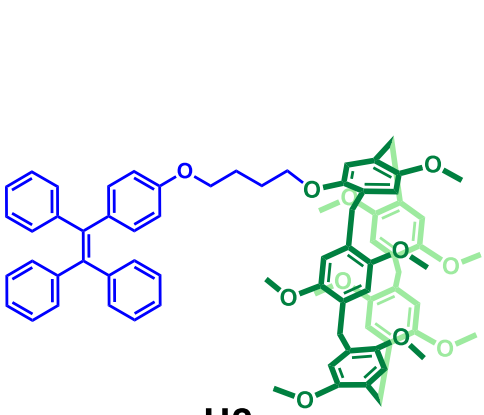
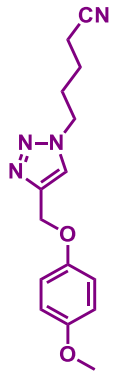


Figure S25. Fluorescence emission spectra of **H1**, **H2**, **H3** in THF and chloroform, respectively. (λ_{ex} = 350 nm; λ_{ex} = 490 nm; slit widths: Ex. 5 nm, Em. 5 nm; 25 °C, concentration: [**H1**] = 100 μM, [**H2**] = 100 μM, [**H3**] = 100 μM).

5. Isothermal Titration Calorimetry (ITC)

In the ITC experiments,[S3] the **H2** solution in chloroform was placed in the reaction cell and the chloroform solution of **G1** was placed in the syringe and then were added into the cell by sequential injections. The binding isotherm data were fitted by "one set of binding sites" model.





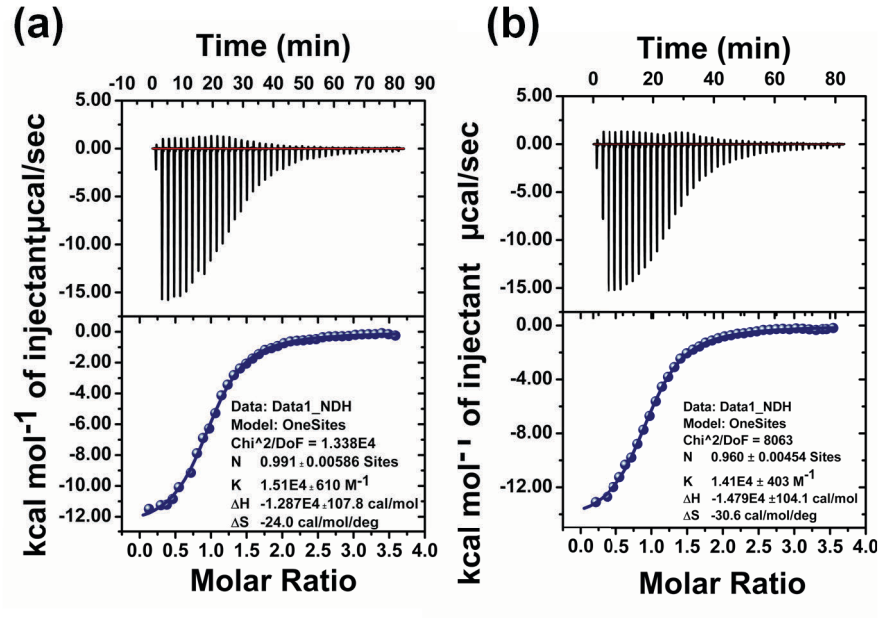


Figure S26. (a) **H2** (1.01 mM) with **G1** (20.20 mM) in $CHCl_3$ at 25 °C. raw ITC data for 41 sequential injections (0.7 μL per injection) of **G1** solution (20.20 mM) into **H2** solution (1.01 mM) with 1.0 second duration time between each injection and net reaction heat obtained by subtracting the dilution heat from the reaction heat, fitted by "one set of binding sites" model. (b) Repeated ITC experiment to (a). Average datas: K_s (M^{-1})=1.46 ± 0.05 × 10^{-4} M^{-1}, ΔH^o = – 57.76 ± 4.19 kJ mol^{-1}, $T\Delta S^o$ = – 34.07 ± 0.12 kJ mol^{-1}. (1 cal/mol=4.1868 J/mol, T=298 K)

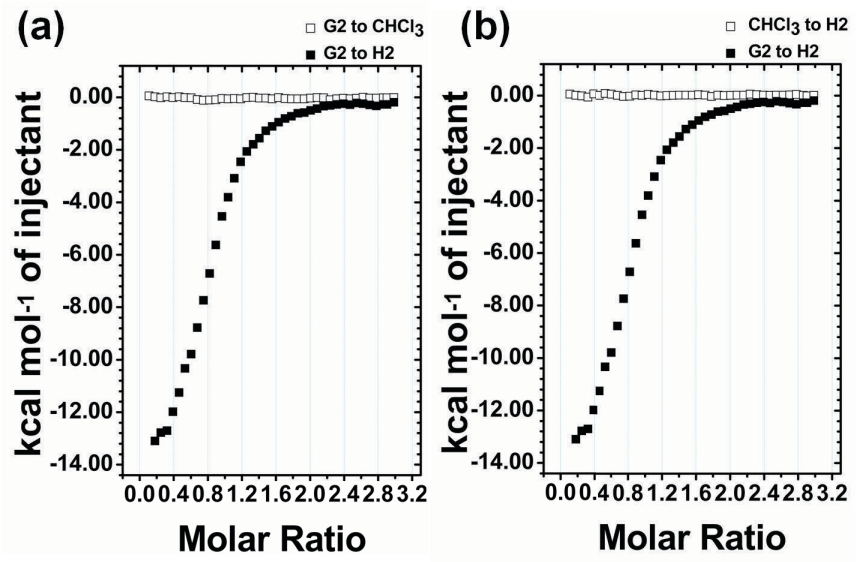


Figure S27. Heat effects of the dilution of (a) injecting **G2** into $CHCl_3$ and (b) $CHCl_3$ into **H2,** and the complexation reaction of **G1** (20.20 mM) with **H2** (1.01 mM) for each injection during a calorimetric titration at 25 °C.

6. Fluorescence Experiments for the Detection of the Supramolecular Assembly

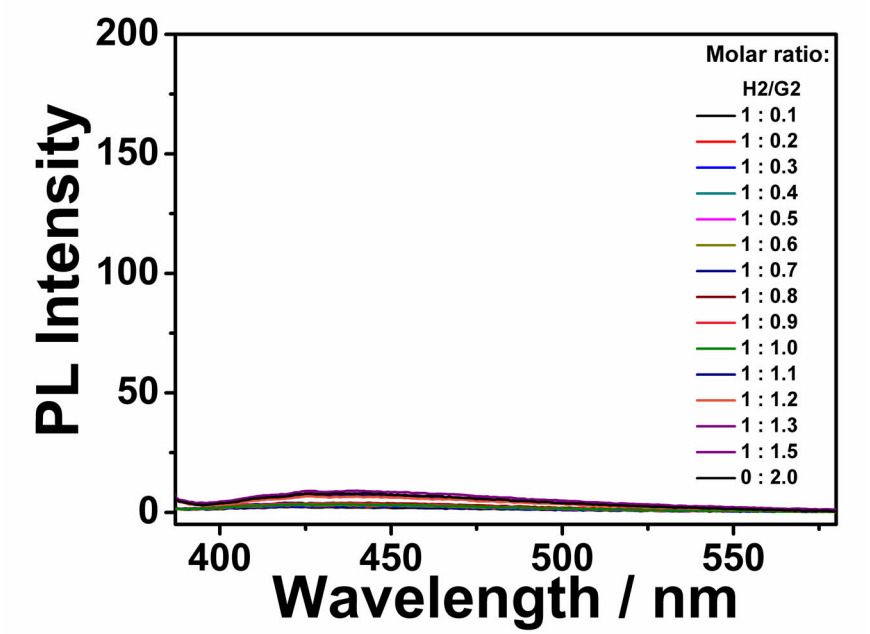


Figure S28. Fluorescence emission spectra of **G2** ⊂ **H2** (λ_{ex} = 373 nm; slit widths: Ex. 5 nm, Em. 5 nm; 25 °C, concentration: [**H2**] = 10.0 μM, [**G2**] = 1.0 μM, 2.0 μM, 3.0 μM, 4.0 μM, 5.0 μM, 6.0 μM, 7.0 μM, 8.0 μM, 9.0 μM, 10.0 μM, 11.0 μM, 12.0 μM, 13.0 μM, 15.0 μM, 17.0 μM, 20.0 μM; [**H2**] = 0 μM, [**G2**] = 20.0 μM)

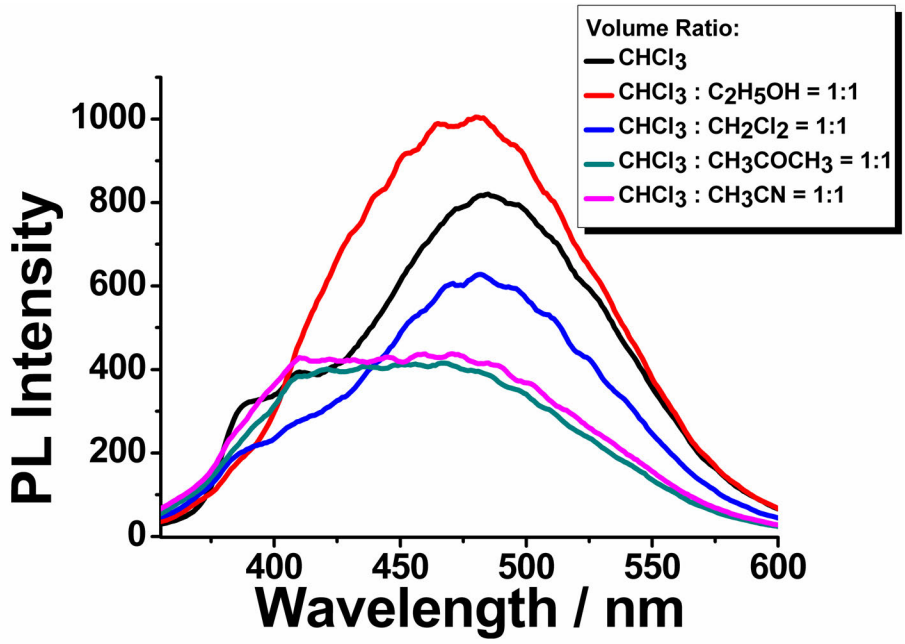


Figure S29. Fluorescence emission spectra of **G2** ⊂ **H1** in different solvents. (λ_{ex} = 332 nm; λ_{em} = 484 nm; slit widths: Ex. 5 nm, Em. 5 nm; 25 °C, concentration: [**H1**] = 10.0 μM, [**G2**] = 20.0 μM).

7. Experiments for Thermal Stability of the Supramolecular Gel

From the TGA data, a negligible thermal decomposition at the temperatures ranging from 150 °C to 300 °C, and a dramatic thermal decomposition from a weight loss of 34.9% to 65.1% from 322 °C to 467 °C, resulting from the decomposition of pillarene derivatives. Moreover, differential scanning calorimetry (DSC) studies were performed to gain further evidence on the thermal stability of the supramolecular organogels. When the gel was heated, there are three obvious peaks at 177.1 °C, 182.2 °C, 195.7 °C, respectively, which ascribed to the transition process from gel to sol. More sophisticated peaks from 175 °C to 200 °C can be attributed to the transitions from different aggregated states. However, during the process of bringing down the temperature, no peaks corresponding to the transition of sol to gel was found. This is because the supramolecular polymerization between tetramer **H1** and ditopic **G2** might involve multiple non-covalent interactions such as C–H···π interactions and C–H···N/C–H···O hydrogen bonds, and these complicated cooperative interactions result in different aggregation states that are difficult to transform back. This mechanism has also been confirmed by TGA data that the gel has no obvious decomposition from 175 °C to 200 °C.

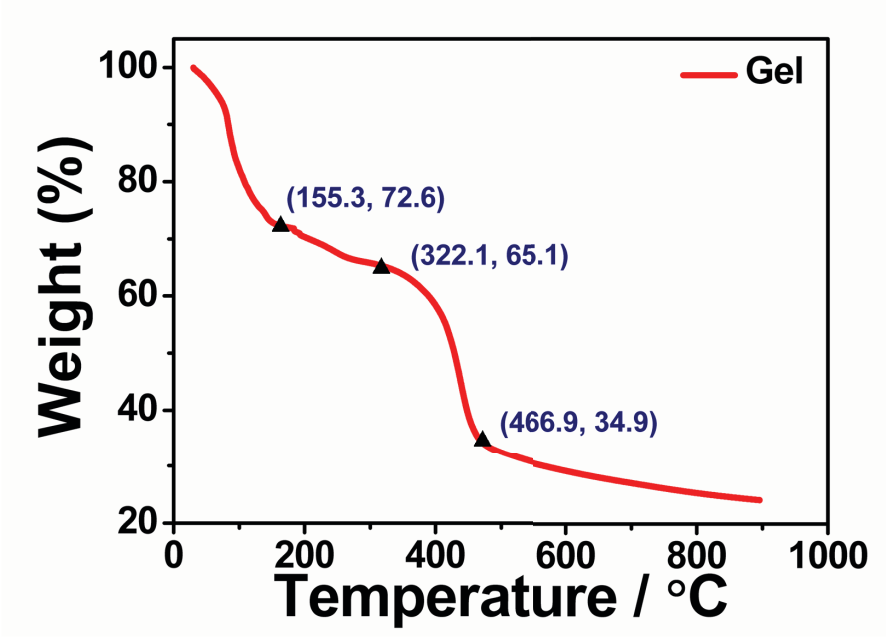


Figure S30. Thermogravimetric analysis (TGA) of the supramolecular organogel formed of **G2** ⊂ **H1**. TGA was performed on a TA Q500 instrument with a heating program consisting of a heating rate of 10 °C/min from 25 °C to 900 °C. The quality of the sample is 16.3680 mg before the temperature starting ramping up.

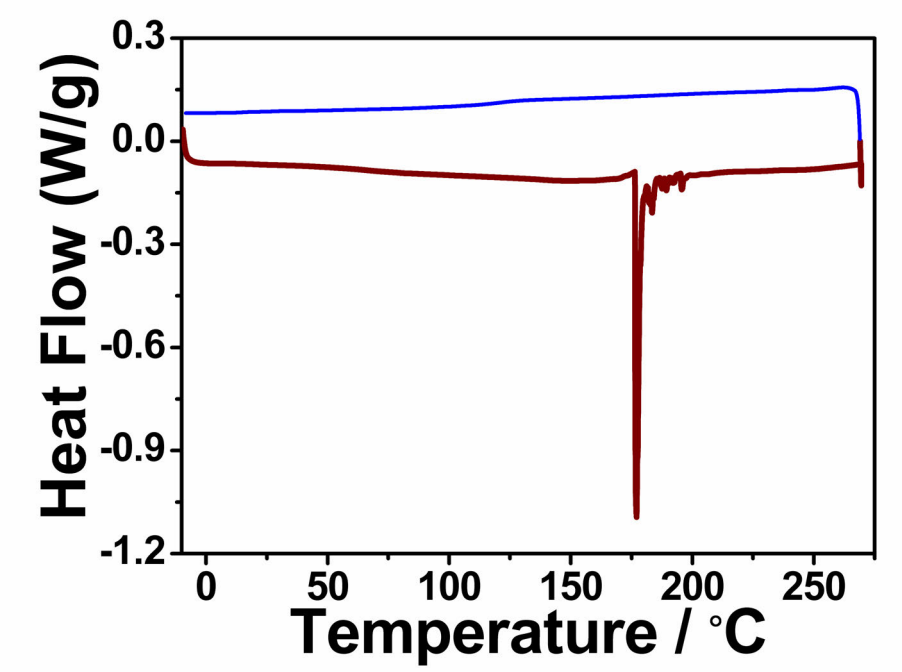


Figure S31. Differential scanning calorimetry (DSC) of the supramolecular organogel. The experiment was studied on a Netzsch DSC 204 with a scanning rate of 5 °C /min from -10 °C to 270 °C and then cooling back. The quality of the sample is 5.27 mg at the beginning.

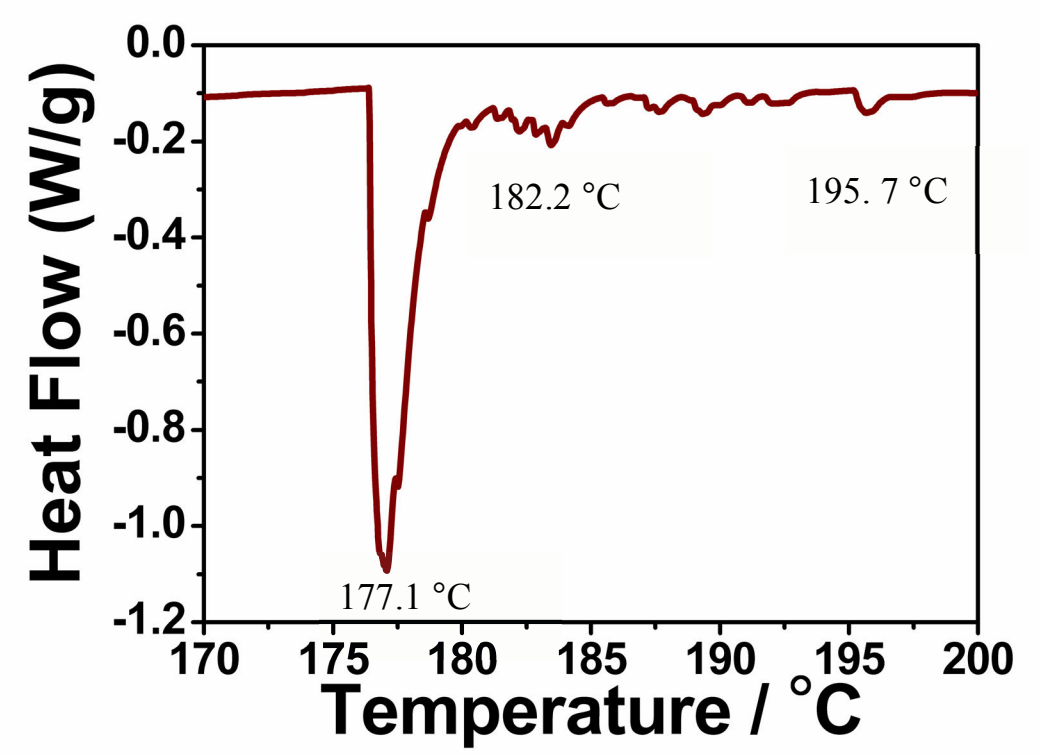


Figure S32. Partial spectrum of DSC shown in ***Figure S25*** at the temperature ranging from 151.6 °C to 202.0 °C.

8. References

S1. X. F. Duan, J. Zeng, J. W. Lu and Z. B. Zhang, *J. Org. Chem.*, 2006, **71**, 9873.

S2. K. Wang, L. L. Tan, D. X. Chen, N. Song, G. Xi, S. X. A. Zhang, C. J. Li and Y. W. Yang, *Org. Biomol. Chem.*, 2012, **10**, 9405.

S3. The ITC data were obtained using a MicroCal ITC isothermal calorimeter at 25 °C and are corrected for the heat generated from dilution of the host. Detailed experimental procedures for ITC determinations and the operation of ITC200 instruments can be found on the MacroCal ITC manual provided by General Electric Company. Data were analysed by non-linear least square fitting using the Origin software supplied by MicroCal: T. Wiseman, S. Williston, J. F. Brandts and L.-N. Lin, *Anal. Biochem.*, 1989, **179**, 131–137. For ITC experimental design and data analysis, please also refer to M. W. Freyer and E. A. Lewis, *Methods in Cell Biology*, 2008, vol. 84, chapter 4, DOI: 10. 1016/S0091-679X(07)84004-0, Elsevier Inc.