Electronic Supplementary Information

Photo-controlled fluorescence on/off switching of a pseudo[3]rotaxane between an AIE-active pillar[5]arene host and a photochromic bithienylethene guest

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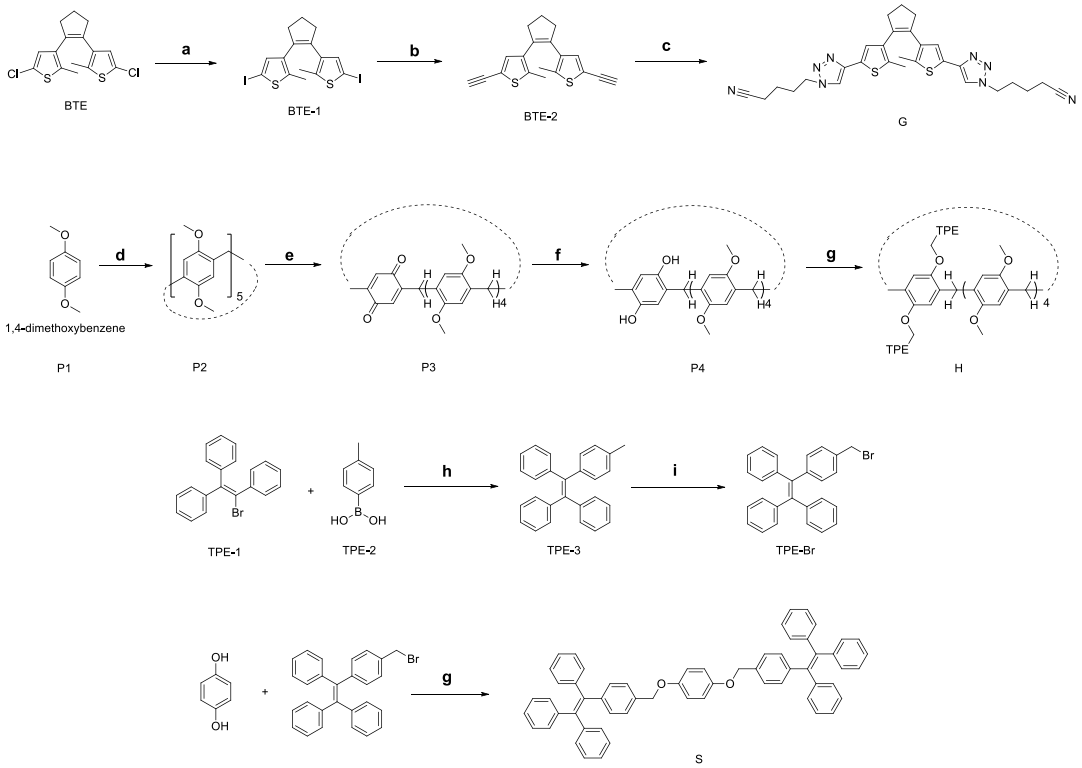
1. Materials and instruments

Most of chemicals were purchased from ***Energy***, ***Aladdin*** and ***Aldrich***. All solvents were purified by normal procedures and handled under moisture free atmosphere. The other materials were commercial products and were used without

further purification. NMR spectra were recorded on a Bruker Avance III 400 MHz spectrometer with TMS as internal standard. UV-Visible absorption spectra were measured on a Shimadzu UV-2550 spectrophotometer. Fluorescence spectra were measured on an Agilent Cary Eclipse Fluorescence Spectrophotometer. Mass spectra were recorded on a Shimadzu QP1000 spectrometer. Photographs were taken by Canon EOS 60D digital cameras.

2. Synthesis of target compounds



Scheme 1. Synthesis of **G** , **H** and **S**. a) *t*-BuLi, I_2; b) (1) 2-methylbut-3-yn-2-ol, triethylamine, CuI, $Pd(PPh_3)Cl_2$; (2) KOH, toluene; c) 5-bromopentanenitrile, CuI; d) $(CH_2O)_n$, $BF_3{\cdot}Et_2O$, 1,2-DCE; e) $(NH_4)_2Ce(NO_3)_6$, DCM; f) $Na_2S_2O_4$, H_2O, DCM; g) TPE-Br, $CsCO_3$, MeCN; h) $Pd(PPh_3)_4$, 2M K_2CO_3, EtOH, toluene; i) NBS, BPO, CCl_4.

2.1 Synthesis of 1,2-bis(5-iodo-2-methylthiophen-3-yl)cyclopent-1-ene (BTE-1)

To the solution of BTE (1.00 g, 3.06 mmol) in 10 mL THF at -78 ^{o}C under nitrogen atmosphere, 9.90 mL *t*-BuLi (1.3 M in hexane, 12.83 mmol) was added slowly. After stirring at -78 ^{o}C 30 min later, I_2 (2.33 g, 9.16 mmol) was added quickly. Then the mixture was allowed to warm to room temperature gently. After the reaction was complete, the mixture was poured into 15 mL NaOH aqueous (2 M) and extracted with EA three times. The combined organic layers were washed with brine then dried over $MgSO_4$. The collected organic layer was evaporated under vacuum; the residue was then purified by column chromatography on silica gel with petroleum ether as eluent to afford BTE-1 as white solid in 96% (1.52 g) yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.92 (s, 2H), 2.75 (t, *J* = 7.5 Hz, 4H), 2.13 – 1.97 (m, 2H), 1.91 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.7, 137.5, 137.5, 133.9, 68.2, 38.4, 22.9, 14.2.

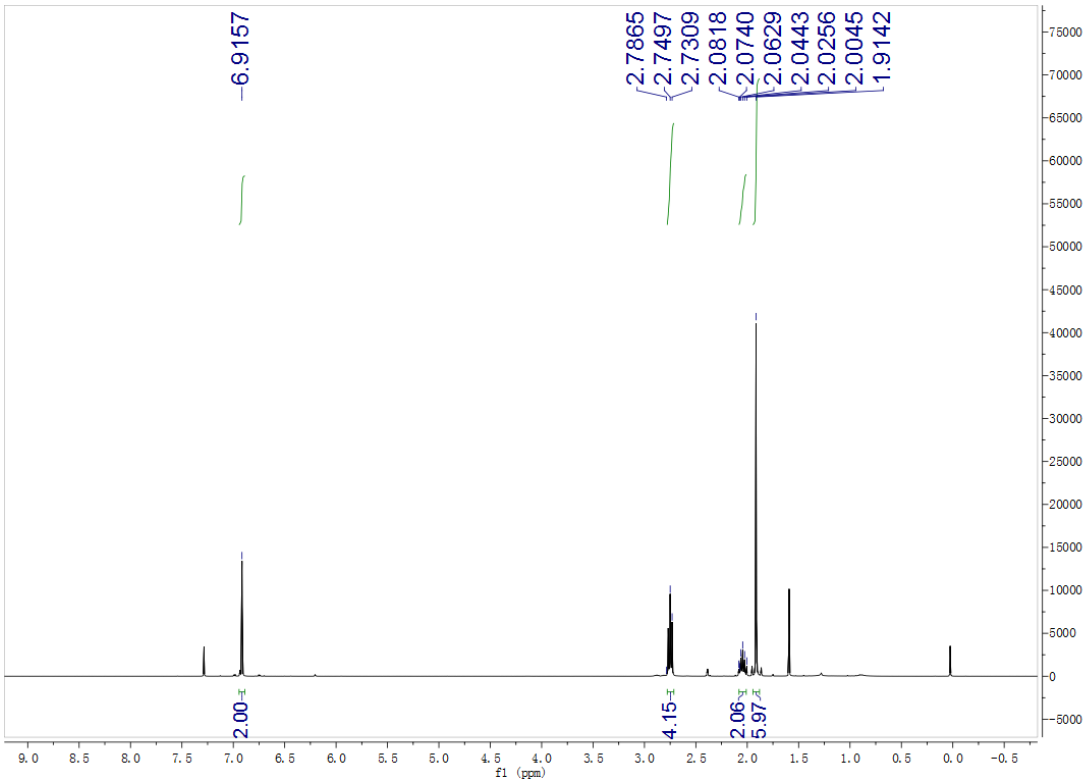


Fig. S1. ^{1}H NMR of **BTE-1** in $CDCl_3$

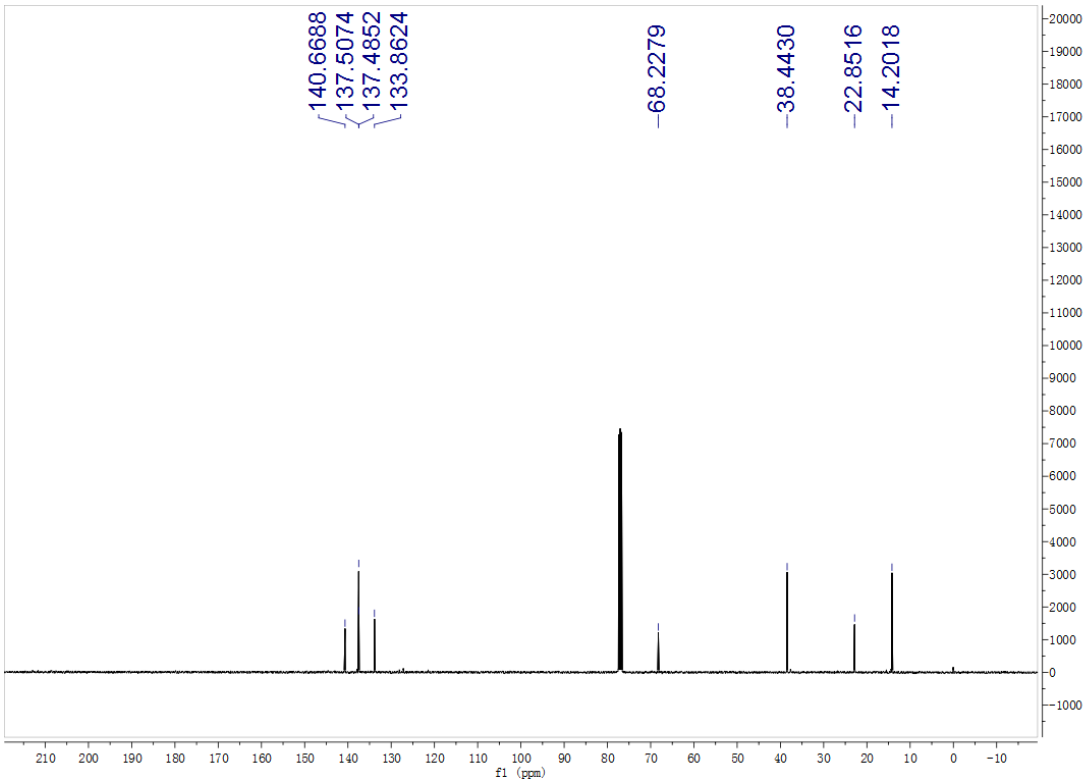


Fig. S2. ^{13}C NMR spectra of **BTE-1** in $CDCl_3$

2.2 Synthesis of 1,2-bis(5-ethynyl-2-methylthiophen-3-yl)cyclopent-1-ene (BTE-2)

BTE-1 (0.51 g, 1.00 mmol), 2-methylbut-3-yn-2-ol (0.34 g, 4.00 mmol) and Et_3N (15 mL) was dissolved in THF (30 mL), CuI (0.76 g, 4.00 mmol) and $Pd(PPh_3)_2Cl_2$ (0.14 g, 0.20 mmol) was added. Then the mixture was stirred at 40 ^oC under nitrogen atmosphere for 36 h. After cooling to room temperature, the mixture was poured in to water and extracted with EA three times. The combined organic layers were washed with brine then dried over $MgSO_4$. The collected organic layer was evaporated under vacuum, the residue was then purified by column chromatography on silica gel with petroleum ether/ ethyl acetate (5/1) as eluent to afford crude product. After the crude product was dissolved in toluene (20 mL), KOH (0.20 g, 3.57 mmol) was added and heated to reflux for 3 h under nitrogen atmosphere. The salt was removed by filtration

when the mixture was cooling to room temperature. The filtrate was evaporated under vacuum; the residue was then purified by column chromatography on silica gel with petroleum ether as eluent to afford BTE-2 as white solid in 36% (0.11 g) yield for two steps. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.99 (s, 2H), 3.31 (s, 2H), 2.77 (t, *J* = 7.5 Hz, 4H), 2.12 – 2.00 (m, 2H), 1.92 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.3, 135.5, 134.5, 134.1, 117.9, 80.7, 77.3, 38.5, 22.8, 14.3. HRMS (ESI, m/z): $[M + H]^+$ calcd for $C_{19}H_{16}S_2$: 309.0766, found: 309.0762.

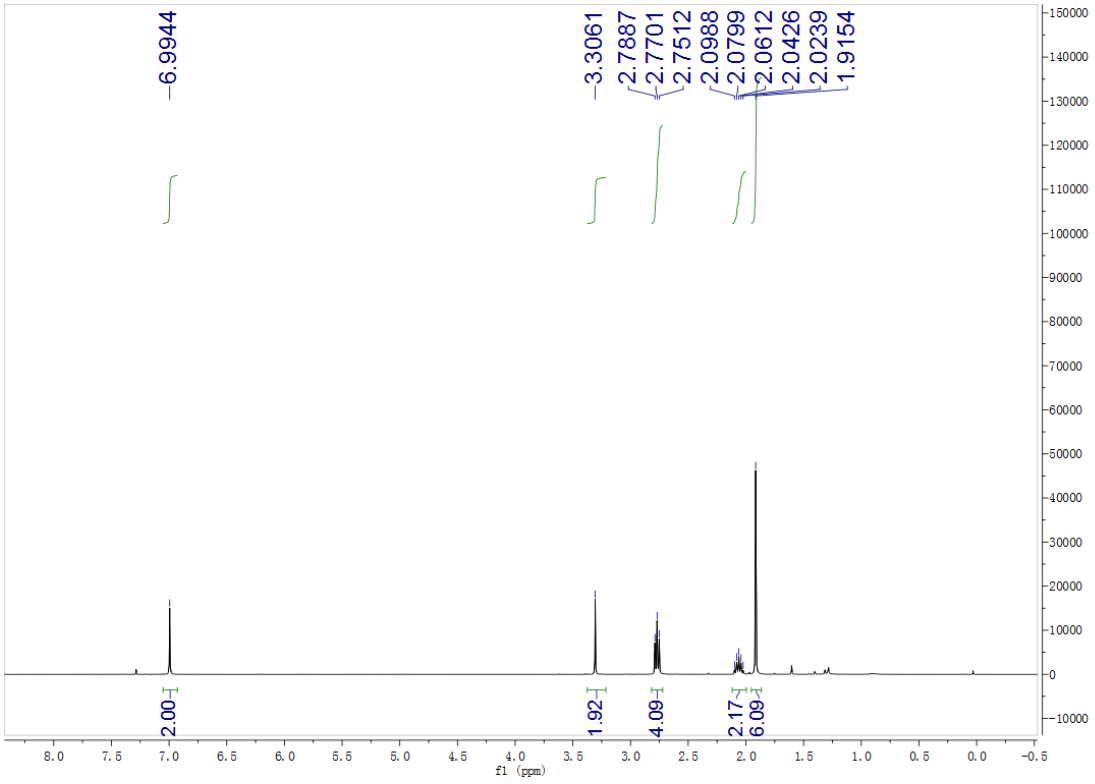


Fig. S3. ^{1}H NMR spectra of **BTE-2** in $CDCl_3$

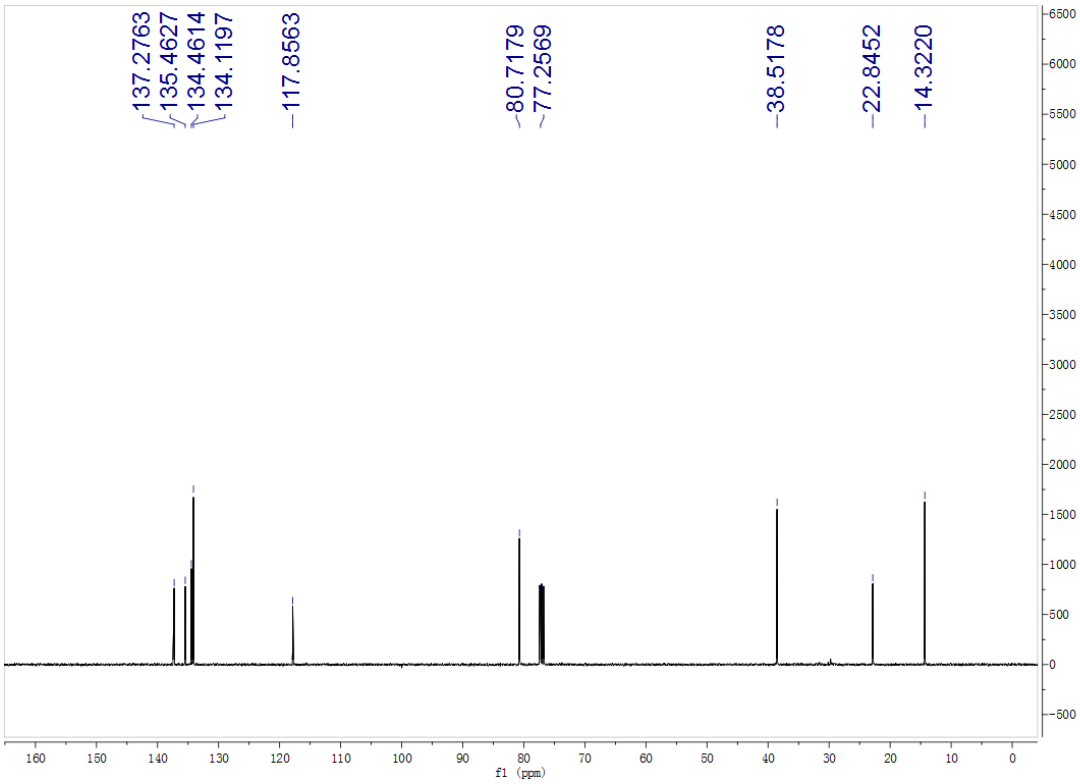


Fig. S4. ^{13}C NMR spectra of **BTE-2** in $CDCl_3$

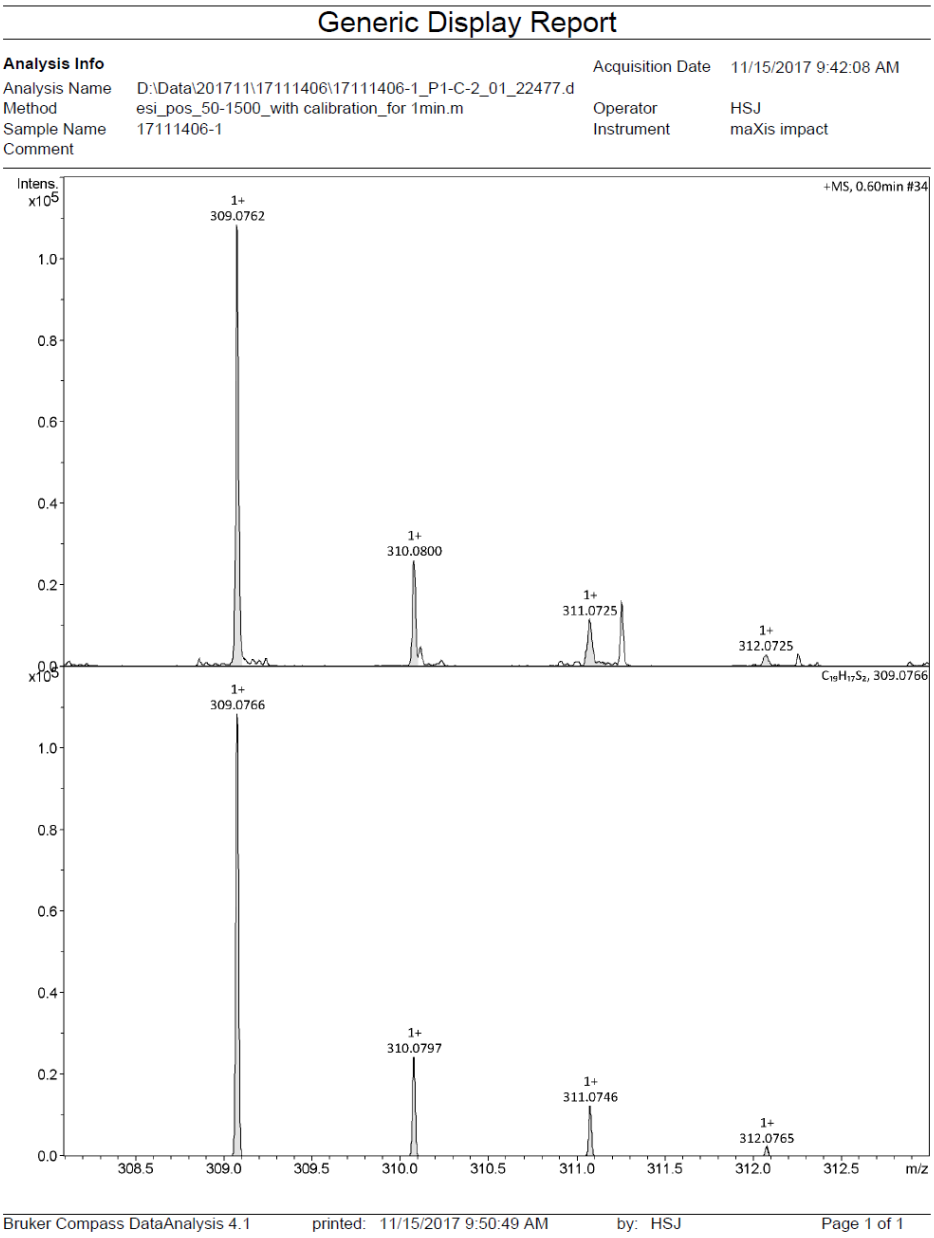


Fig. S5. HRMS spectra of **BTE-2**

2.3 Synthesis of 5,5'-(4,4'-(4,4'-(cyclopent-1-ene-1,2-diyl)bis(5-methylthiophene-4,2-diyl))bis(1H-1,2,3-triazole-4,1-diyl))dipentanenitrile (G)

BTE-2 (0.31 g, 1.00 mmol), 5-azidopentanenitrile (0.27 g, 2.20 mmol) and CuI

(0.019, 0.10 mmol) was dissolved in THF (20 mL), then the mixture was heated to reflux under nitrogen atmosphere for 8 h. After restore to room temperature, 15 mL water was added to quench the reaction. The mixture was extracted with EA three times. The combined organic layers were washed with brine then dried over $MgSO_4$. The collected organic layer was evaporated under vacuum; the residue was then purified by column chromatography on silica gel with ethyl acetate/dichloromethane (1/10) as eluent to afford **G** as white solid in 98% (0.54 g) yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (s, 2H), 7.09 (s, 2H), 4.43 (t, *J* = 6.8 Hz, 4H), 2.83 (t, *J* = 7.4 Hz, 4H), 2.43 (t, *J* = 7.0 Hz, 4H), 2.20 – 2.04 (m, 6H), 2.00 (s, 6H), 1.75 – 1.67 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.2, 136.2, 134.8, 134.6, 128.2, 125.3, 119.0, 118.7, 49.3, 38.5, 29.1, 23.0, 22.3, 16.7, 14.4. HRMS (ESI, m/z): $[M + Na]^+$ calcd for $C_{29}H_{32}N_8NaS_2$: 579.2084, found: 579.2094.

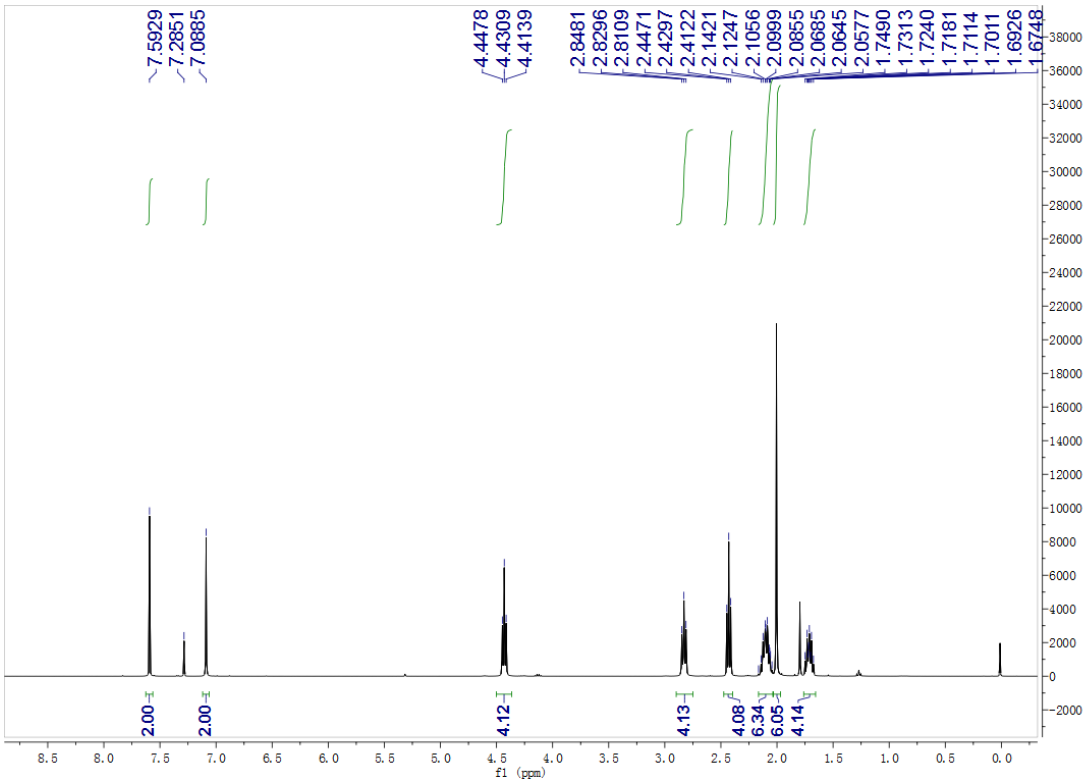


Fig. S6. ^{1}H NMR spectra of **G** in $CDCl_3$

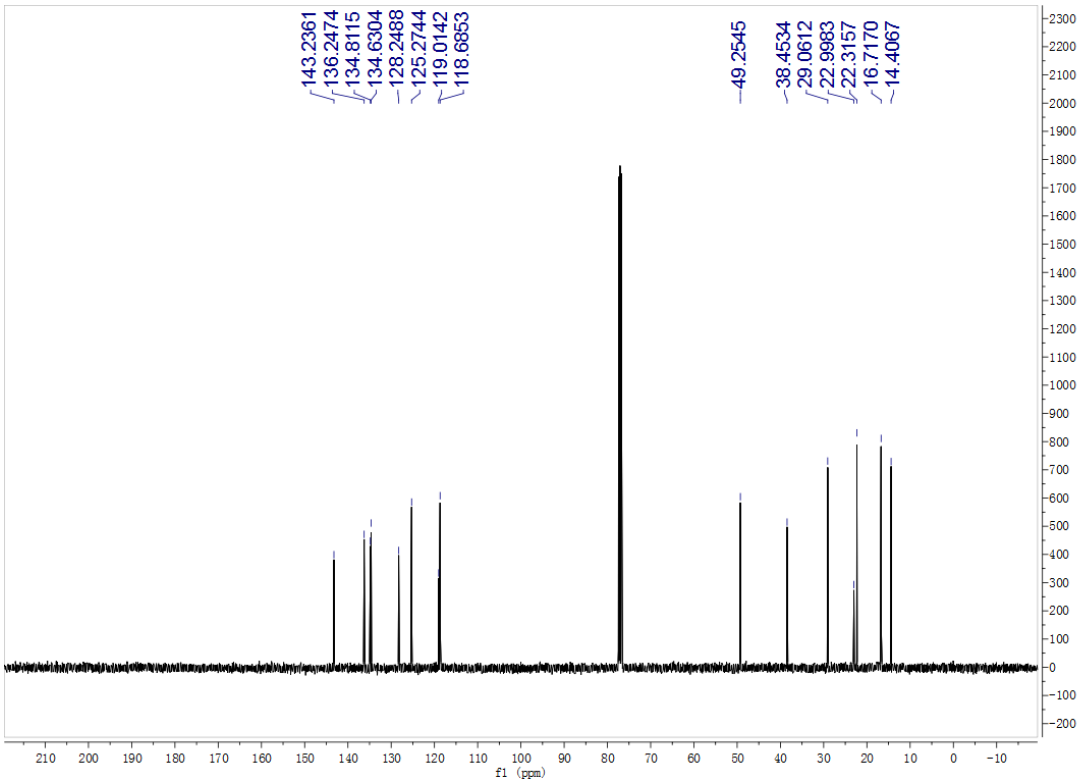


Fig. S7. ^{13}C NMR spectra of **G** in $CDCl_3$

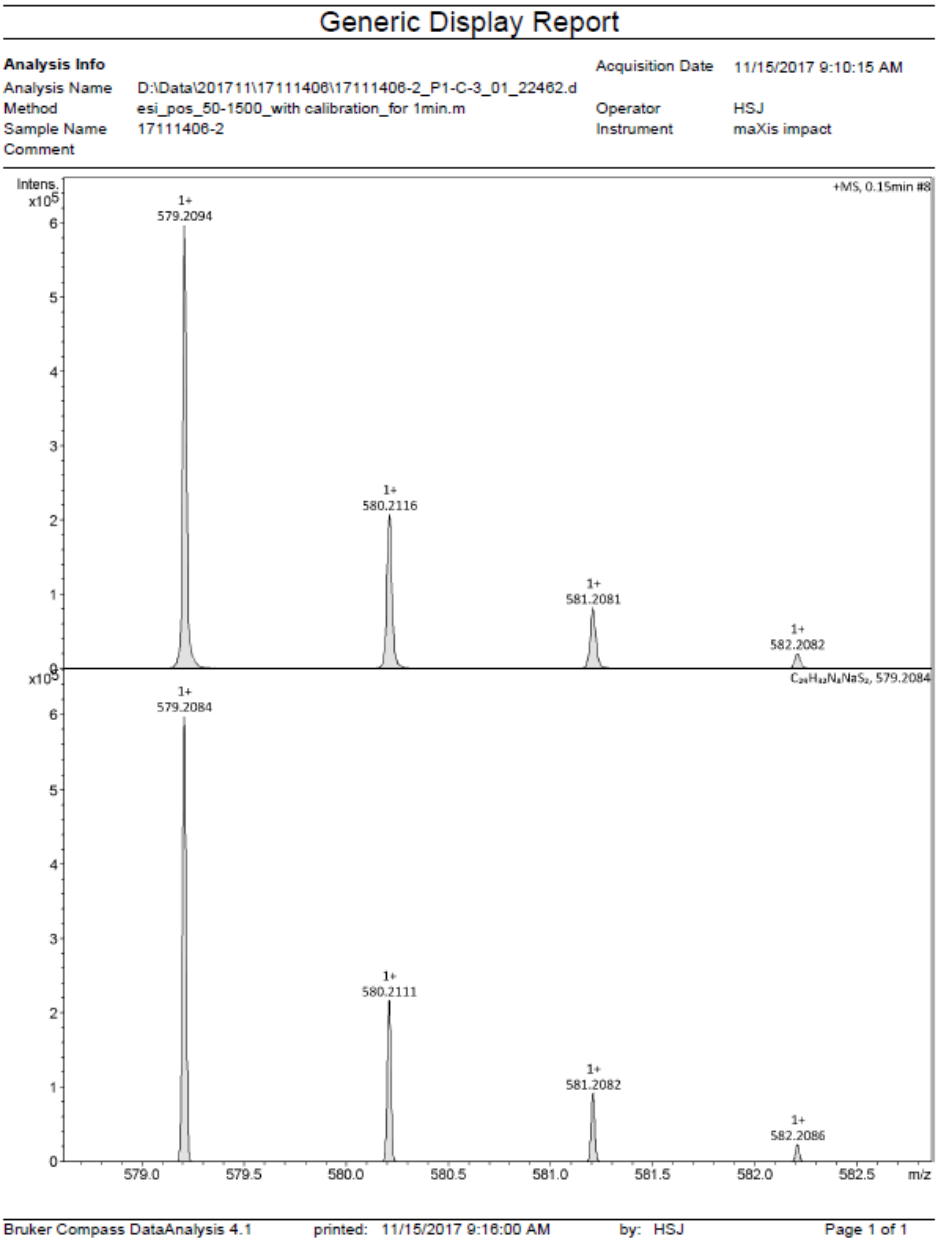


Fig. S8. HRMS spectra of **G**

2.4 Synthesis of compound P2

The mixture of P1 (4.14 g, 0.030 mmol), $(CH_2O)_n$ (2.88 g, 0.090 mmol) and 1,2-DCE (220 mL) was keep at 29 ^oC for 20 min. Then 4.16 mL $BF_3{\cdot}Et_2O$ was added quickly. 3min latter, 20 mL EtOH was added to quench the reaction. White solid was collected

by filtration, washed with EtOH (20 mL) three times. The solid was then dispersed to 150 mL DCM and stirred for 20 min at room temperature vigorously. Then filtrate was collected and washed with 10% NaOH aqueous solution, brine three times successively. The organic layer was dried over $MgSO_4$ and evaporated by reduced pressure to obtained P2 (3.09 g) as white solid in 85% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.89 (s, 10H), 3.79 (s, 10H), 3.74 (s, 30H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 128.2, 113.4, 55.5, 29.3.

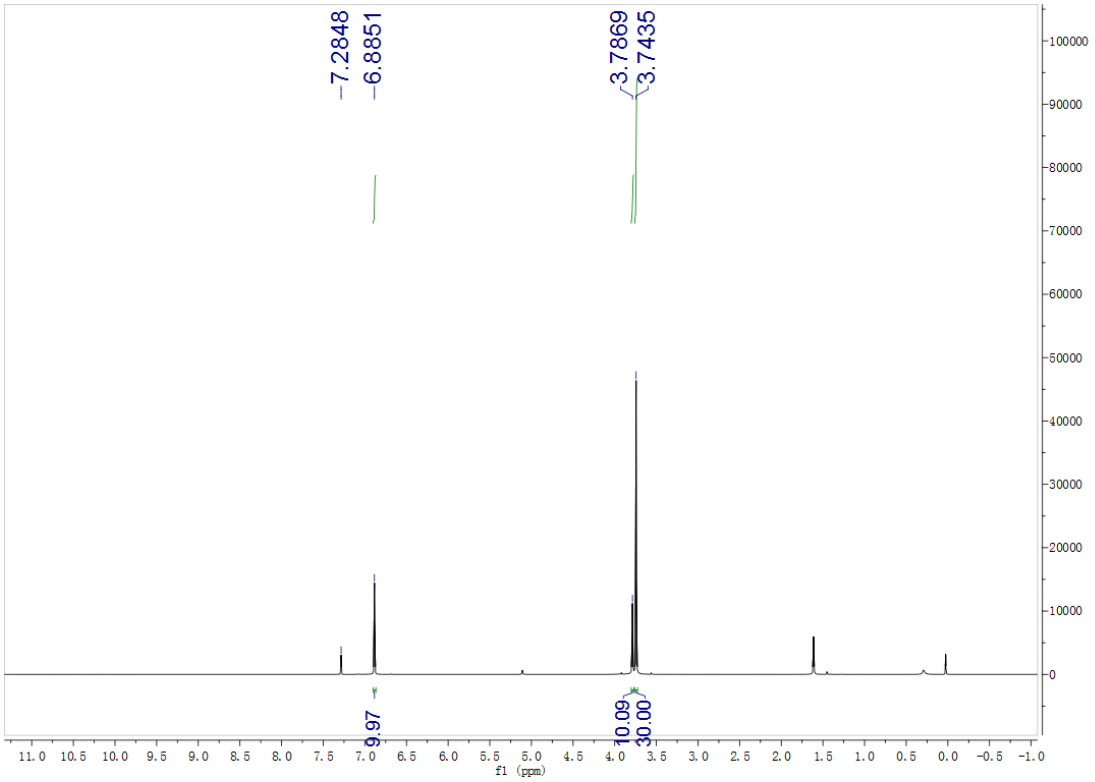


Fig. S9. ^{1}H NMR spectra of **P2** in $CDCl_3$

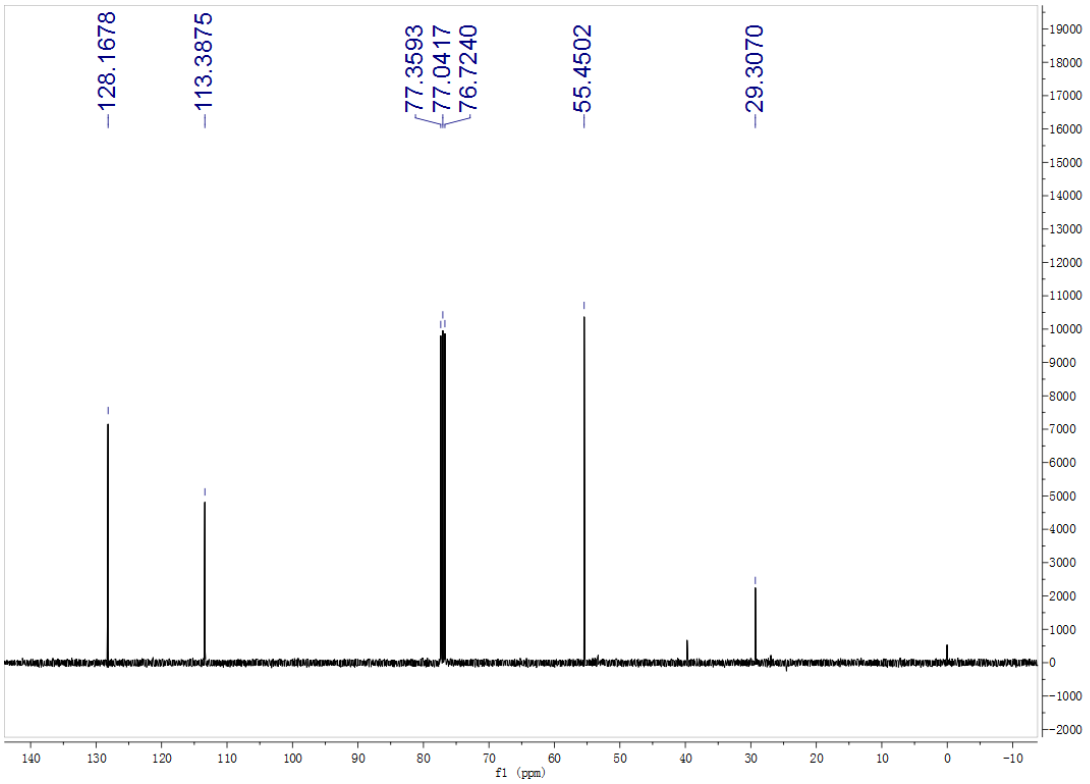


Fig. S10. ^{13}C NMR spectra of **P2** in $CDCl_3$

2.5 Synthesis of compound P3

To the solution of P2 (0.80 g, 1.07 mmol) in 25 mL DCM, $(NH_4)_2Ce(NO_3)_6$ (1.17 g, 2.14 mmol) in 50 mL H_2O aqueous solution was added dropwise. The reaction was monitor by TLC 20 min latter. Organic layer was separated when P2 was almost disappeared and washed by brine three times. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel with a 2:1 mixture of petroleum ether/dichloromethane as eluent to afford a crimson solid. Then the solid was recrystallized with dichloromethane/MeOH to afford **P3** in 65% yield (0.50 g). ^1H NMR (400 MHz, $CDCl_3$) δ 6.87 (s, 2H), 6.84 (s, 2H), 6.82 (s, 2H), 6.70 – 6.69 (m, 4H), 3.82 – 3.81 (m, 6H), 3.77 (s, 6H), 3.74 (m, 12H), 3.66 (s, 6H), 3.61 (s, 4H).

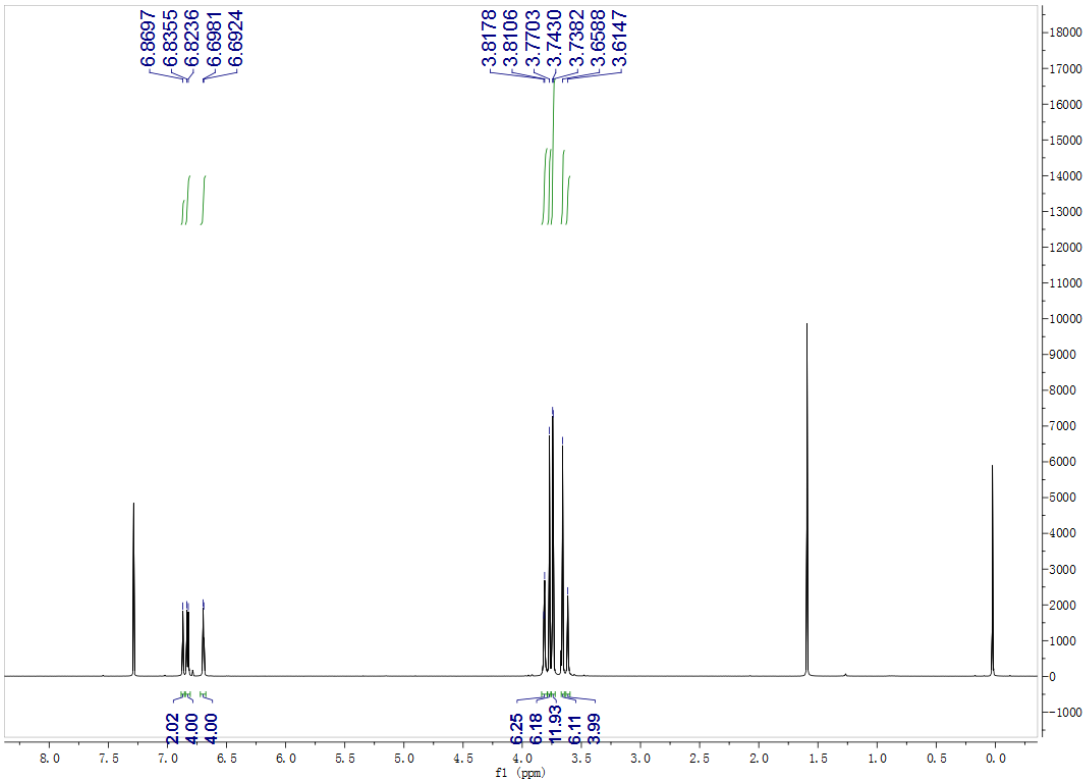


Fig. S11. ^{1}H NMR spectra of **P3** in $CDCl_3$

2.6 Synthesis of compound P4

The solution of $Na_2S_2O_4$ (3.84 g, 22.24 mmol) was added to solution of P3 (0.80 g, 1.11 mmol) in 50 mL DCM. The mixture was stirred at room temperature for 6h under nitrogen atmosphere. Organic layer was separated and washed by brine three times. The crude product compound P4 was obtained by evaporating all the solvent under reduced pressure and directly used for the next reaction without further purification.

2.7 Synthesis of compound H

TPE-Br (1.28 g, 3.00 mmol), P4 (0.72 g, 1.00 mmol), and $CsCO_3$ (0.33 g, 1.00 mmol) was added to anhydrous MeCN (25 mL), the mixture was stirred at 80 ^{o}C under nitrogen atmosphere for 24h. 50 mL H_2O was added when the mixture was cooling to room temperature. Organic layer was separated and washed by brine three times. After removal of the solvent under reduced pressure, the residue was purified

by column chromatography on silica gel with a 20:1 mixture of petroleum ether/ ethyl acetate as eluent to afford **H** as white solid in 21% yield (0.30 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 – 7.21 (m, 4H), 7.18 – 7.05 (m, 34H), 6.88 (s, 2H), 6.76 (m, 6H), 6.67 (s, 2H), 4.86 – 4.83 (m, 2H), 4.78 – 4.75 (m, 2H), 3.91 – 3.88 (m, 2H), 3.83 – 3.65 (m, 20H), 3.61 (s, 6H), 3.33 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.8, 150.7, 150.3, 143.7, 143.7, 143.2, 141.2, 140.5, 136.0, 131.4, 131.3, 131.3, 128.7, 128.2, 128.1, 128.1, 128.0, 127.8, 127.7, 127.7, 126.7, 126.5, 126.5, 126.5, 115.4, 114.1, 114.1, 114.0, 70.6, 55.8, 55.8, 55.6, 29.8, 29.7, 29.6. HRMS (ESI, m/z): $[M + Na]^+$ calcd for $C_{97}H_{86}NaO_{10}$: 1433.6113, found: 1433.6146.

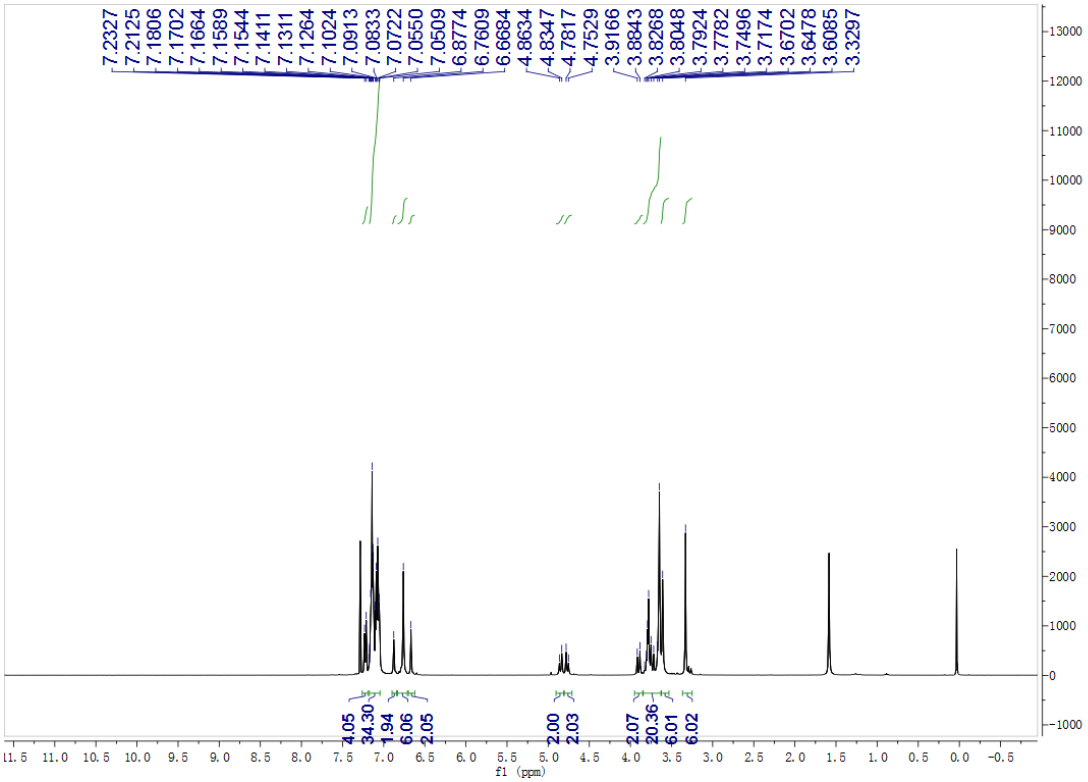


Fig. S12. ^{1}H NMR spectra of **H** in $CDCl_3$

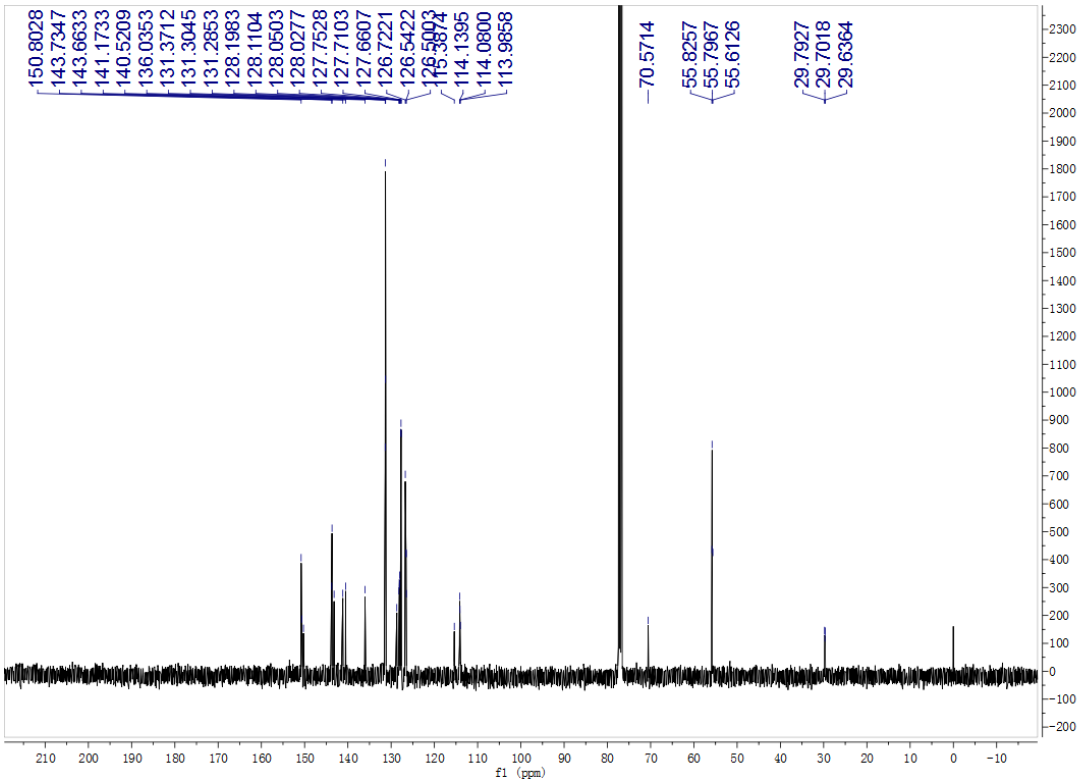


Fig. S13. ^{13}C NMR spectra of **H** in $CDCl_3$

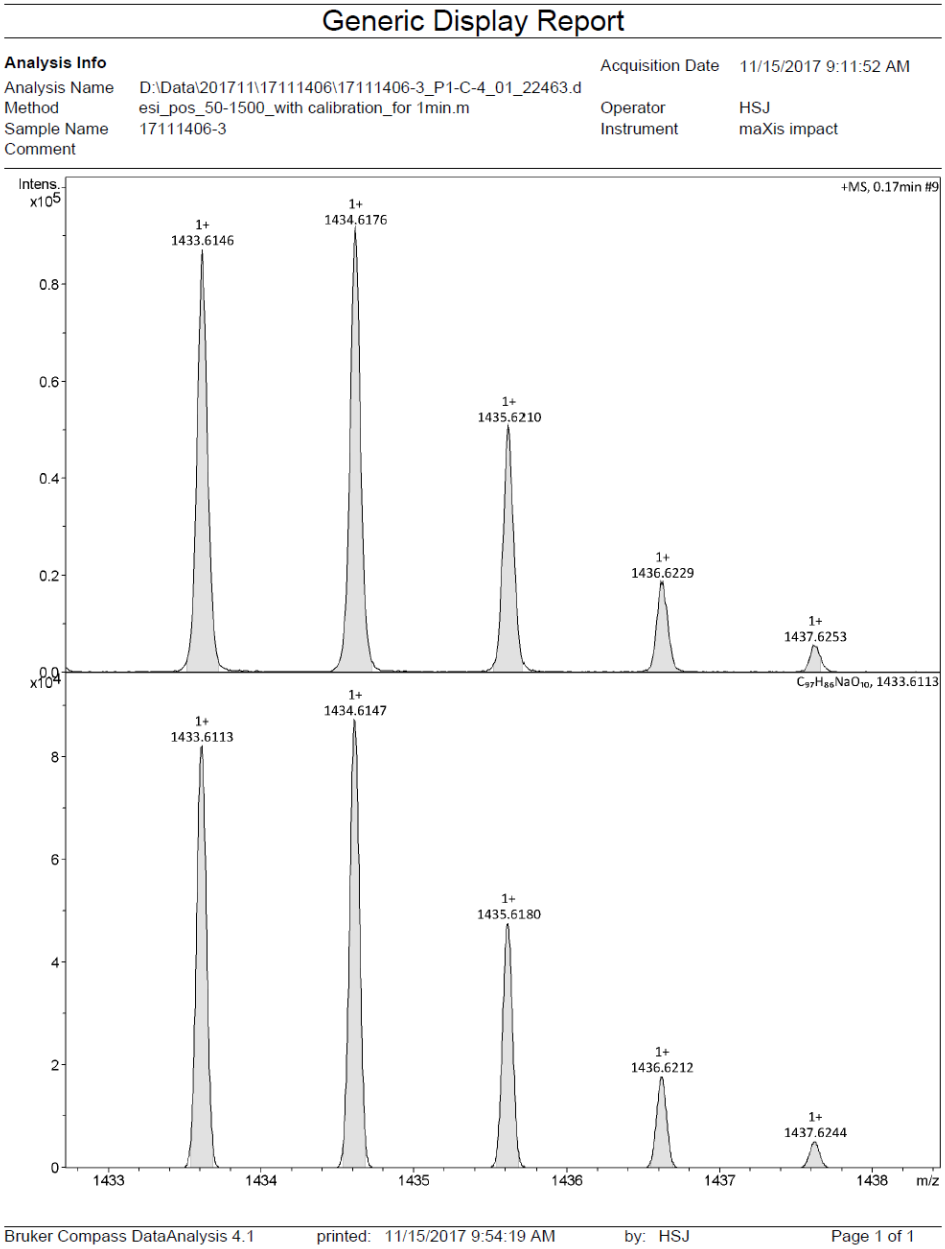


Fig. S14. HRMS spectra of **H**

2.8 Synthesis of (2-(p-tolyl)ethene-1,1,2-triyl)tribenzene (TPE-3)

To the mixture of TPE-1 (3.35 g, 10.8 mmol), TPE-2 (1.35 g, 10.00 mmol), K_2CO_3 aqueous solution (2 M, 15 mL), ethyl alcohol (15 mL) and toluene (50 mL), $Pd(PPh_3)_4$ (0.10 g, 0.10 mmol) was added. The mixture was stirred for 12 h under

nitrogen atmosphere at reflux. After cooling to room temperature, the reaction mixture was poured into water, extracted with dichloromethane three times and the combined organic layers were washed with brine then dried over $MgSO_4$. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel with petroleum ether as eluent to afford TPE-3 as white solid in 92% yield (3.19 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 – 7.09 (m, 9H), 7.09 – 7.02 (m, 6H), 6.93 (m, 4H), 2.28 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.0, 143.9, 140.9, 140.7, 140.5, 136.1, 131.4, 131.3, 131.2, 128.4, 127. 7, 127.6, 126.3, 126.3, 21.2.

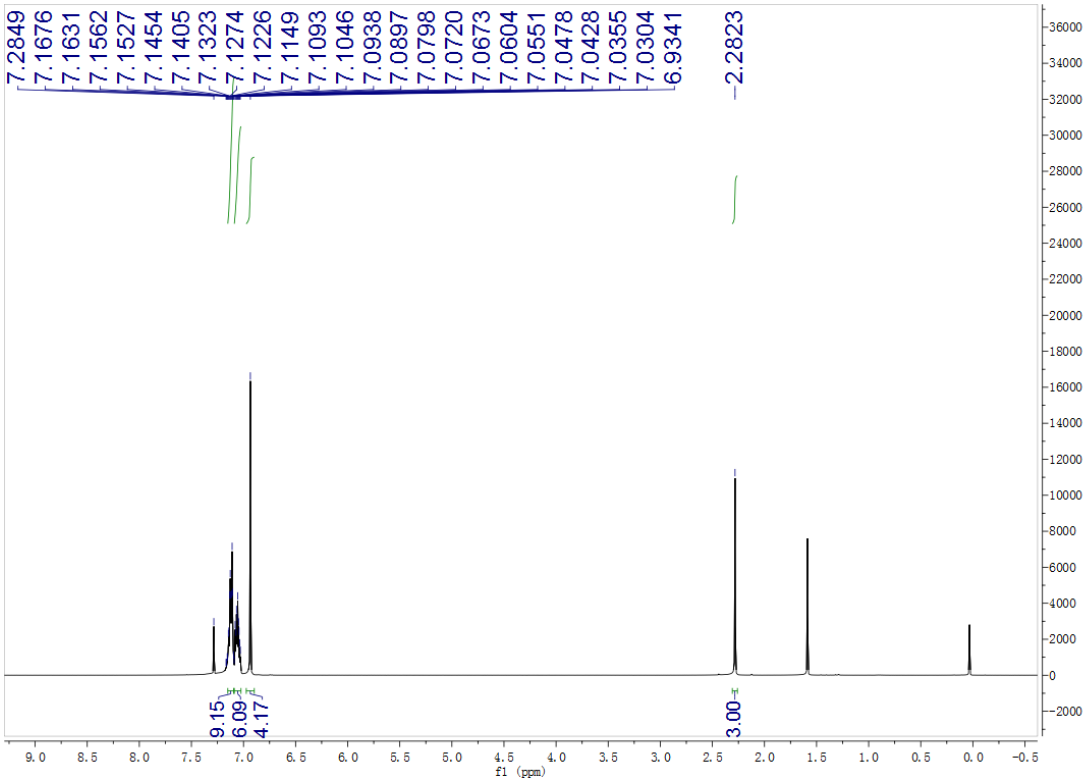


Fig. S15. ^{1}H NMR spectra of **TPE-3** in $CDCl_3$

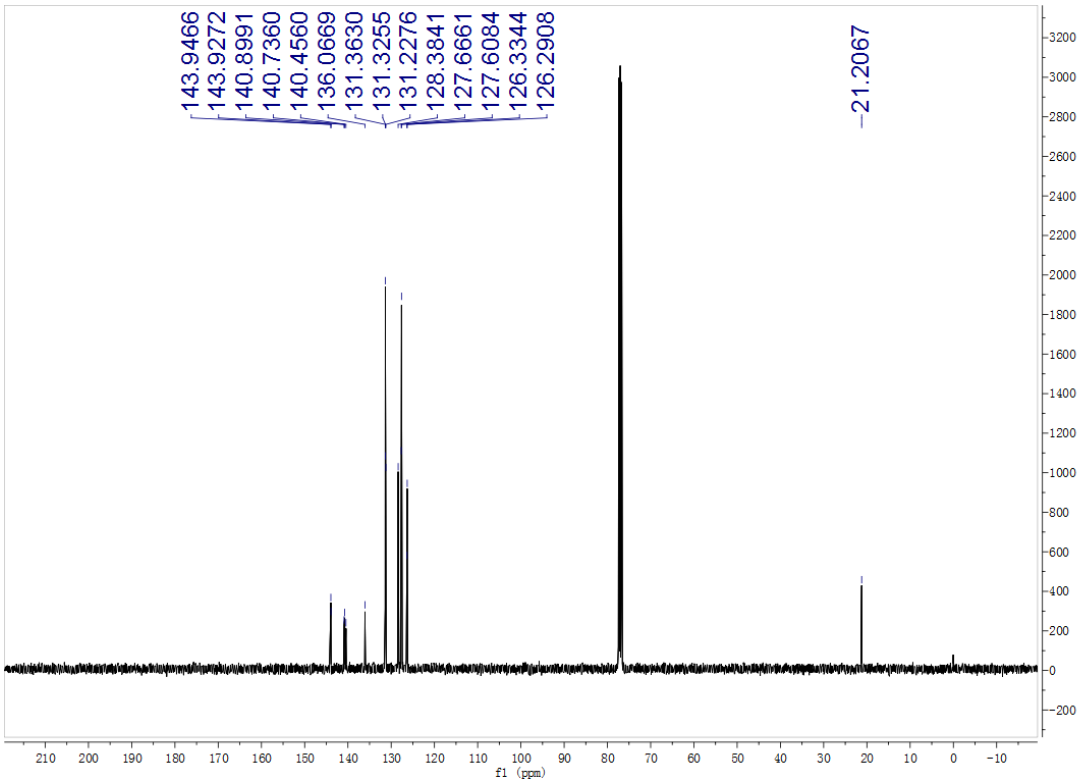


Fig. S16. ^{13}C NMR spectra of **TPE-3** in $CDCl_3$

2.9 Synthesis of (2-(4-(bromomethyl)phenyl)ethene-1,1,2-triyl)tribenzene (TPE-Br)

BPO (0.10 g, 0.40 mmol) was added to the mixture of TPE-3 (1.73 g, 5.00 mmol) and NBS (0.89 g, 5.00 mmol) in CCl_4 (30 mL). Then the mixture was stirred at reflux for 12h. After cooling to room temperature, the reaction mixture was poured into water, extracted with dichloromethane three times and the combined organic layers were washed with brine then dried over $MgSO_4$. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel with petroleum ether as eluent to afford TPE-Br as white solid in 24% yield (0.50 g). ^1H NMR (400 MHz, CDCl3) δ 7.16 – 7.11 (m, 11H), 7.08 – 7.02 (m, 8H), 4.44 (s, 2H). 13C NMR (101 MHz, CDCl3) δ 144.0, 143.6, 143.5, 143.4, 141.6, 140.2, 135.7, 131.70, 131.4, 131.3, 128.4, 127.8, 127.8, 127.7, 126.6, 126.6, 126.6, 33. 7.

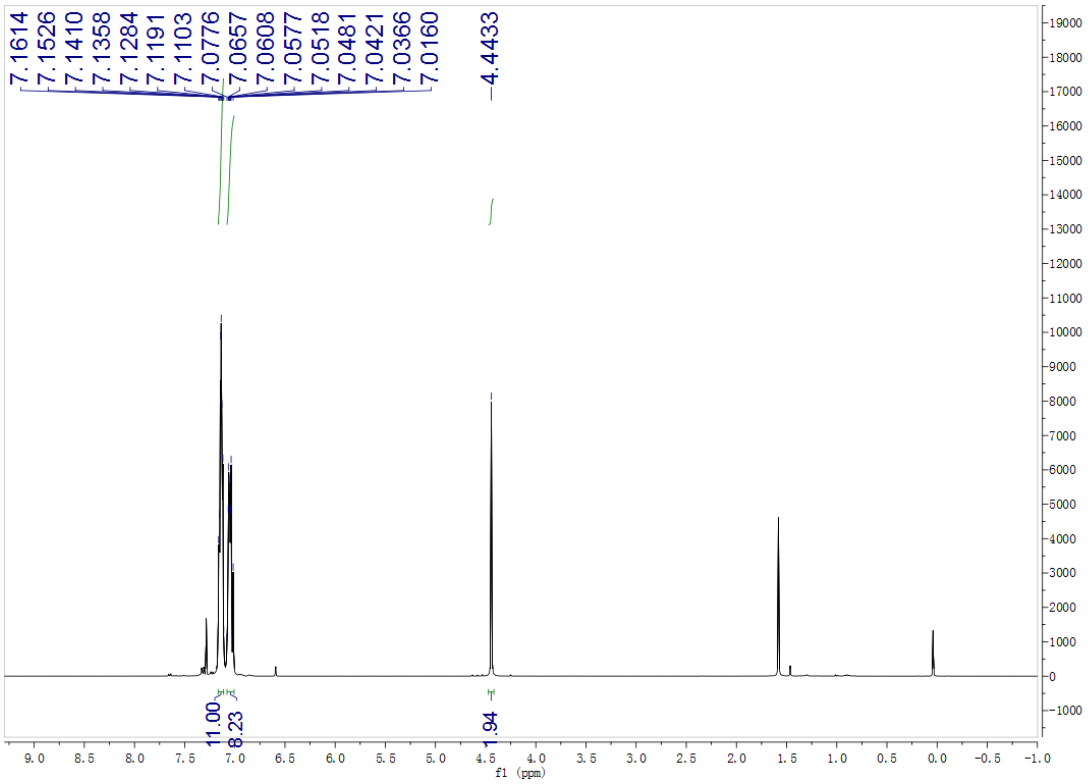


Fig. S17. ^{1}H NMR spectra of **TPE-Br** in $CDCl_3$

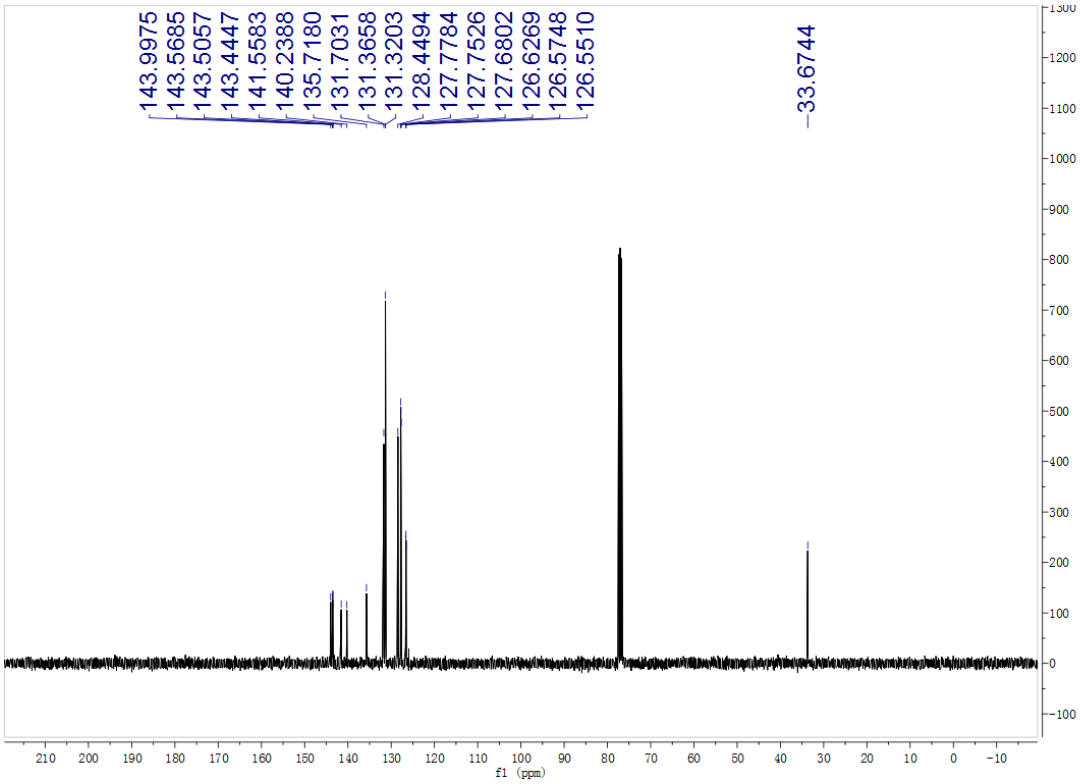


Fig. S18. ^{13}C NMR spectra of **TPE-Br** in $CDCl_3$

2.10 Synthesis of 1,4-bis((4-(1,2,2-triphenylvinyl)benzyl)oxy)benzene (S)

TPE-Br (1.28 g, 3.00 mmol), hydroquinone (0.11 g, 1.00 mmol), and $CsCO_3$ (0.32 g, 1.00 mmol) was added to anhydrous MeCN (25 mL), the mixture was stirred at 80 ^oC under nitrogen atmosphere for 24h. 50 mL H_2O was added when the mixture was cooling to room temperature. Organic layer was separated and washed by brine three times. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel with a 20:1 mixture of petroleum ether/ ethyl acetate as eluent to afford **H** as white solid in 58% yield (0.46 g). ^1H NMR (400 MHz, $CDCl_3$) δ 7.19 – 7.03 (m, 38H), 6.88 (s, 4H), 4.94 (s, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.2, 143.7, 143.7, 143.6, 143.4, 141.2, 140.5, 135.3, 131.5, 131.4, 131.3, 127.7, 127.7, 127.6, 126.9, 126.5, 115.9, 70.6. HRMS (ESI, m/z): $[M + Na]^+$ calcd for $C_{60}H_{46}NaO_2$: 821.3390, found: 821.3393.

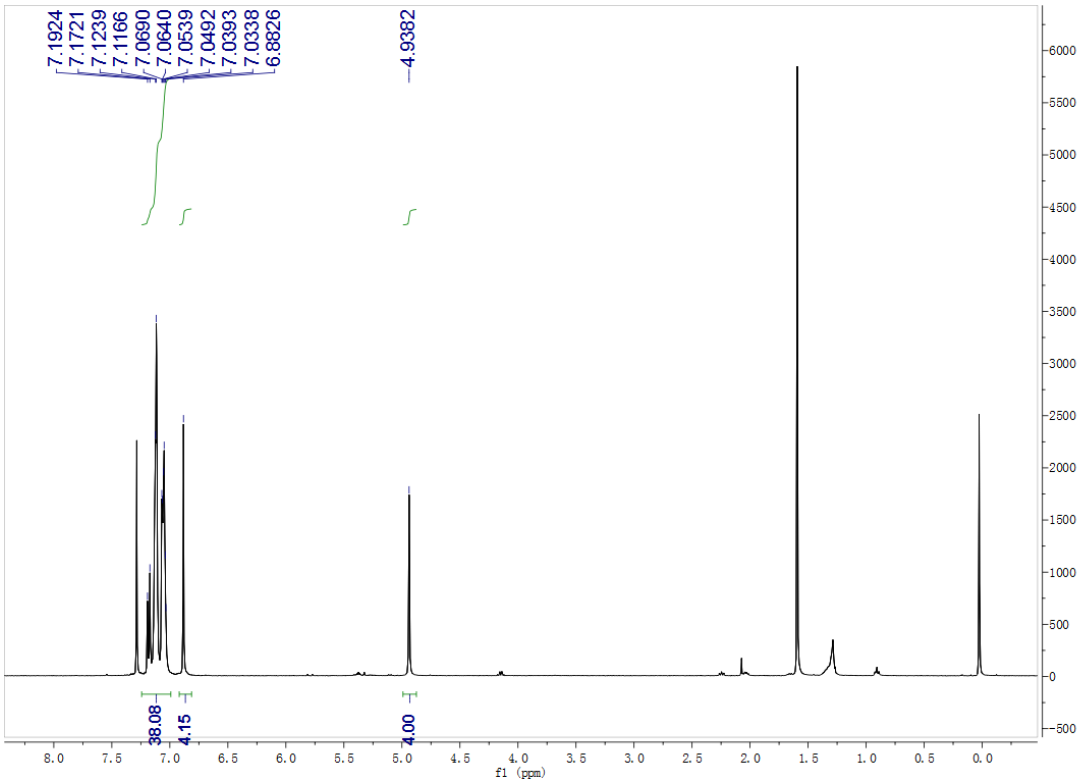


Fig. S19. ^{1}H NMR of **S** in $CDCl_3$

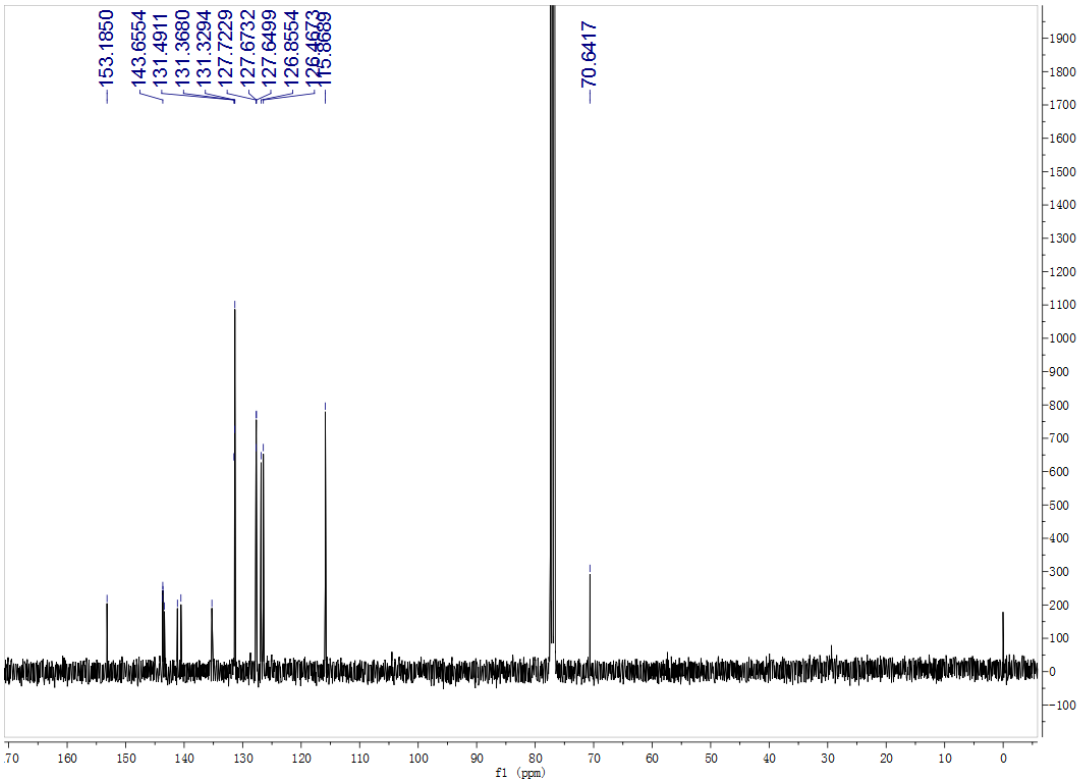


Fig. S20. ^{13}C NMR of **S** in $CDCl_3$

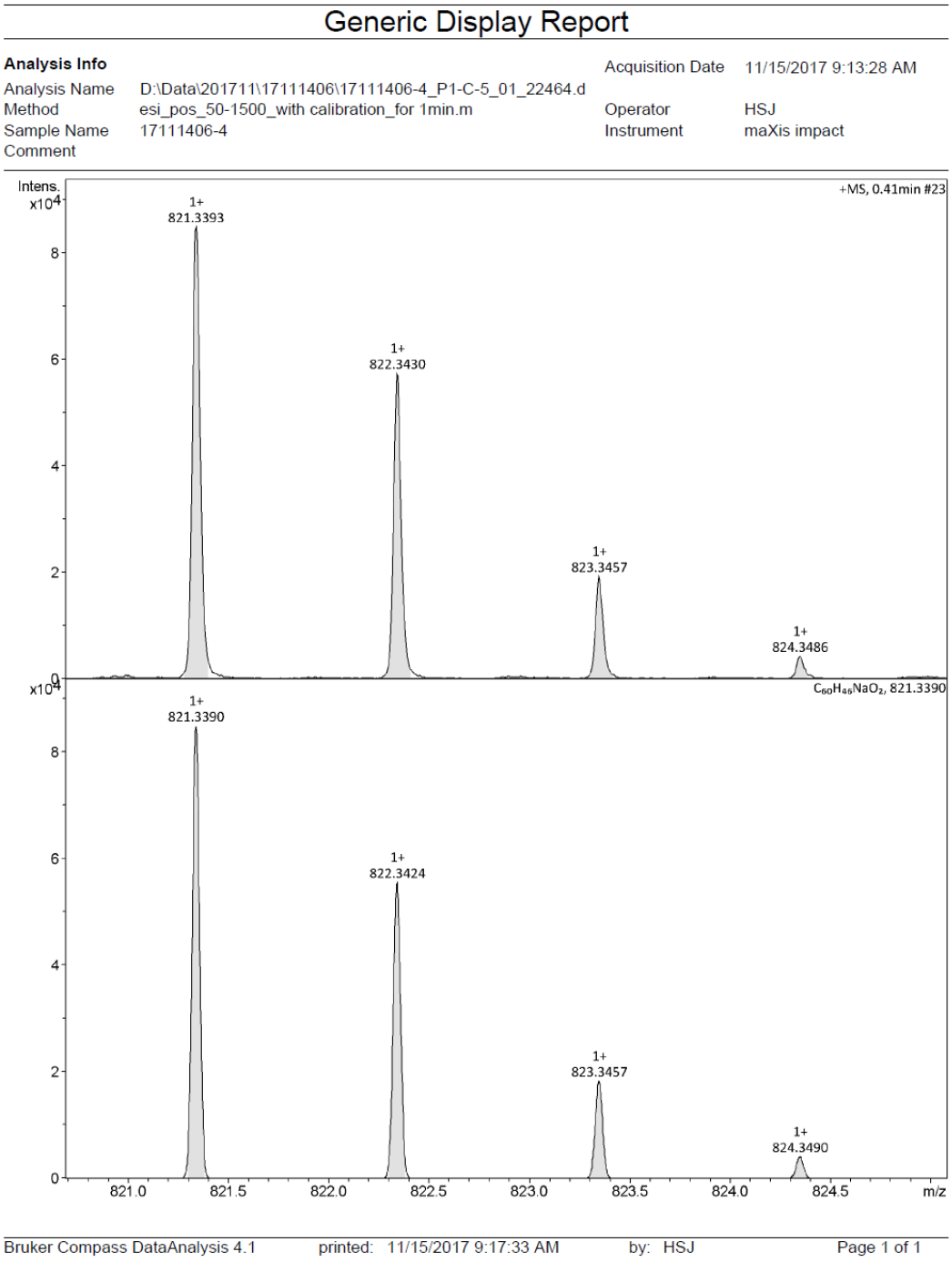


Fig. S21. HRMS of **S**

3. Rotating Frame Overhauser Effect Spectroscopy (ROESY)

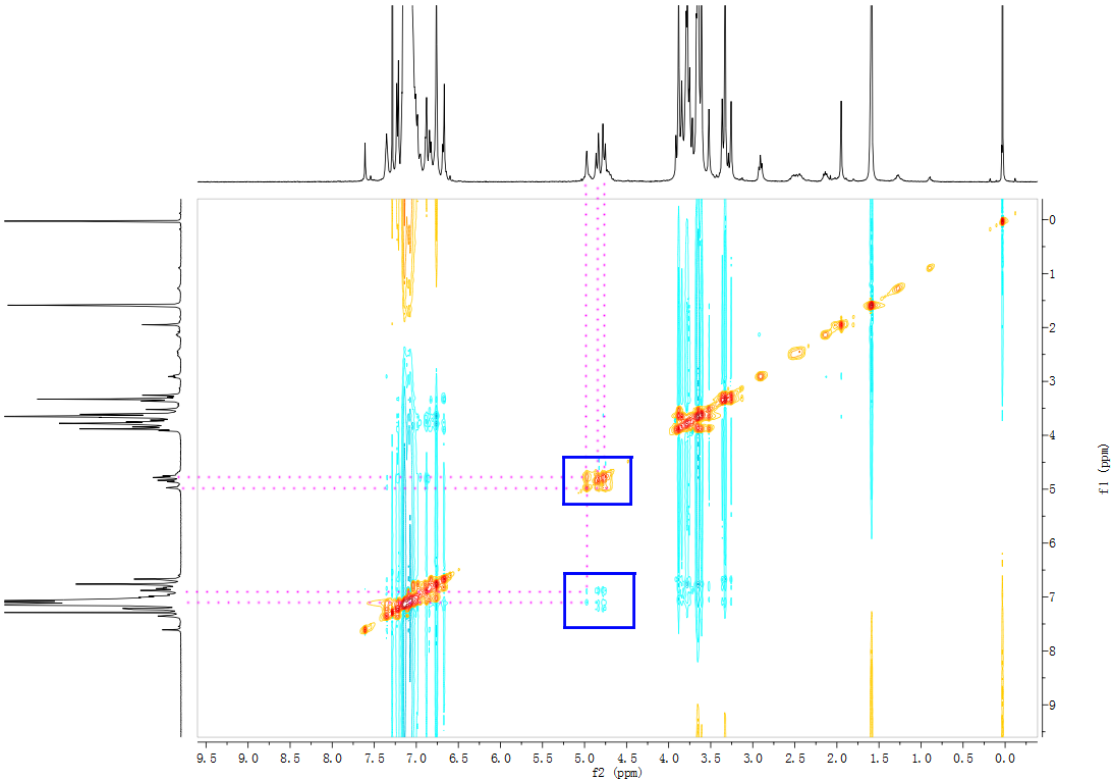


Fig. S22 ROESY spectra of the **G** ⊂ **H** assembly in $CDCl_3$ ($n_{\mathbf{G}}$: $n_{\mathbf{H}}$=1:2).

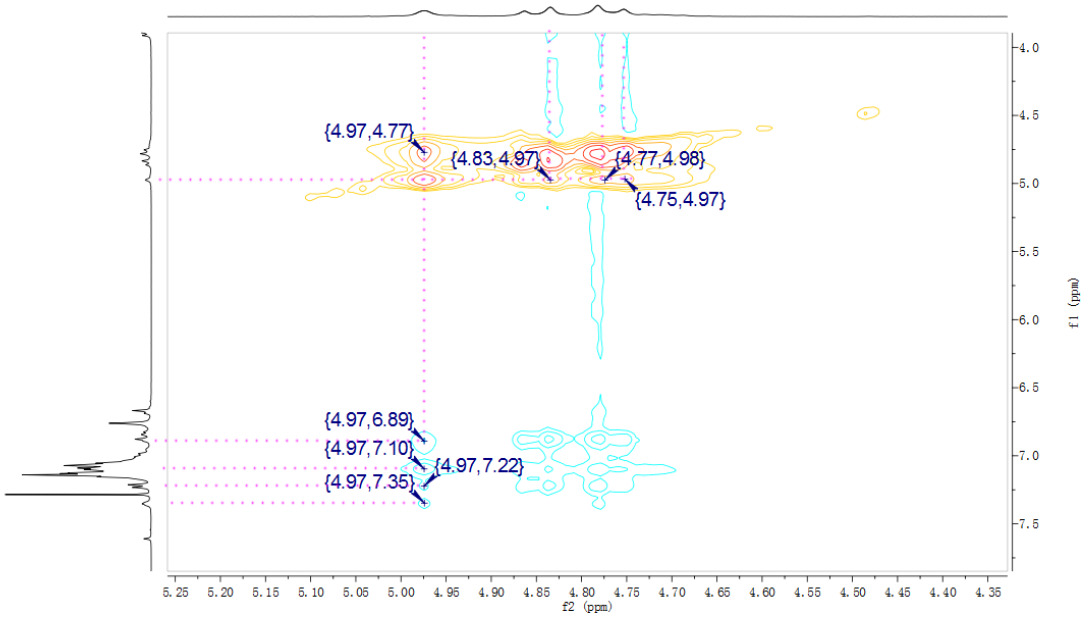


Fig. S23. Partial ROSEY spectra of the **G** ⊂ **H** assembly in $CDCl_3$ ($n_{\mathbf{G}}$: $n_{\mathbf{H}}$=1:2).

4. AIE properties of H and G ⊂ H assembly

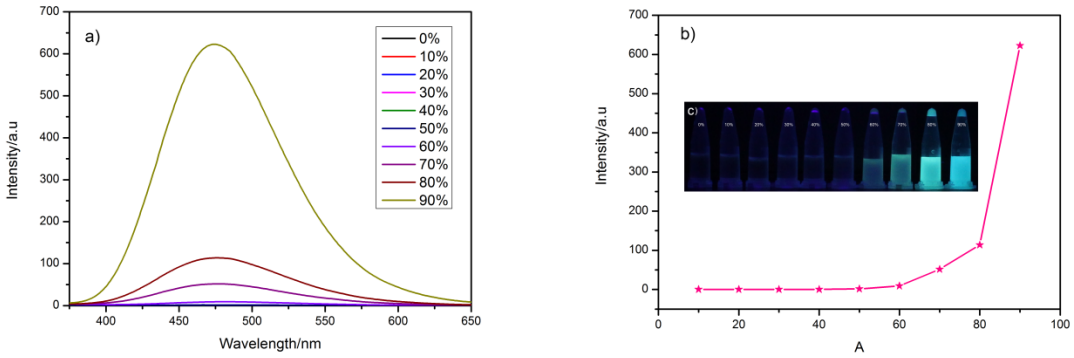


Fig. S24. (a) Fluorescence spectra of **H** in different H_2O/THF (v/v) solutions; (b) The dependence of the fluorescence emission intensity on the f_w. [**H**] = 10^{-5} M; c) Insert: Photographs of **H** in different H_2O/THF solutions under UV light (300 nm). λ_{ex} = 300 nm.

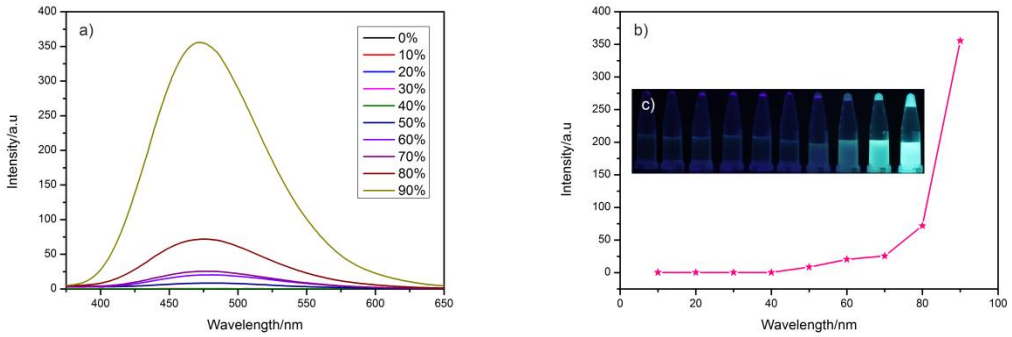


Fig. S25. a) Fluorescence spectra of **G** ⊂ **H** assembly in different H_2O/THF (v/v) solutions ([**G**] = 0.5×10^{-5} M, [**H**] = 10^{-5} M); (b) The dependence of the fluorescence emission intensity on the f_w; c) Insert: Photographs of **H** in different H_2O/THF solutions under UV light (300 nm). λ_{ex} = 300 nm.

5. *^{1}H NMR spectra of G and H in THF-d_8/D_2O (v/v = 50%) mixed solution.*

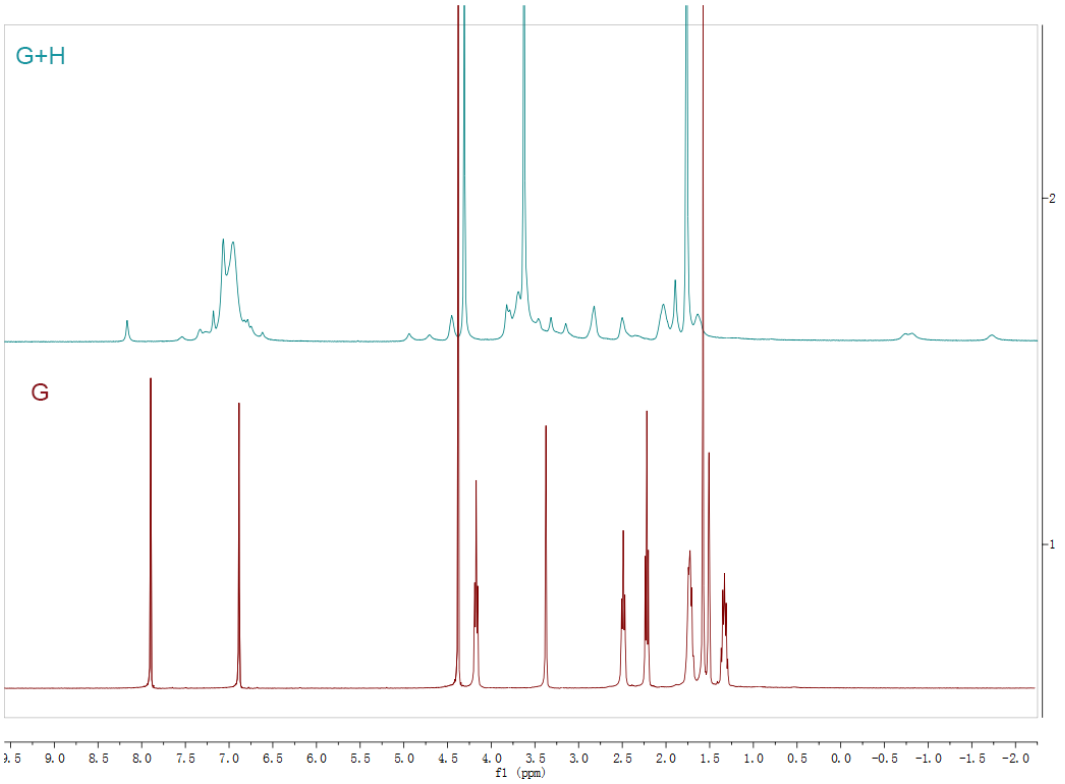


Fig. S26. ^{1}H NMR spectra of **G** and **G** + **H** ([**H**] = 0.01 mmol, [**G**] = 0.005 mmol) in THF-d_8/D_2O = 50/50.

6. *Emission spectra of S and S + G*

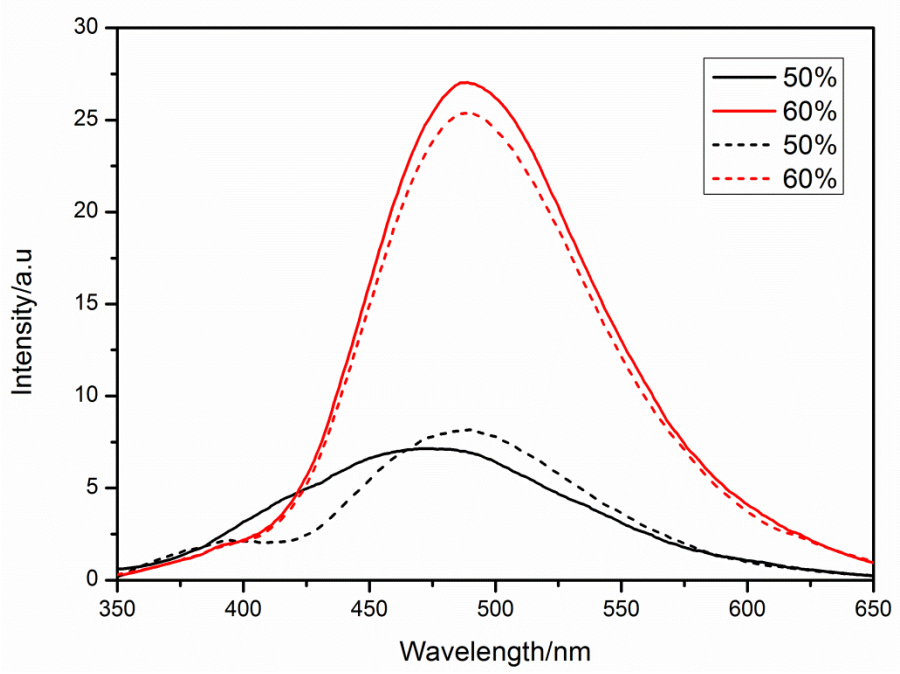


Fig. S27. Emission spectra of **S** (1.0×10^{-5} M, solid lines) and **G** + **S** (1.0×10^{-5} M, dashed lines) in H_2O/THF.

7. Normalized UV-Vis and fluorescence emission spectra of G, G-C and H

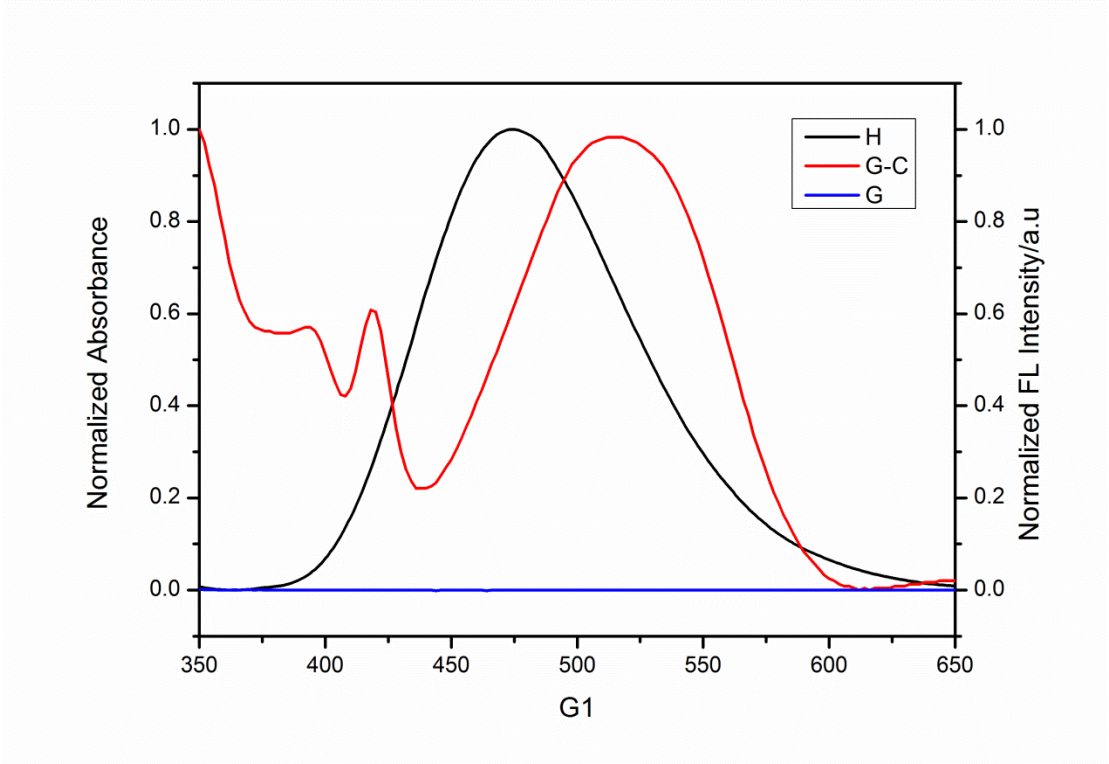


Fig. S28. Normalized UV-Vis spectra (left axis) of **G** in open form (blue line) and close form (red line) and fluorescence emission (black line, right axis) of **H**.

8. SEM images

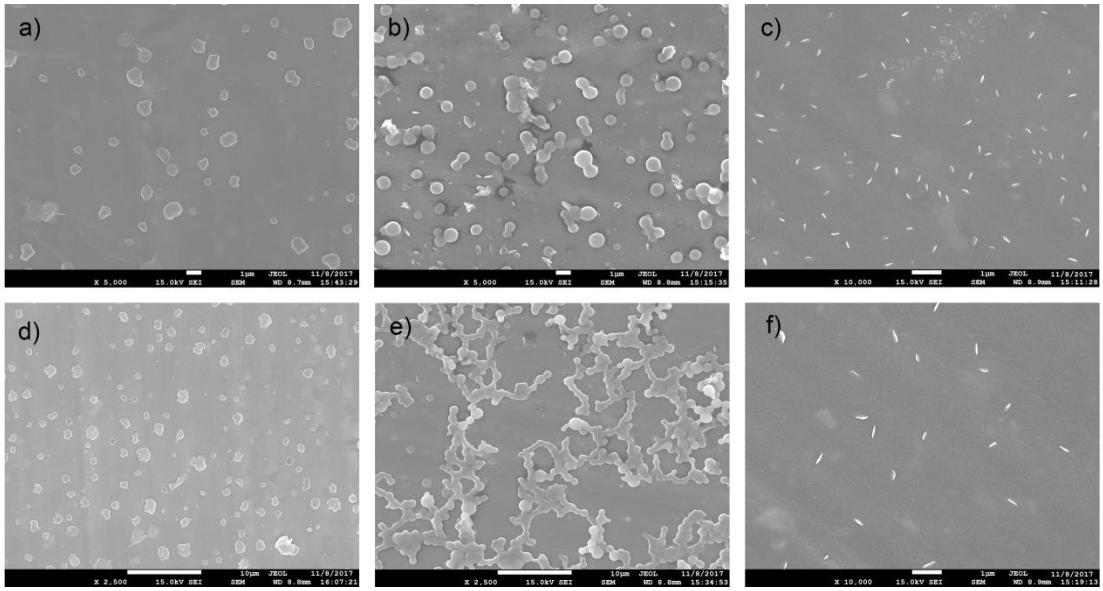


Fig. S29. a) SEM images of **H** ([**H**] = 10^{-5} M) in 50% water fraction solution; b) SEM images of **G** ⊂ **H** ([**H**] = 10^{-5}, [**G**] =0.5×10^{-5} M) in 50% water fraction solution; c) SEM images of **G** ⊂ **H** ([**H**] = 10^{-5}, [G] =0.5×10^{-5} M) in 50% water fraction solution after irradiation of 254 nm light; d) SEM images of **H** ([**H**] = 10^{-5} M) in 60% water fraction solution; e) SEM images of **G** ⊂ **H** ([**H**] = 10^{-5}, [**G**] =0.5×10^{-5} M) in 60% water fraction solution; f) SEM images of **G** ⊂ **H** ([**H**] = 10^{-5}, [**G**] =0.5×10^{-5} M) in 60% water fraction solution after irradiation of 254 nm light.

9. Normalized UV-Vis absorption spectra of G, G-C in PMMA film and fluorescence emission of H in PMMA film

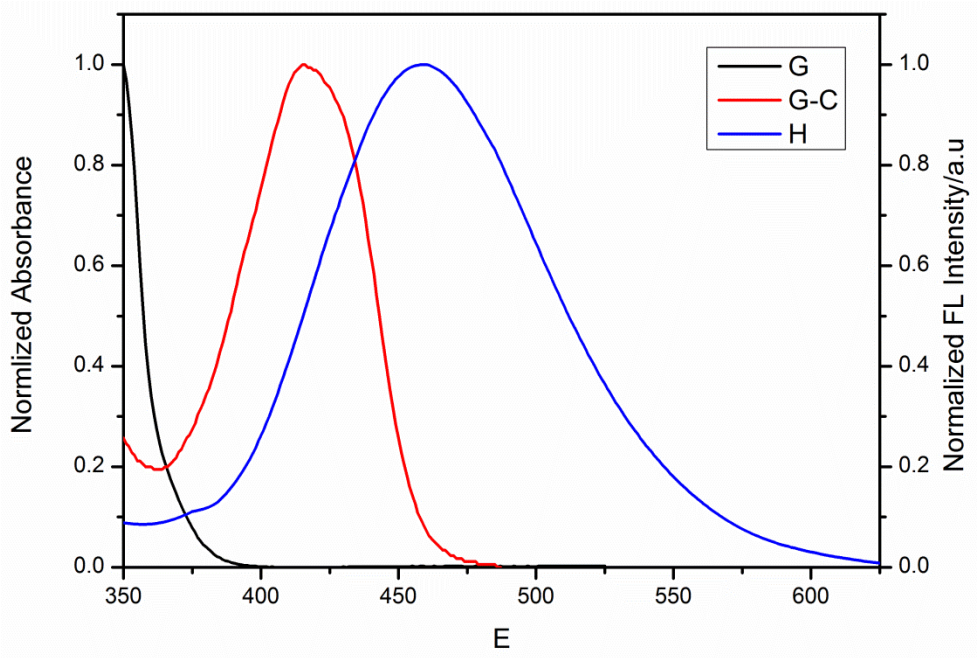


Fig. S30. Normalized UV-Vis spectra (left axis) of **G** (blue line) and **G-C** (red line) in PMMA film and fluorescence emission (black line, right axis) of **H** in PMMA film.

10. UV-Vis spectra changes of G

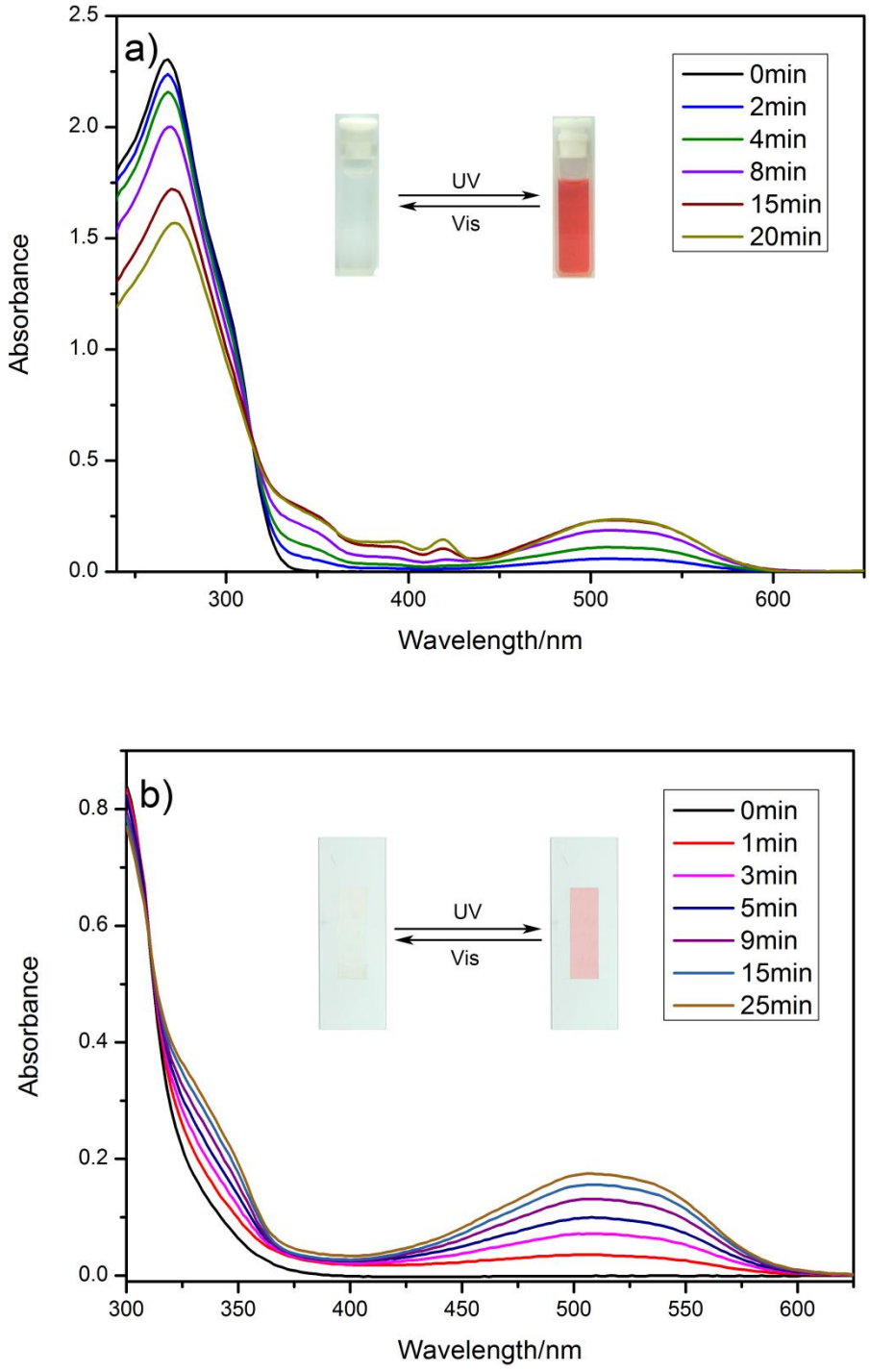


Fig. S31. UV-Vis spectra changes of **G** (0.5×10^{-5} M) in the solution of $CHCl_3$ (a) and PMMA film (1 wt%) (b) upon irradiation with 254 nm light. Inset: Changes of the photograph of **G** in solution (a) and in PMMA film (b) upon alternating UV and visible light irradiation.

11. Association constant (K_a) determination for the complexation between G and H

In addition to the corresponding signals for the uncomplexed **H** and **G**, a new species has occurred in the mixed solution of **G** and **H** in $CDCl_3$, indicating slow exchange on the NMR timescale. And the forces stabilizing the complex are very significant, since the percentage of the free guest is very small in the presence of **H** host. From integrations of all peaks, the stoichiometry of the complex was determined to be 2 : 1.

The association constant (K_a) can be determined using the ^{1}H NMR single point method since the NMR response is slow on the NMR timescale. At low concentrations, such as 10.0 mM, the percentage of the free guest is larger than 50% in the presence of 1.0 eq. **H** host, which is inside the limits of the Weber rule that such determinations should be done within the limits of 20−80% complexation. The K_a value for **G** ⊂ **H** complex was determined to be 5.1×10^6 M^{-2} in $CDCl_3$.

$$K_a = \frac{[G \cdot 2H]}{[G][H]^2}$$