

**Pillar[5]arene based supramolecular polymer for the singlet oxygen reservoir**

Bing Lu,<sup>\* ‡</sup> Jian Wang,<sup>‡</sup> Zhecheng zhang, Xin Yan, Qin Zhao,<sup>\*</sup> Yue Ding, Jin Wang,  
Yang Wang, Yong Yao<sup>\*</sup>

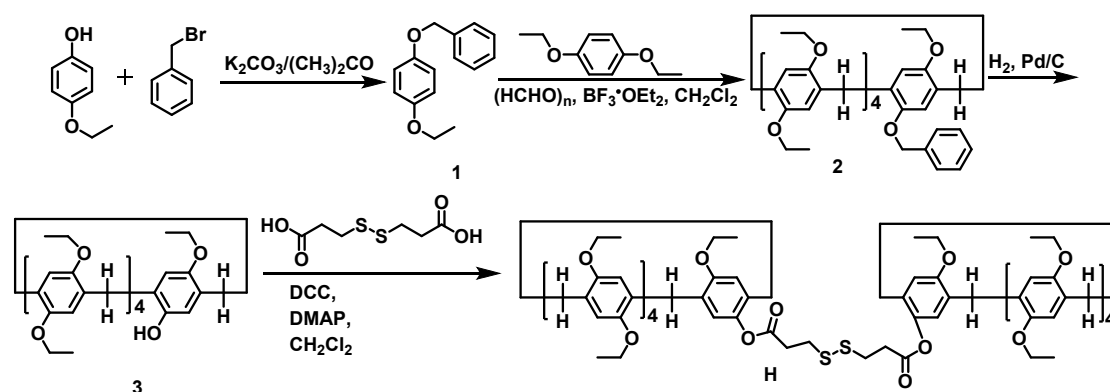
School of Chemistry and Chemical Engineering, Nantong University, Nantong,  
Jiangsu, 226019, P. R. China.

## Materials and characterization methods

Unless stated otherwise, all the chemical reagents and solvents were obtained commercially and used without further purification. All the organic reagents were purchased from Meryer Chemical Inc and TCI Chemical Inc. The  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded using a Bruker AVANCE 400 MHz spectrometer. Scanning electron microscopy (SEM) investigations were carried out on a HitachiS-3400 SEM instrument. UV-Vis spectra were recorded in a quartz cell (light path 10 mm) on a Shimadzu UV-3600 spectrophotometer equipped with a PTC-348WI temperature controller. Fluorescence spectra were recorded in a conventional quartz cell (light path 10 mm) on a Varian Cary Eclipse equipped with a Varian Cary single-cell peltier accessory to control temperature.

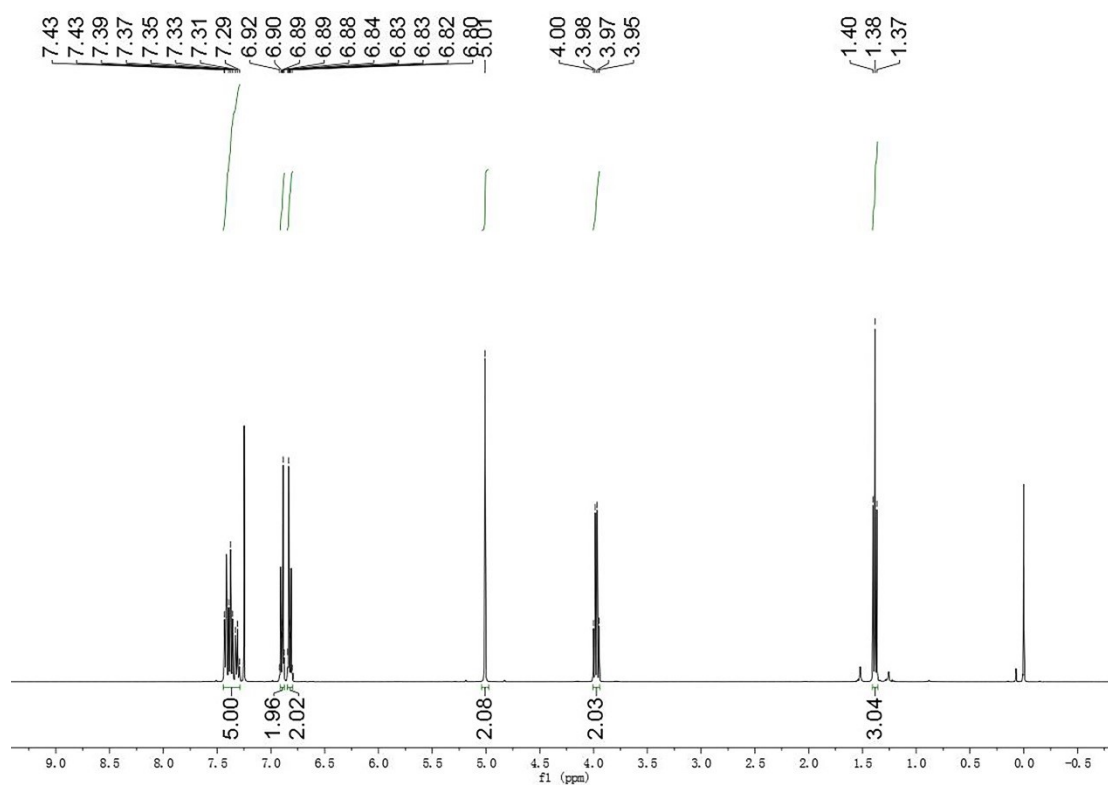
## Synthesis

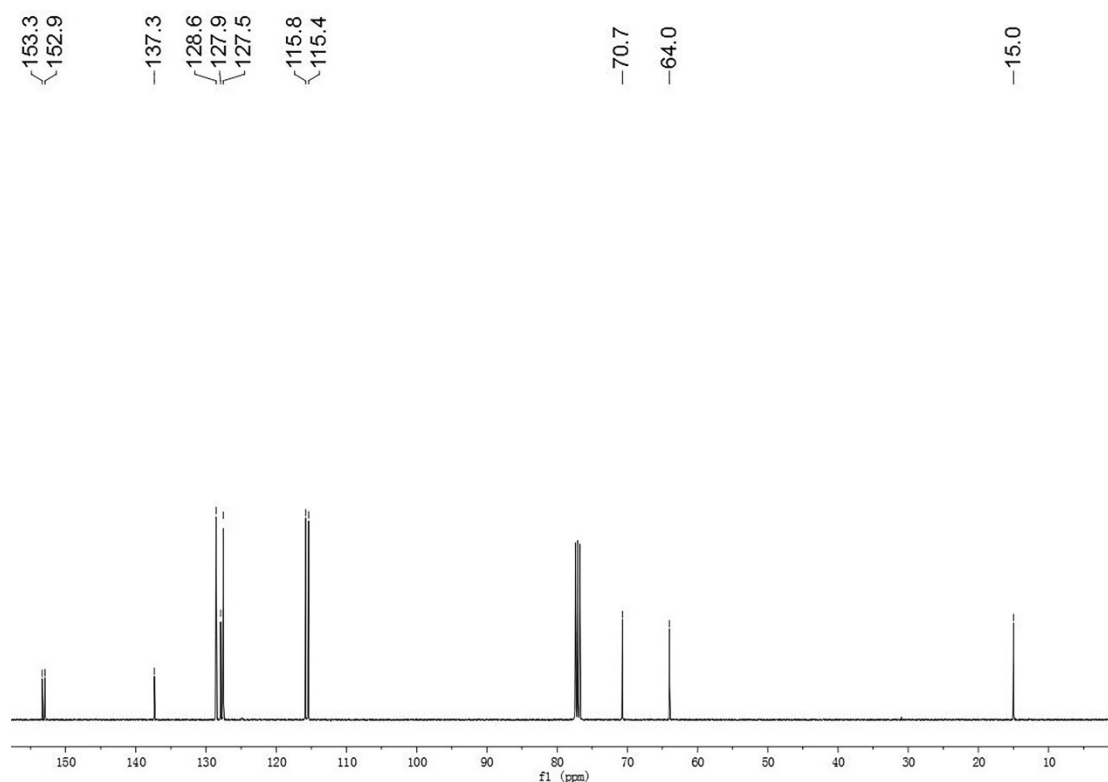
**Scheme S1** The synthetic routes for host molecule **H**.



**Compound 1** To a round bottom flask were added 4-ethoxyphenol (2.76 g, 20.00 mmol), benzyl bromide (3.42 g, 20.00 mmol),  $\text{K}_2\text{CO}_3$  (5.56 g, 40.00 mmol) and acetone (60 mL). The mixture was stirred and refluxed for 18 h. After removal of the solvent under reduced pressure, the residue was purified by column chromatography

on silica gel using petroleum ether/dichloromethane (10 : 1) as eluent to give a white solid (3.97 g, 87%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.43 – 7.29 (m, 5H), 6.92 – 6.88 (m, 2H), 6.84 – 6.79 (m, 2H), 5.01 (s, 2H), 4.00 – 3.94 (q,  $J = 7.0$  Hz, 4H), 1.38 (t,  $J = 7.0$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 153.3, 152.9, 137.3, 128.6, 127.9, 127.5, 115.8, 115.4, 70.7, 64.0, 15.0.



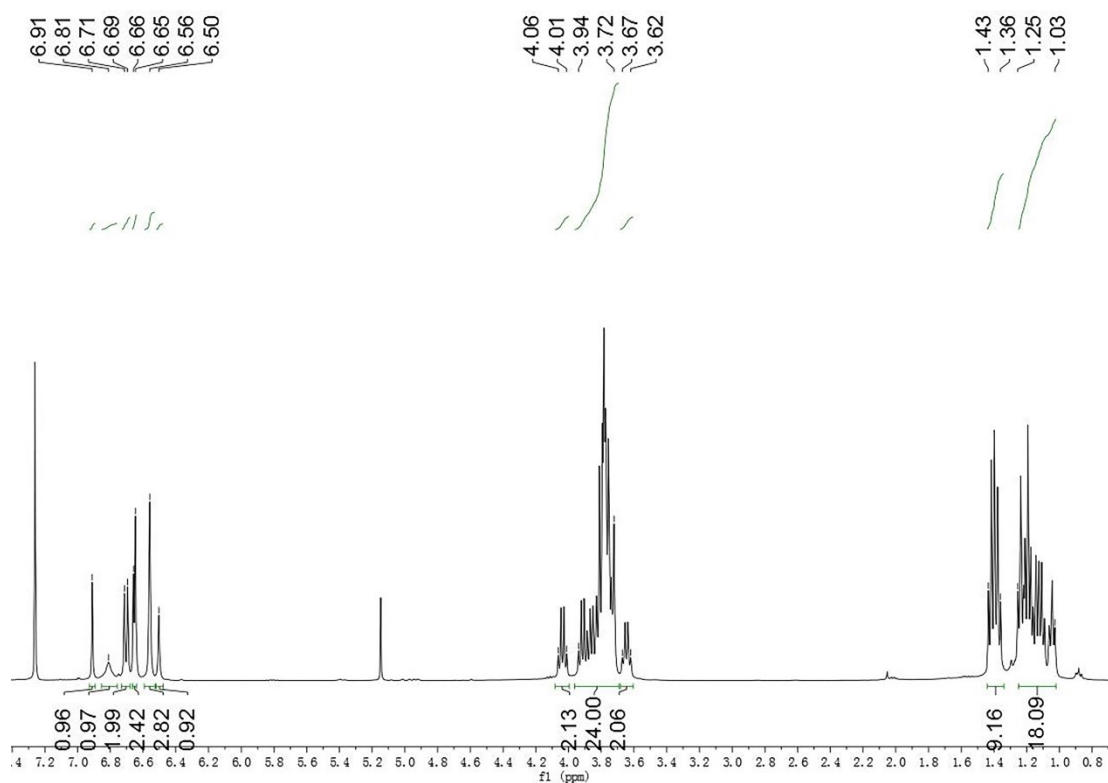


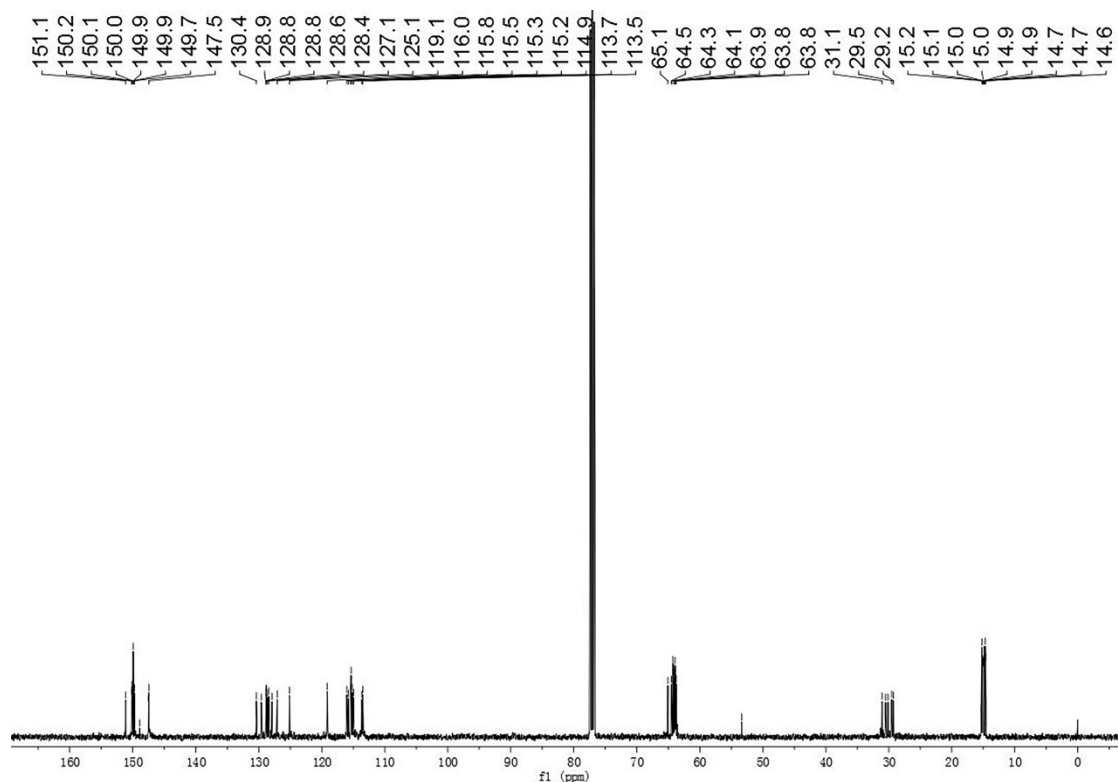
**Fig. S1**  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra of compound 1

**Compound 2** Boron trifluoride diethyl etherate (1.13 g, 8 mmol) were added to a solution of compound 1 (228 mg, 1.00 mmol), 1,4-diethoxybenzene (1.33 g, 8.00 mmol), paraformaldehyde (740 mg, 25.00 mmol) in  $\text{CH}_2\text{Cl}_2$  (60 mL). The mixture was stirred at room temperature for 1 h. Then saturated  $\text{Na}_2\text{CO}_3$  aqueous (30 mL) was poured into the reaction mixture and the mixture was then extracted with  $\text{CH}_2\text{Cl}_2$  ( $2 \times 30$  mL). After removal of the solvent under reduced pressure, the crude product was obtained by column chromatography on silica gel using using petroleum ether/dichloromethane (30 : 1) as eluent. The  $^1\text{H}$  NMR was not obtained due to the presence of the inseparable byproduct.

**Compound 3** To a round bottom flask were added compound 2 (103 mg, 0.11 mmol), Pd/C (80 mg), tetrahydrofuran (2 mL) and methanol (1 mL). The reaction

mixture was stirred at room temperature under an atmosphere of hydrogen for 24 h. Pd/C was filtered through Celite. The filtrate was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel using petroleum ether/dichloromethane (5 : 1) as eluent to give a white solid (29 mg, 31%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 6.91 (s, 1H), 6.81 (s, 1H), 6.70 (d, *J* = 8.1 Hz, 2H), 6.65 (d, *J* = 4.9 Hz, 2H), 6.56 (s, 3H), 6.50 (s, 1H), 4.06 – 4.01 (m, , 2H), 3.94 – 3.72 (m, 24H), 3.67 – 3.62 (m, 2H), 1.43 – 1.36 (m, 9H), 1.25 – 1.03 (s, 18H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 151.1, 150.2, 150.1, 150.0, 149.9 (2C), 149.7, 148.9, 147.5(2C), 130.4, 129.6, 128.9, 128.8 (3C), 128.6, 128.4, 127.9, 127.1, 125.1, 119.1, 116.0, 115.8, 115.5, 115.3, 115.2, 114.9, 113.7, 113.5, 65.1, 64.5, 64.3, 64.1, 63.9, 63.8 (2C), 53.3, 31.1, 30.5, 30.1, 29.5, 29.2, 15.3, 15.2, 15.1, 15.0 (2C), 14.9 (2C), 14.7 (2C), 14.6.

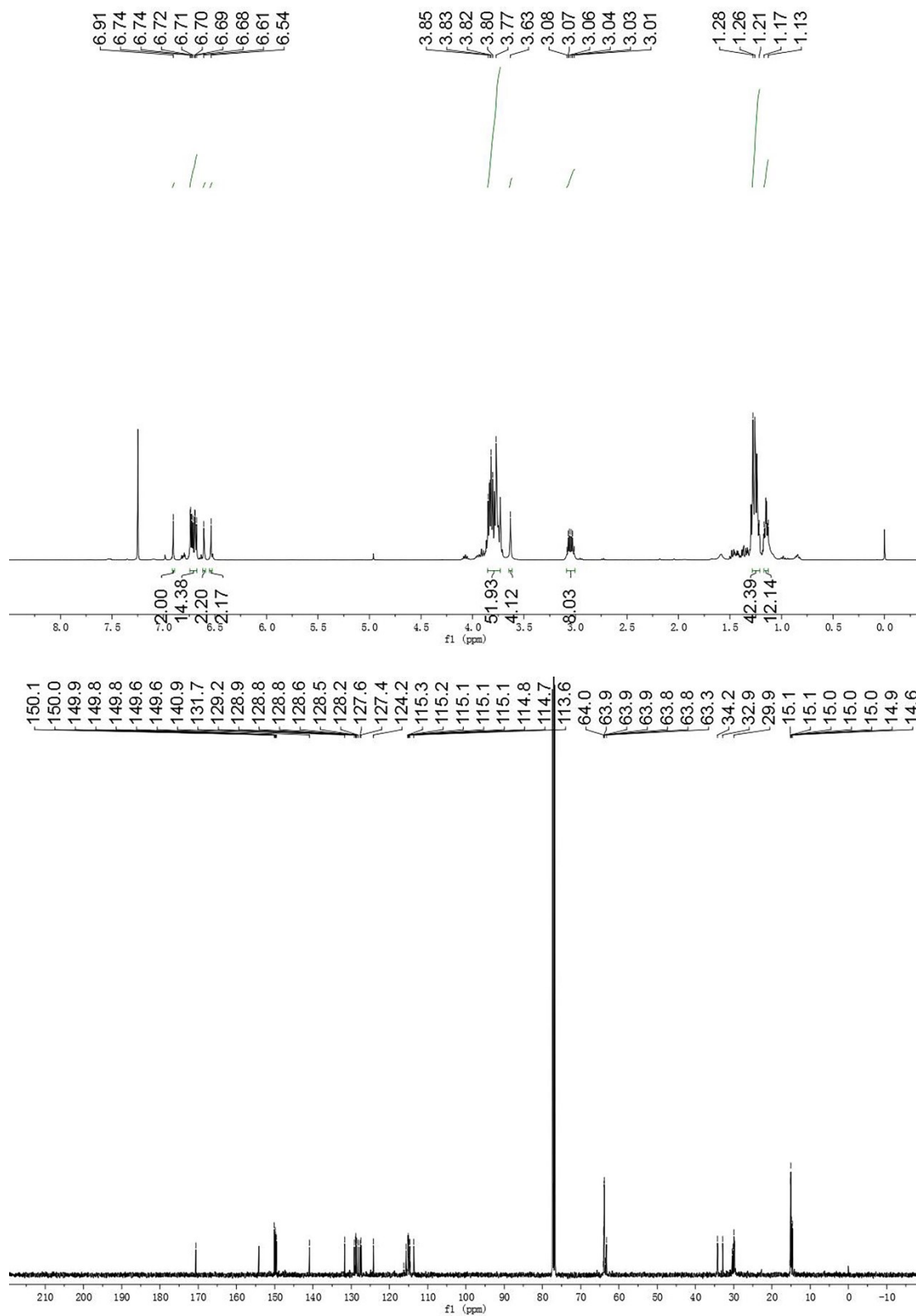




**Fig. S2**  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra of compound 3

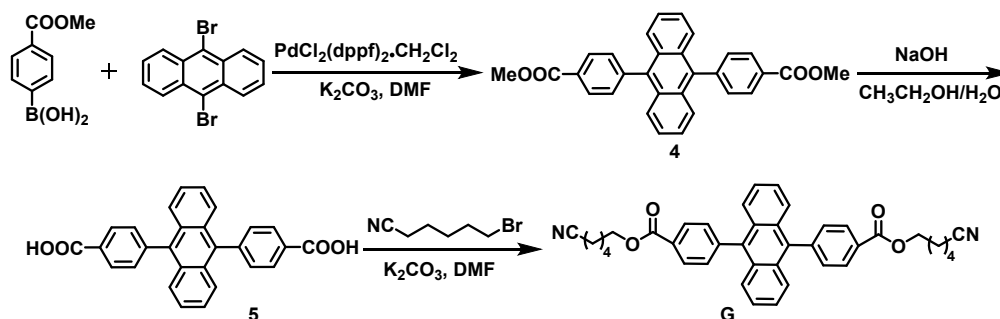
**Compound H** To a round bottom flask were added compound 3 (104 mg, 0.12 mmol), 3,3'-disulfanediyldipropionic acid (126 mg, 0.60 mmol), DCC (248 mg, 1.20 mmol), 4-DMAP (3.00 mg, 0.025 mmol) and  $\text{CH}_2\text{Cl}_2$  (12 mL). The mixture was stirred at room temperature for 12 h. Then the solvent was removed and the residue was purified by silica gel column chromatography using petroleum ether/dichloromethane (10 : 1) as eluent to give a white solid (71 mg, 63%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 6.91 (s, 2H), 6.74 – 6.67 (m, 14H), 6.61 (s, 2H), 6.54 (s, 2H), 3.85 – 3.77 (m, 52 H), 3.63 (s, 4H), 3.08 – 3.01 (m, 8H), 1.28 – 1.21 (t,  $J = 12.5$  Hz, 42H), 1.17 – 1.13 (m, 12H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 170.6, 150.1, 150.0, 149.9, 149.8 (3C), 149.6 (2C), 140.9, 131.7, 129.2, 128.9, 128.8 (2C), 128.6, 128.5, 128.2, 127.4, 124.2, 116.2, 115.6, 115.3, 115.2, 115.1 (3C), 114.8, 114.7, 114.6, 113.6,

64.1, 64.0, 63.9 (3C), 63.8 (2C), 63.6, 63.3, 34.2, 32.9, 30.4, 30.2, 29.9, 29.7, 15.3, 15.2, 15.1 (2C), 15.0 (3C), 14.9, 147.7, 14.6.



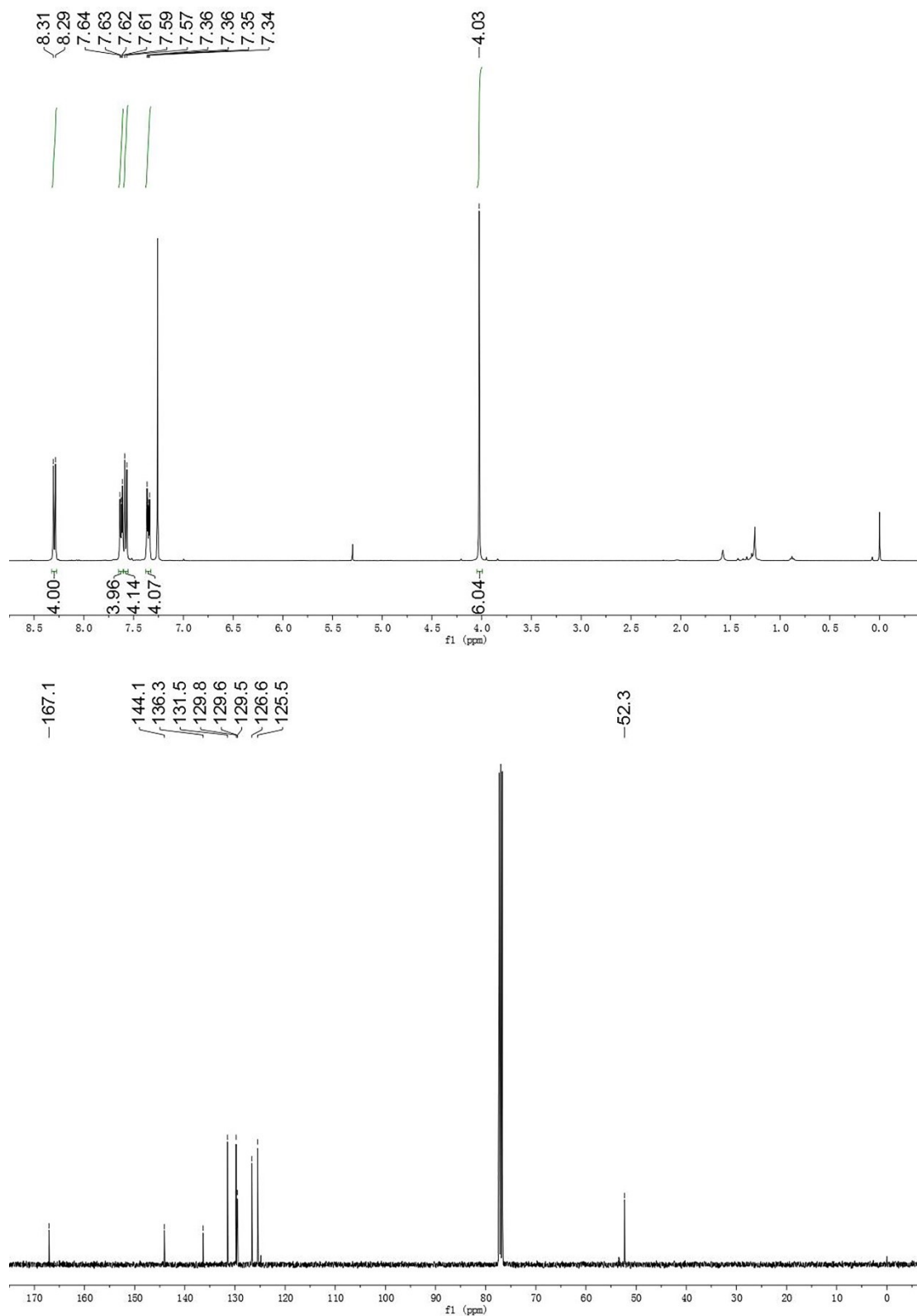
**Fig. S3**  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra of compound H

**Scheme S2** The synthetic routes for host molecule **G**.



**Compound 4** To a three-necked round bottom flask were charged 9,10-dibromoanthracene (1.00 g, 3.00 mmol), (4-(methoxycarbonyl)phenyl)boronic acid (1.45 g, 7.5 mmol),  $\text{Pd}(\text{dppf})\text{Cl}_2 \cdot \text{CH}_2\text{Cl}_2$  (253 mg, 0.3 mmol),  $\text{K}_2\text{CO}_3$  (1.66 g, 2 M aq.) and DMF (30 mL) under the protection of argon. The mixture was stirred at 115 °C for 27 h. After the reaction mixture was cooled to room temperature, the mixture was extracted with  $\text{CH}_2\text{Cl}_2$  ( $2 \times 50$  mL). After removing the solvent, the residue was purified by column chromatography on silica gel using dichloromethane as the eluent yielding a yellow solid (844 mg, 63%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.30 (d,  $J = 8.3$  Hz, 4H), 7.64 – 7.57(m, 8H), 7.36 – 7.34 (m, 4H), 4.03 (s, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 167.1, 144.1, 136.3, 131.5, 129.8, 129.6, 129.5, 126.6, 125.5, 52.3.

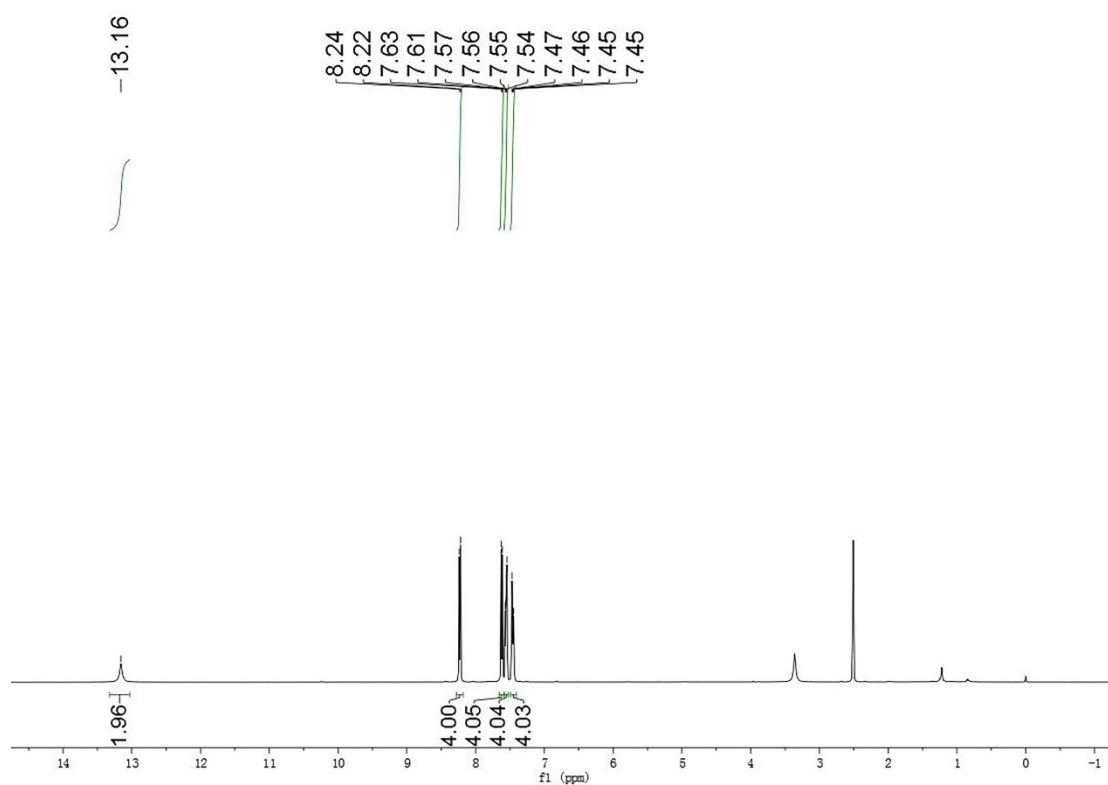


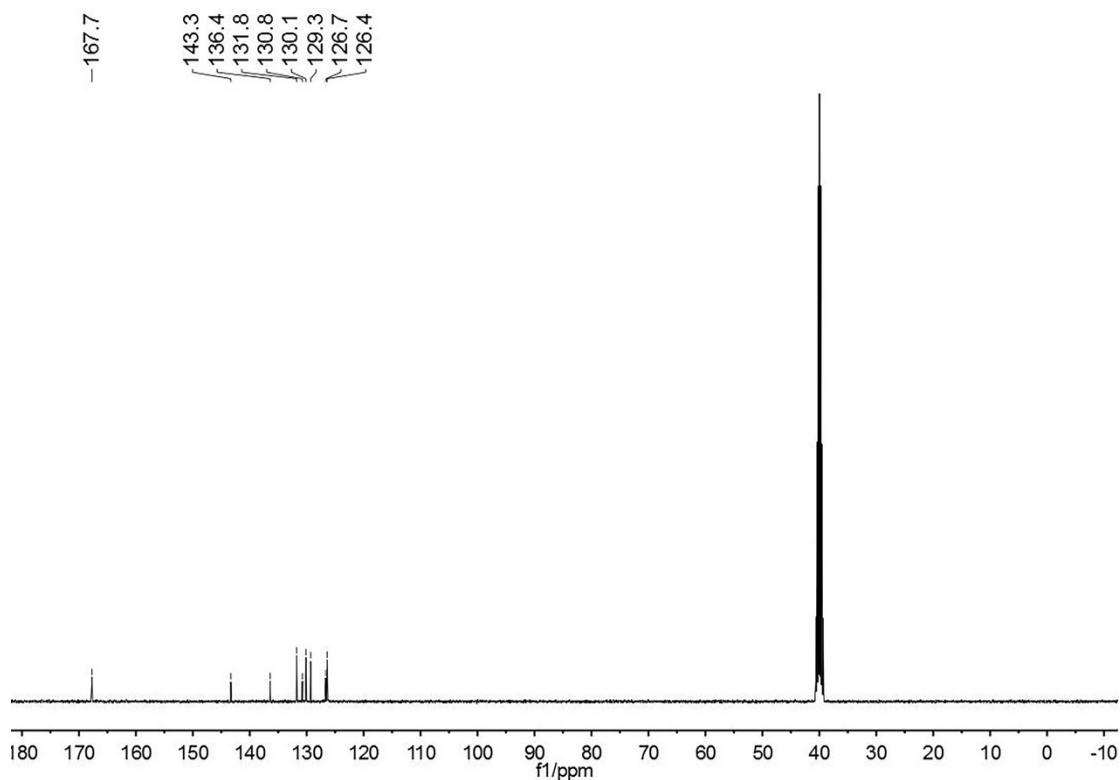


**Fig. S4** <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of compound 4

**Compound 5** To a round bottom flask were added compound 4 (474 mg, 1.00

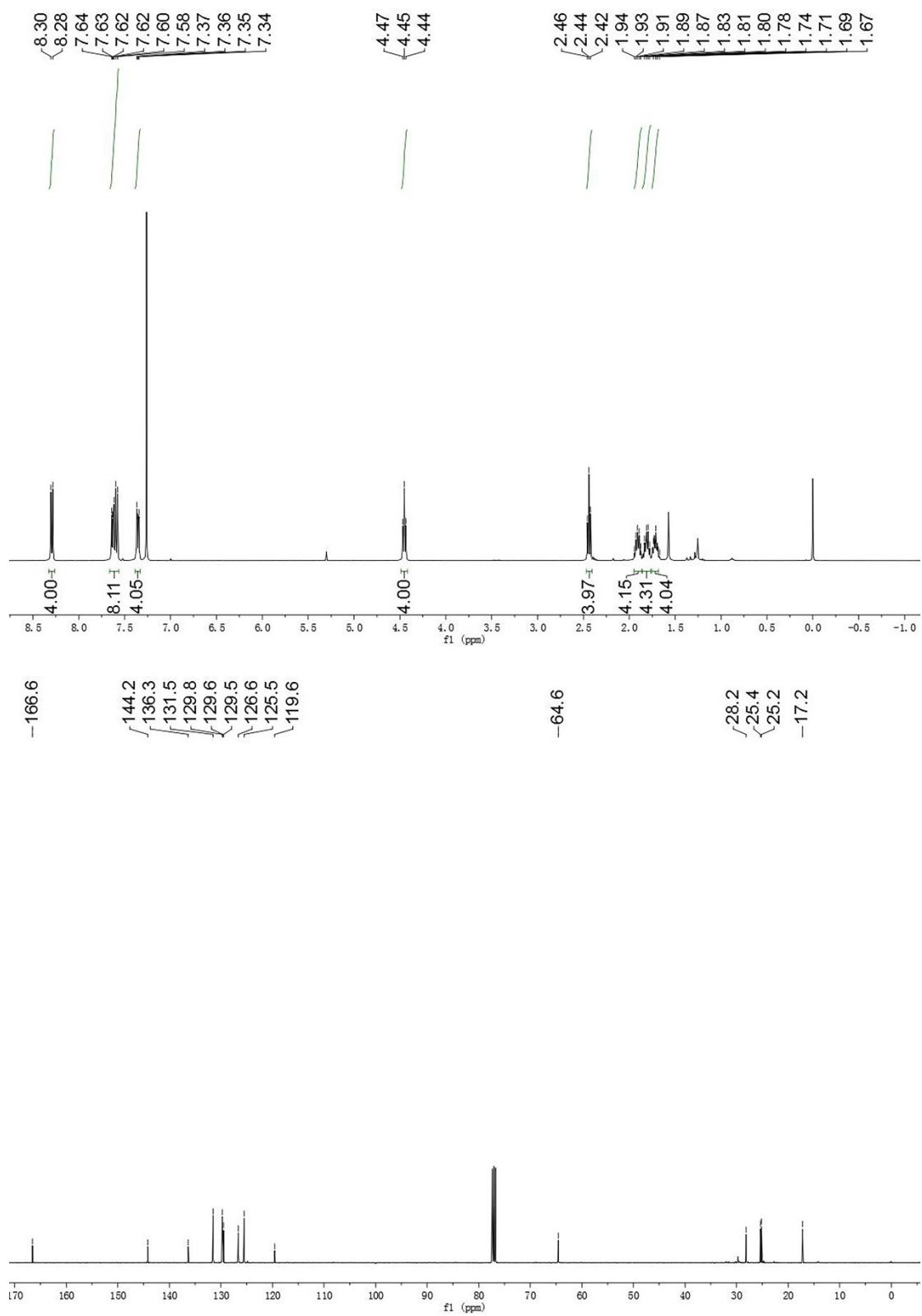
mmol), NaOH (180 mg, 4 M aq.) and ethanol (90 mL). The mixture was refluxed overnight. After the reaction mixture was cooled to room temperature, ethanol was removed by rotary evaporator. Then 2 M HCl was added to the mixture. Compound 5 (376 mg, 90%) was obtained by filtration under vacuum.  $^1\text{H}$  NMR (400 MHz, DMSO)  $\delta$ : 132.16 (s, 2H), 8.23 (d,  $J = 8.1$  Hz, 4H), 7.63 – 7.54 (m, 8H), 7.47 – 7.45 (m, 4H);  $^{13}\text{C}$  NMR (400 MHz, DMSO)  $\delta$ : 167.7, 143.3, 136.4, 131.8, 130.8, 130.1, 129.3, 126.7, 126.4.





**Fig. S5**  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra of compound 5

**Compound G** To a round bottom flask were added compound 5 (418 mg, 1.00 mmol), 6-bromohexanenitrile (704 mg, 4.00 mmol),  $\text{K}_2\text{CO}_3$  (331 mg, 2.40 mmol) and DMF (5 mL). The mixture was stirred at 90 °C for 12 h. After the reaction mixture was cooled to room temperature, the mixture was extracted with  $\text{CH}_2\text{Cl}_2$  ( $2 \times 15$  mL). After removing the solvent, the residue was purified by column chromatography on silica gel using petroleum ether/dichloromethane (5 : 1) as the eluent yielding a white solid (524 mg, 86%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.29 (d,  $J = 8.2$  Hz, 4H), 7.64 – 7.58 (m, 8H), 7.37 – 7.34 (m, 4H), 4.45 (t,  $J = 6.4$  Hz, 4H), 2.44 (t,  $J = 6.9$  Hz, 4H), 1.94 – 1.87 (m, 4H), 1.83 – 1.78 (m, 4H), 1.74 – 1.67 (t,  $J = 8.8$  Hz, 4H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 166.6, 144.2, 136.3, 131.5, 129.8, 129.6, 129.5, 126.6, 125.5, 119.6, 64.6, 28.2, 25.4, 25.2, 17.2.



**Fig. S6** <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of compound G

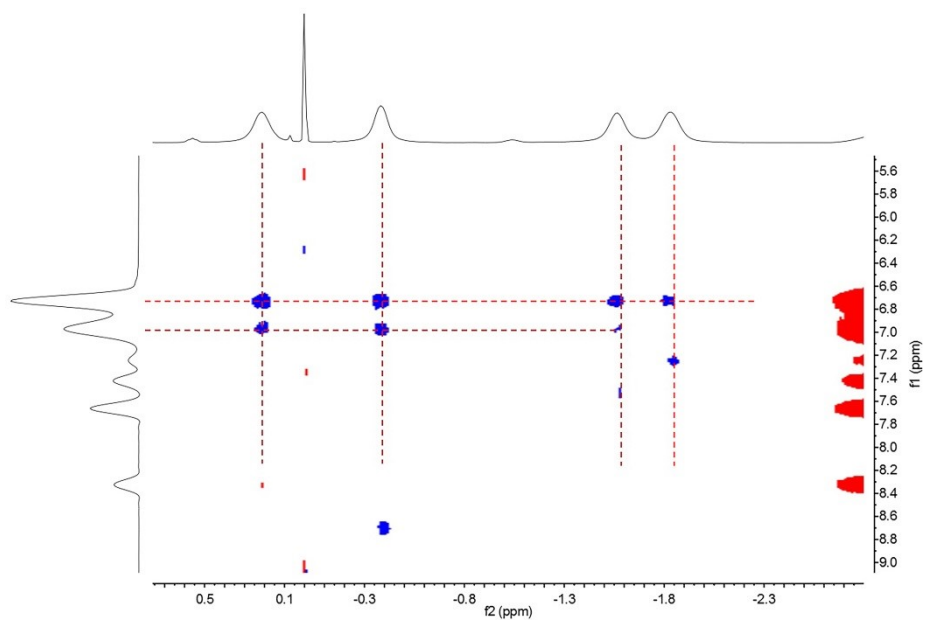


Fig. S7 Partial NOESY spectrum of  $H_M$  and  $G$  in  $CDCl_3$ .

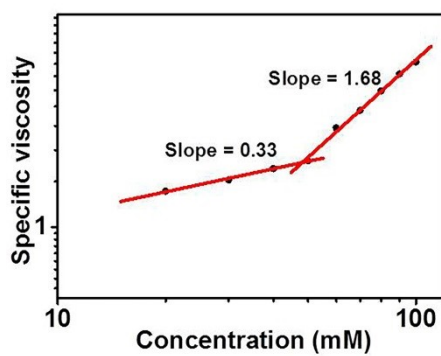
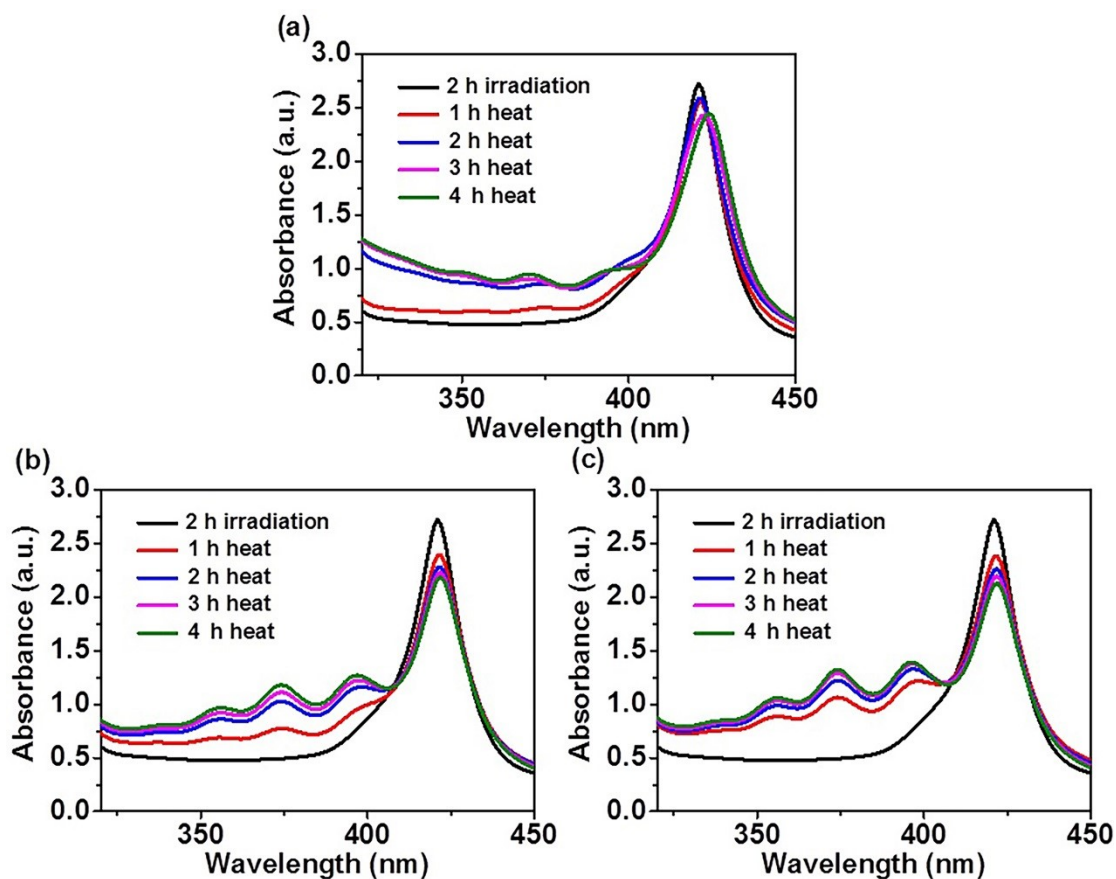
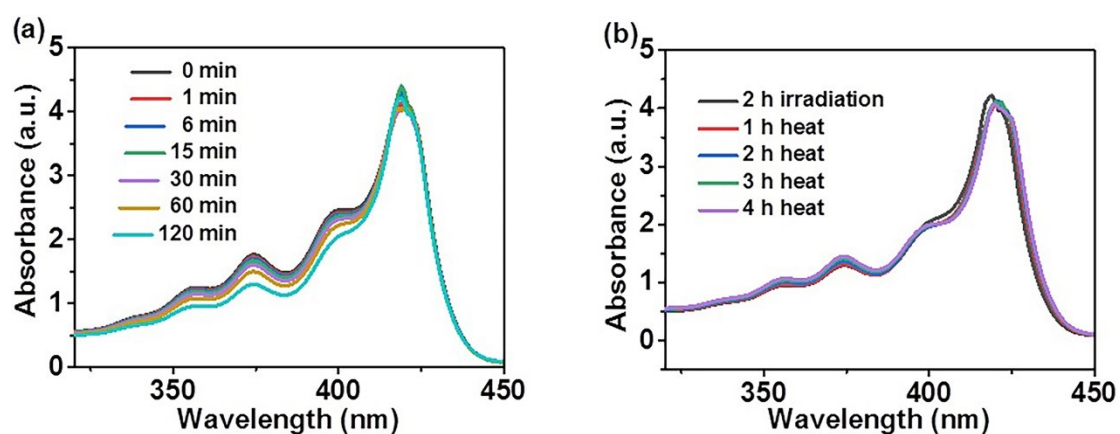


Fig. S8 Specific viscosity (298 K) of 1 : 1 mixture of  $H$  and  $G$  in  $CHCl_3$  versus the monomer concentration.

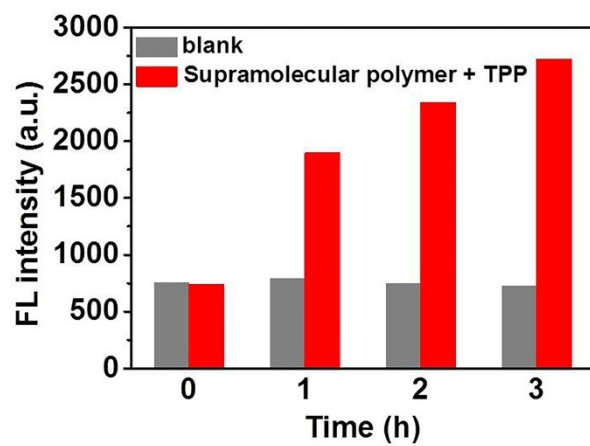


**Fig. S9** UV-Vis absorption curves of **H<sub>2</sub>G** (100  $\mu$ M) and **TPP** (25  $\mu$ M) in DMF after the laser irradiation (660 nm, 1 W) for 2 h and subsequent heating at (a) 90 °C, (b) 100 °C and (c) 110 °C.



**Fig. S10** (a) The UV-Vis spectra of the mixture of **G** (100  $\mu$ M) and **TPP** (25  $\mu$ M) in DMF after different time of laser irradiation. (b) The UV-Vis spectra of the mixture of

G (100  $\mu\text{M}$ ) and TPP (25  $\mu\text{M}$ ) in DMF after laser irradiation, and laser irradiation subsequent heating at different temperatures.



**Fig. S11** The fluorescence changes of the SOSG (5  $\mu\text{M}$ ) in DMF, and in the irradiated mixture of the supramolecular polymer and TPP nanoparticles after heated at 90  $^{\circ}\text{C}$  for different time.