

Electronic Supplementary Material

Copillar[5]arene-Based Supramolecular Polymer Gel: Controlling Stimuli-Response Properties through a Novel Strategy with Surfactant

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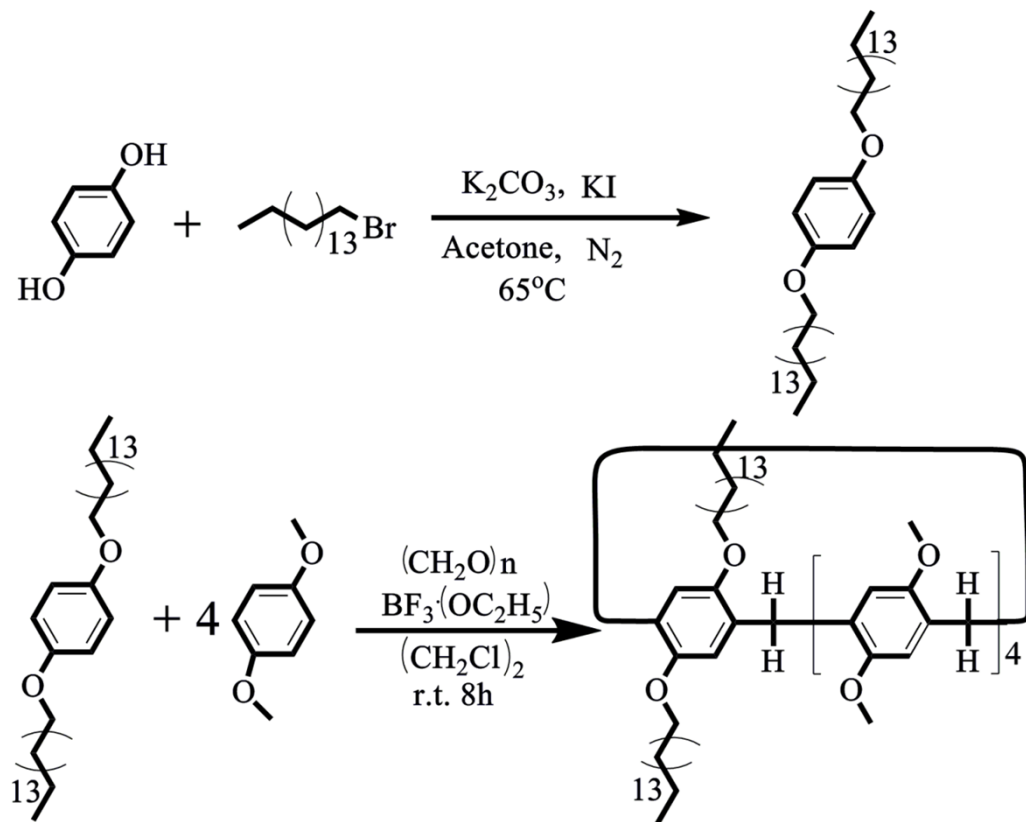
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1. Materials and methods

1, 4-Dimethoxybenzene, boron trifluoride ethyl ether complex, 1-Bromohexadecane, and was reagent grade and used as received. Solvents were either employed as purchased or dried by CaCl_2 . ^1H NMR spectra were recorded on a Mercury-600BB spectrometer at 600 MHz and ^{13}C NMR spectra were recorded on a Mercury-600BB spectrometer at 150 MHz. Chemical shifts are reported in ppm downfield from tetramethylsilane (TMS, δ scale with solvent resonances as internal standards). Melting points were measured on an X-4 digital melting-point apparatus (uncorrected). Mass spectra were performed on a Bruker Esquire 3000 plus mass spectrometer (Bruker-FranzenAnalytik GmbH Bremen, Germany) equipped with ESI interface and ion trap analyzer. XRD patterns were recorded at a scanning rate of 5 $^\circ$ /min in the 2θ range of 2° to 50° with $\text{Cu-K}\alpha$ radiation.

2. Synthesis of Copillar[5]arene DCP5-16



Synthesis of 1,4-bis(hexadecyl)benzene: In a 500 mL round-bottom flask, Hydroquinone (2.2 g, 20.0 mmol), K_2CO_3 (20 g, 140 mmol), KI (2 g, 12mmol), 1- Bromohexadecane (13.4 g, 44 mmol) and acetone (300.0 mL) were added. The reaction mixture was stirred at reflux for 3 days. After the solid

was filtered off, the solvent was removed. The solid was dissolved in CHCl_3 (150 mL) and washed twice with H_2O (200 mL). The organic layer was dried over anhydrous Na_2SO_4 and evaporated to afford the crude product, which was recrystallized with CH_3CN to give 1, 4-bis (hexadecyl) benzene (yield 80%) as a white solid. m.p. $65\text{ }^\circ\text{C}$. ^1H NMR (400MHz, CDCl_3 , 275 K) δ (ppm): 6.82 (d, 4H), 3.96 (t, 4H), 1.75 (t, 4H), 1.43 (t, 4H), 1.26 (t, 48H), 0.86 (s, 6H).

Synthesis of compound DCP5-16: To a solution of 1, 4-bis (hexadecyl) benzene (2.79 g, 5 mmol) and 1, 4-dimethoxybenzene (2.76 g, 20 mmol) in 1, 2-dichloroethane (80 mL), paraformaldehyde (0.75 g, 25 mmol) was added. Then, boron trifluoride diethyl etherate (3.2 mL, 25 mmol) was added to the solution and the mixture was stirred at room temperature for 6 h. The solution was poured into methanol and the resulting precipitate was collected by filtration. The solid was dissolved in CHCl_3 (150 mL) and the insoluble part was filtered off. The resulting solid dissolved in CHCl_3 and washed twice with H_2O (100 mL). The organic layer was dried over anhydrous Na_2SO_4 and evaporated to afford the crude product, which was isolated by flash column chromatography using petroleum ether/ethyl acetate (50:1). The fractions containing the product were combined and concentrated under

vacuum to give DCP5-16 (16%) as a white solid, m.p. 55~56 °C. The proton NMR spectrum of DCP5-16 ^1H NMR (600 MHz, chloroform- d_3 , 293K) δ (ppm): 6.81–6.78 (d, 10H), 3.83 (t, 4H), 3.77 (s, 10H), 3.67 (s, 24H), 1.78 (t, 4H), 1.33– 1.15(m, 52H), 0.87-0.83 (3, 6H). The ^{13}C NMR (150 MHz, CDCl_3 , 293K) δ (ppm): 150.74, 150.69, 150.01, 128.41, 128.27, 128.22, 128.13, 128.09, 68.49, 55.62, 31.88, 29.81, 29.76, 29.72, 29.70, 29.59, 29.49, 29.40, 26.23, 22.63, 14.08. ESI-MS m/z: $[\text{M}+\text{NH}_4]^+$ Calcd for 1188; Found 1188.8, $[\text{M}+\text{Na}]^+$ 1193.8, $[\text{M}+\text{K}]^+$ 1209.7.

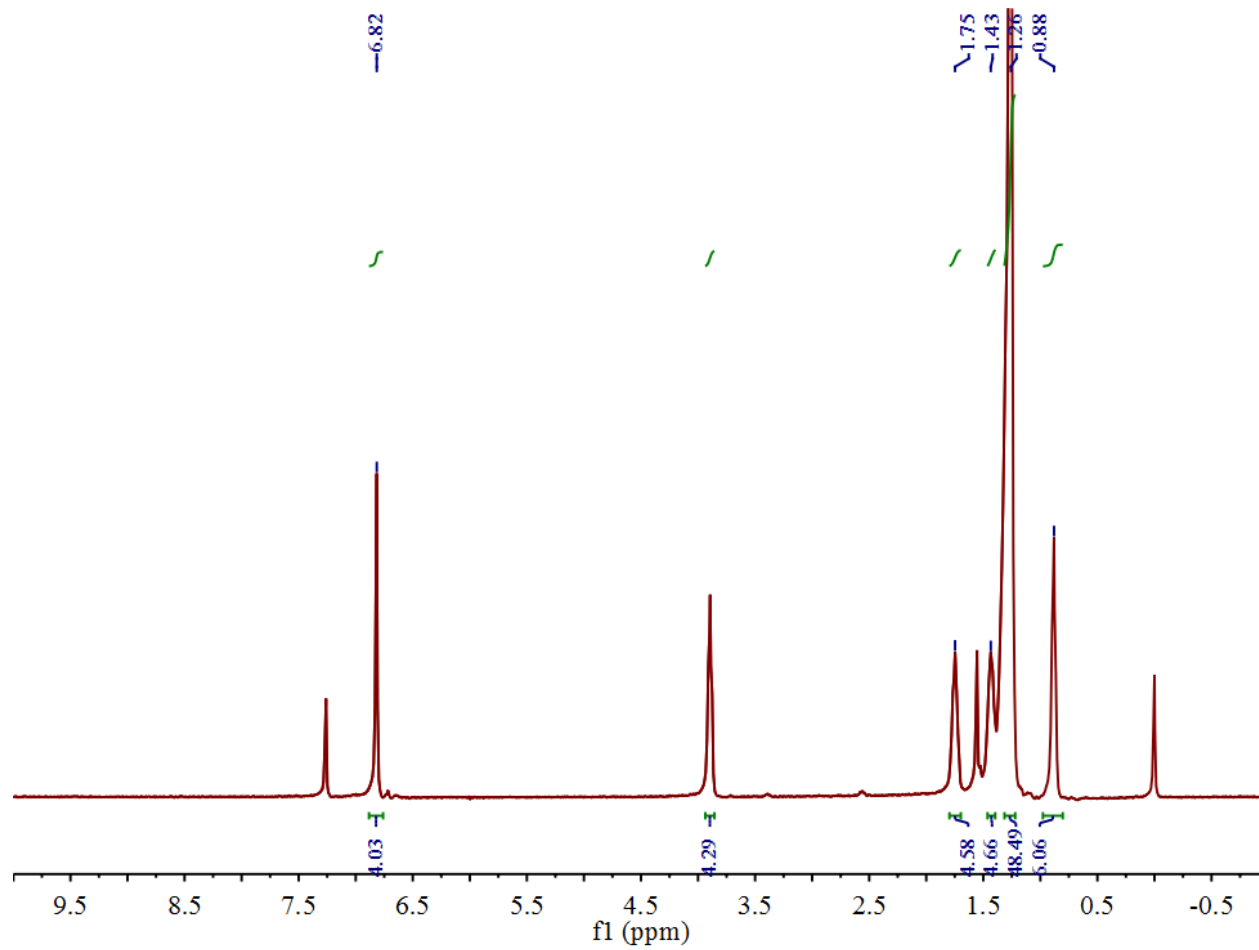


Figure S1 ¹H NMR spectra of 4-bis (hexadecyl) benzene

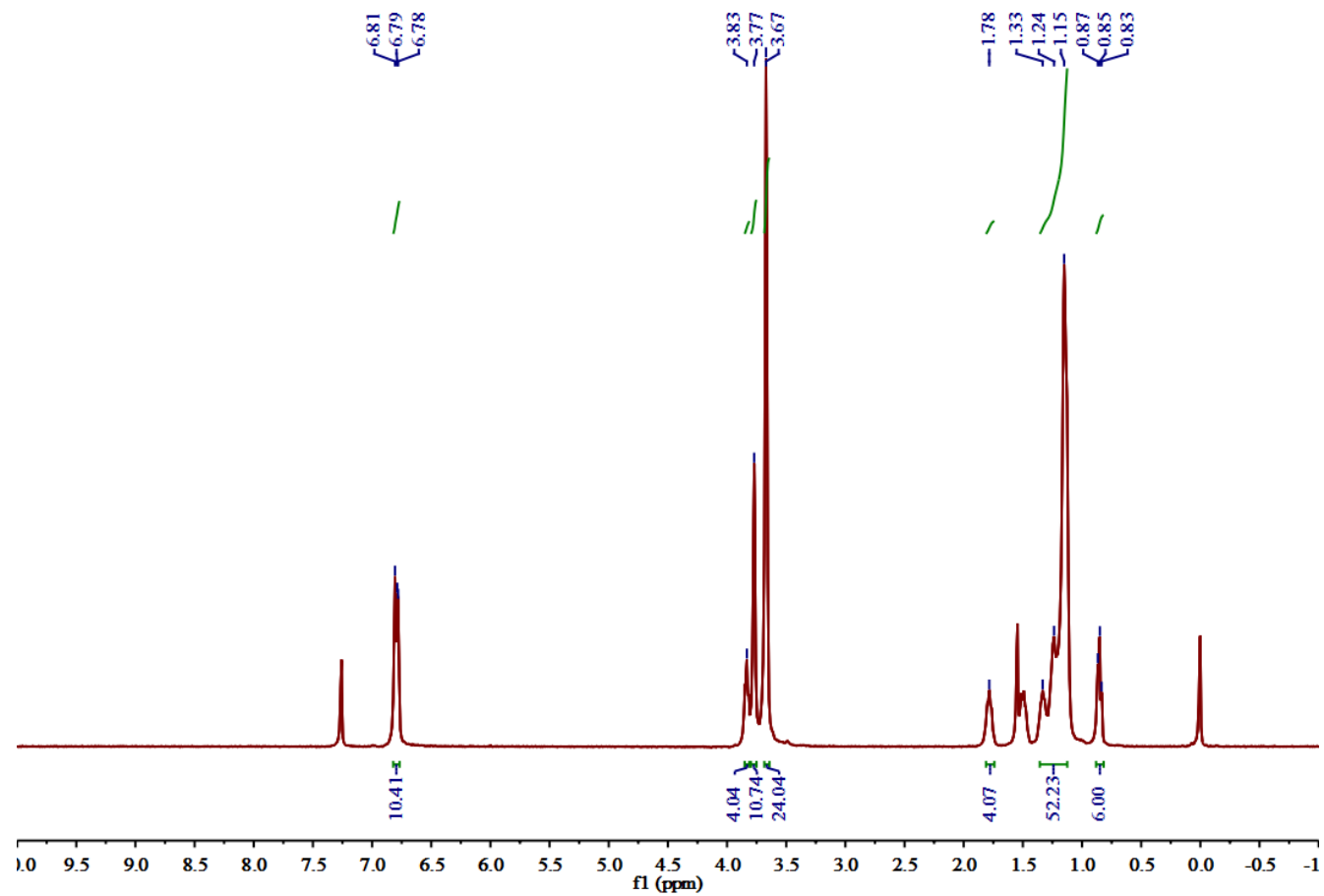


Figure S2 ¹H NMR spectra of DCP5-16

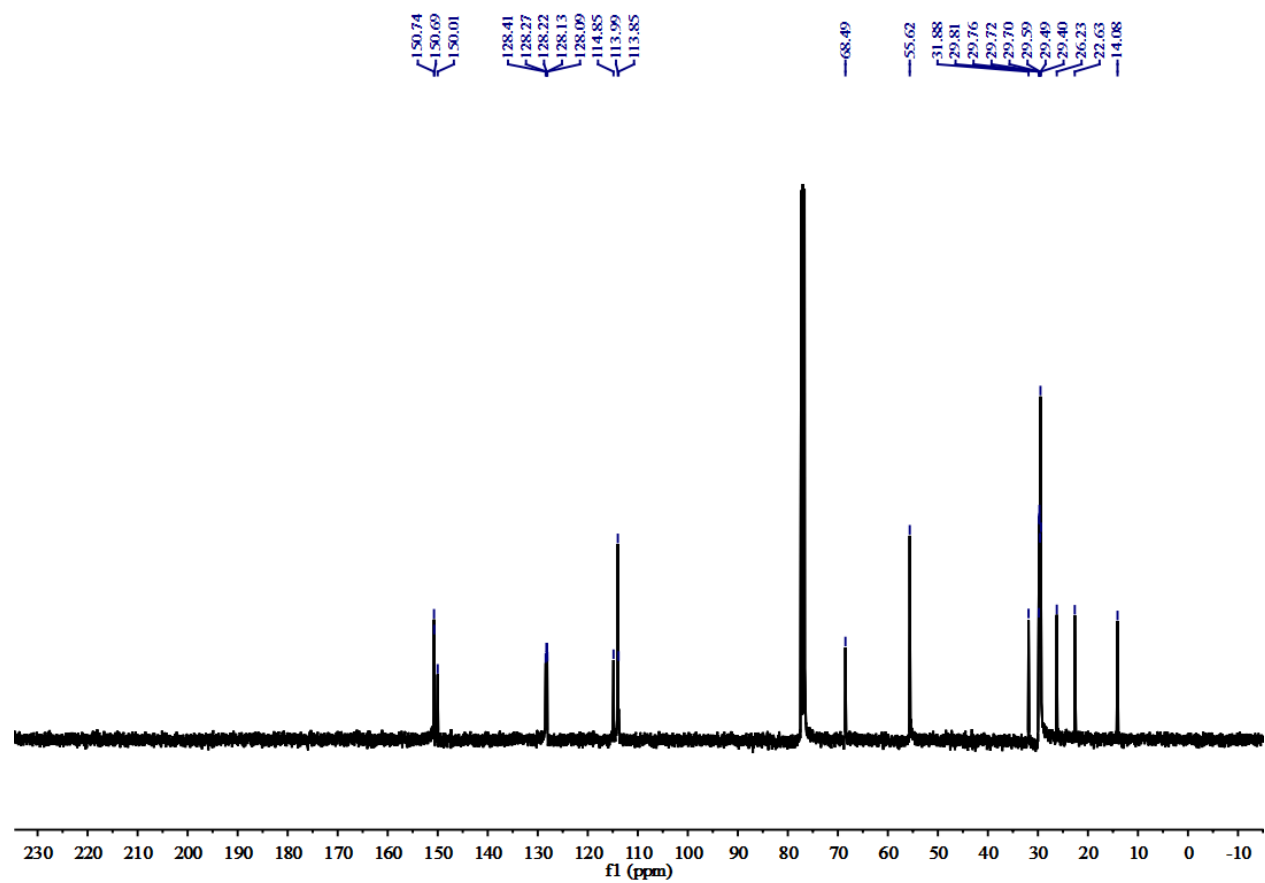


Figure S3 ^{13}C NMR spectra of DCP5-16

lihui-1_140715095035 #1 RT: 0.00 AV: 1 NL: 3.84E4
T: FTMS + c ESI Full ms [800.00-2000.00]

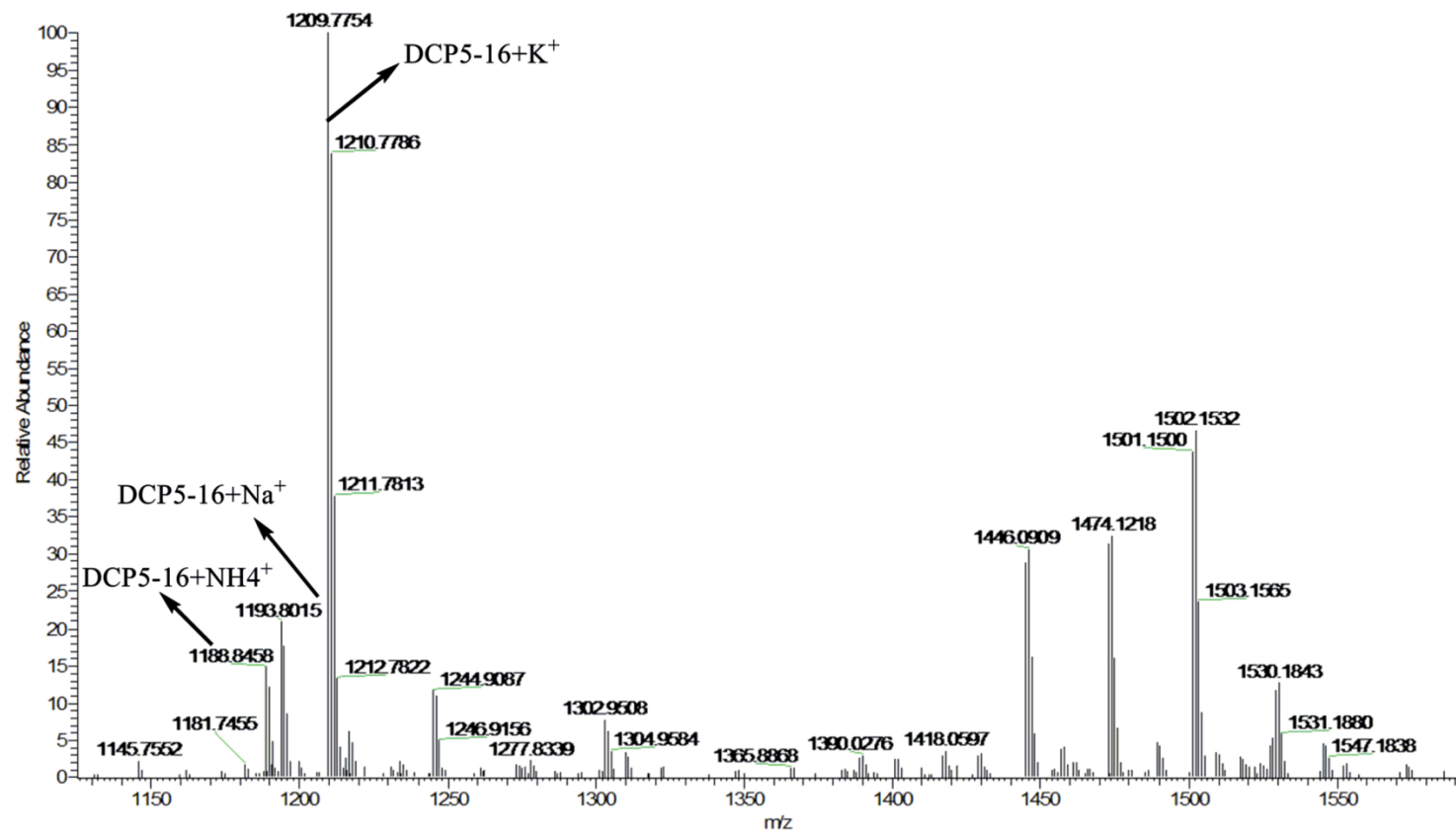


Figure S4 High resolution mass data of gelator DCP5-16.

2#_150407160827 #1 RT: 0.00 AV: 1 NL: 1.20E6
T: FTMS + p ESI Full ms [200.00-4000.00]

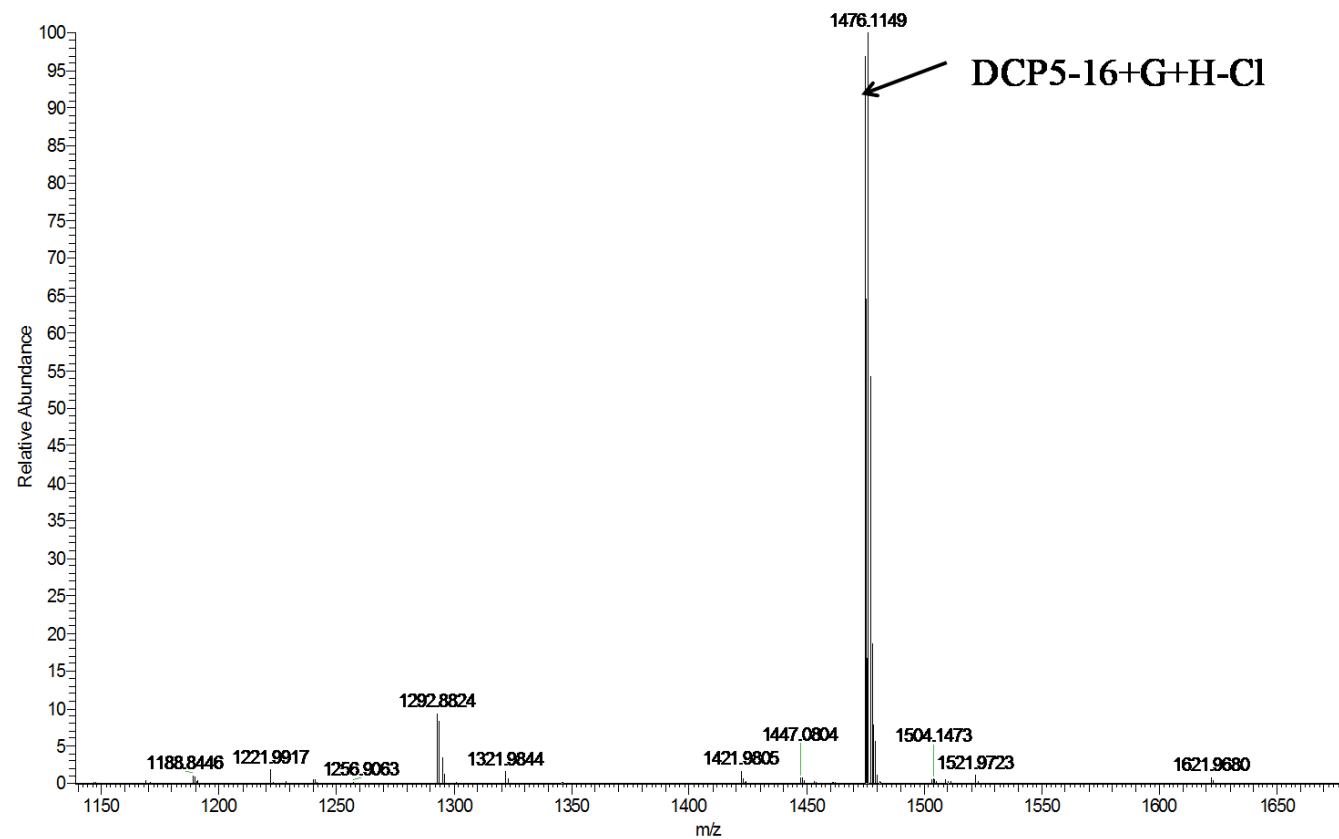


Figure S5 High resolution mass data of gelator DCP5-16 and G.

Table 1 Gelation properties of DCP5-16

DCP5-16

CHCl ₃	S
CH ₃ CN	G
CHCl ₂	S
Acetone	S
H ₂ O	S
DMSO	P
CH ₃ CH ₂ OH	E
CH ₃ OH	E
Ethyl acetate	E
DMF	E

G: gel, S: sol, E: emulsion, P: precipitate. DCP5-16

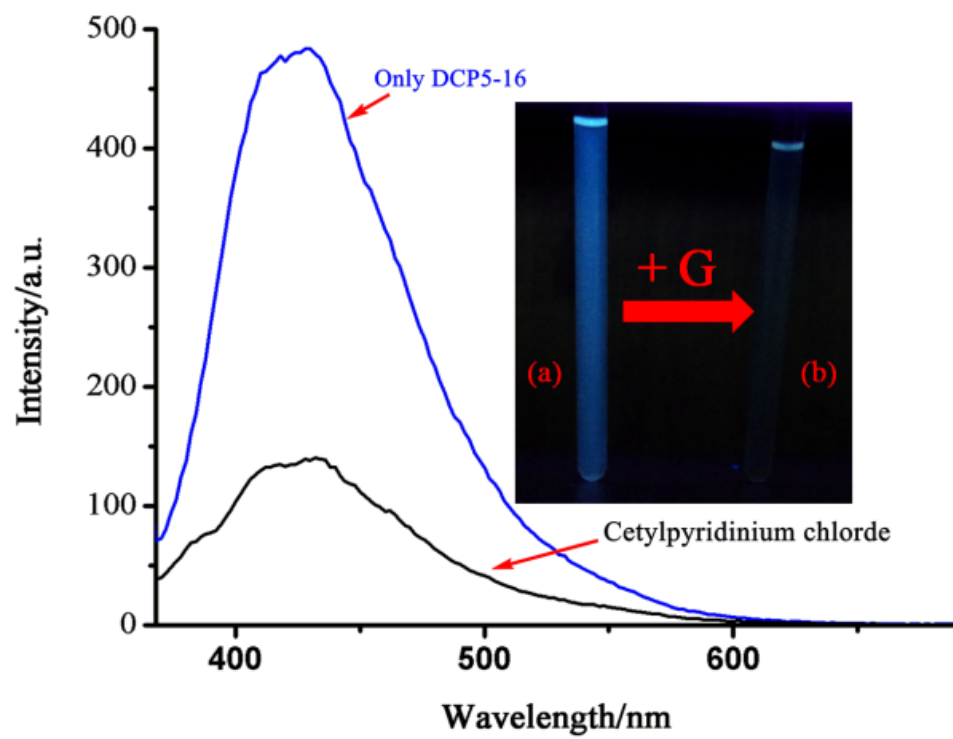


Fig. S6 Fluorescence intensity changes for DCP5–16 in CDCl_3 upon addition of G.

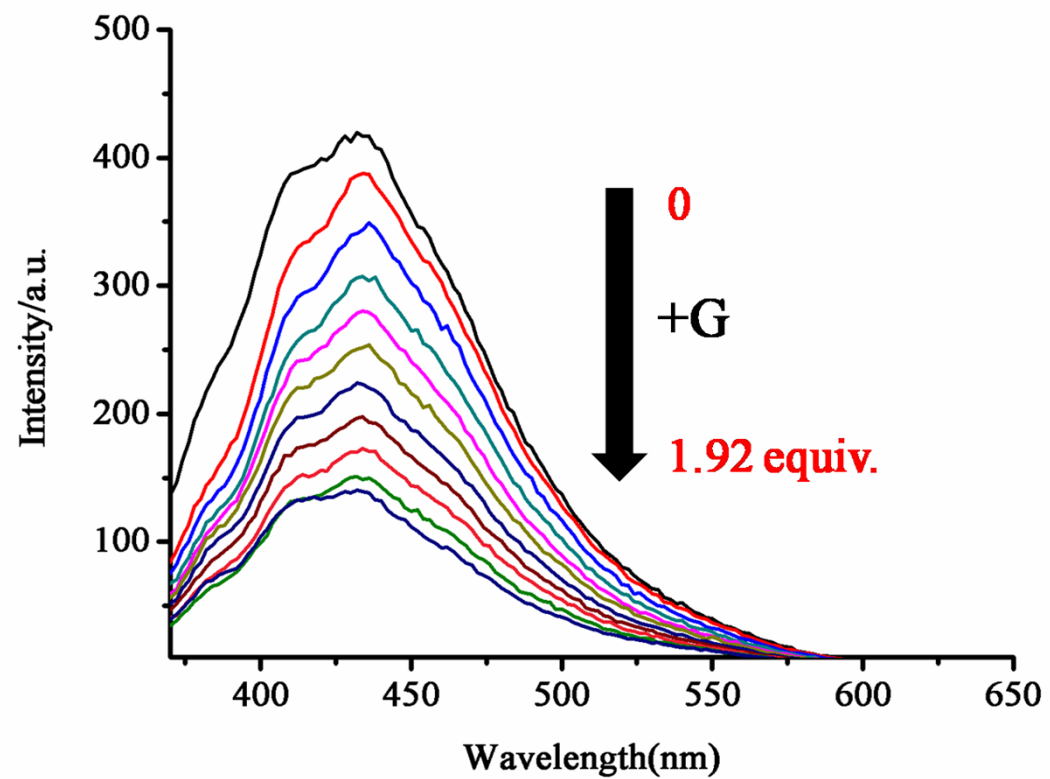


Figure S7 The changes in fluorescence intensity of DCP5-16 upon the titration of G in CH₃CN

Determination of the detection limit

We use the 3δ way to figure out the detection limit. The process of the analysis as follows.

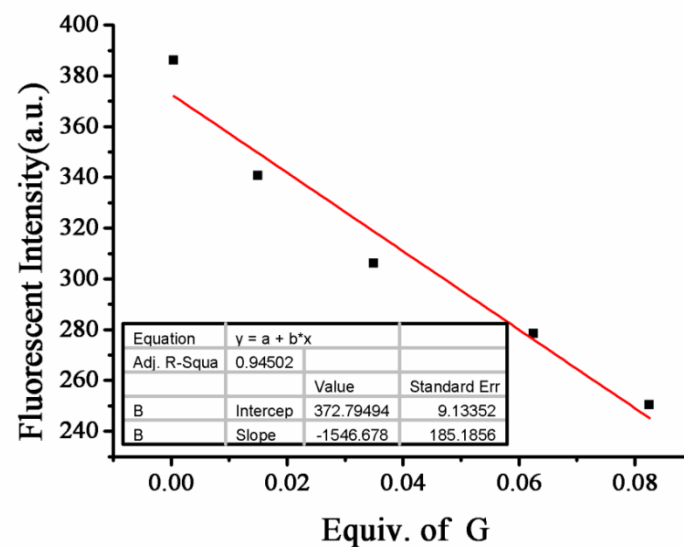


Figure S8 The photograph of the linear range

Linear Equation:

$$Y = -1546.678X + 185.1856$$

$$R^2 = 0.9450$$

$$S = 1.546678 \times 10^9$$

$$\delta = \sqrt{\frac{\sum(F_i - F_0)^2}{N - 1}} = 3.7$$

$$K = 3$$

$$\text{LOD} = K \times \delta / S = 1.72 \times 10^{-8} \text{ M}$$

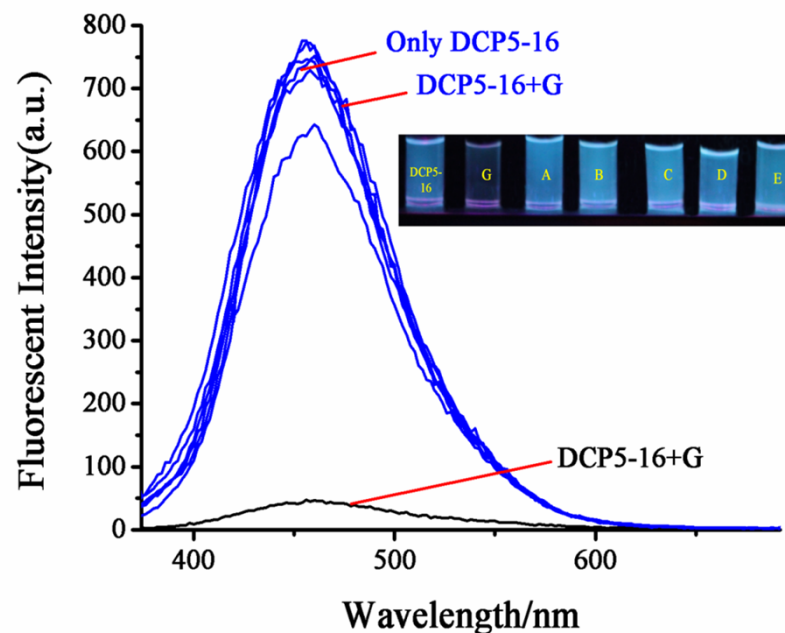


Fig. S9 Fluorescence spectra of DCP5-16 upon an excitation at 355 nm in CHCl_3 . Inset: photograph from left to right shows the change in the fluorescence including: DCP5-16; G) DCP5-16 and hexadecylpyridinium chloride, A) DCP5-16 and hexadecylpyridinium bromide, B) DCP5-16 and hexadecyl trimethyl ammonium bromide C) DCP5-16 and trimethylamine solution D) DCP5-16 and triethanolamine E) DCP5-16 and sodium dodecylbenzenesulfonate.

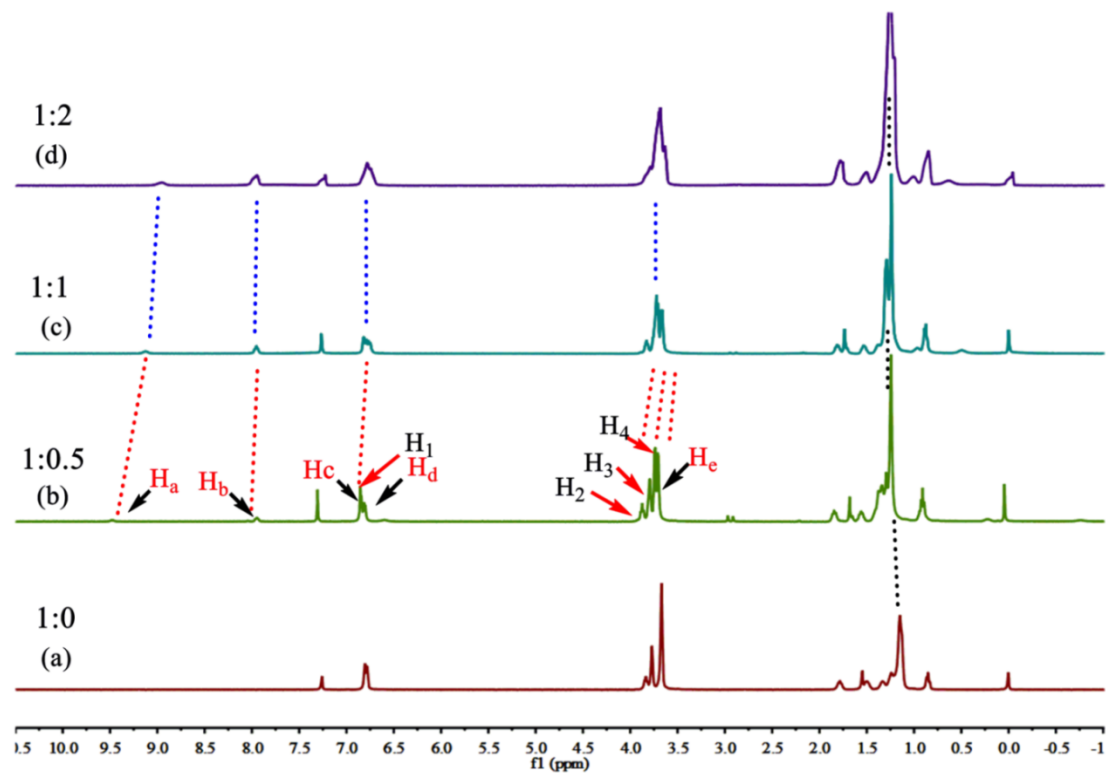


Figure S10 ¹H NMR spectra of DCP5-16 (10 mM, 600 MHz, CDCl₃) in the presence of increasing amounts of G; from bottom to top: 0, 0.5, 1.0 and 2.0 equivalents.