Electronic Supplementary Information

Impediment of photodimerization of coumarin derivative induced by pillar[5]arene-based molecular recognition in water

Chunwen Yang Haixiong Shi Shanshan Li and Qiao Li*

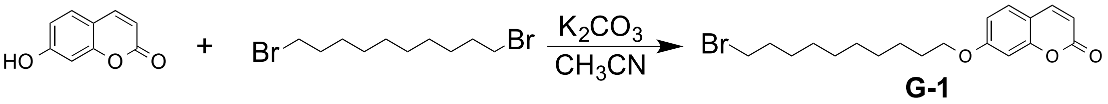
Chunwen Yang Haixiong Shi Shanshan Li and Qiao Li *

College of Chemical Engineering, Lanzhou University of Arts and Science, Lanzhou,
Gansu 730000, P. R. China
Fax and Tel: +869318685568; Email address: gansuchengzhou@126.com

General methods

All reagents were commercially available and used as supplied without further purification. Compounds **WP5** were prepared according to published procedure.[S1] NMR spectra were recorded with a Bruker Avance DMX 400 spectrophotometer. Low-resolution electrospray ionization mass spectra were recorded with a Bruker Esquire 3000 Plus spectrometer. High-resolution mass spectrometry experiments were performed with a Bruker 7-Tesla FT-ICR mass spectrometer equipped with an electrospray source (Billerica, MA, USA). The determination of the critical aggregation concentration (CAC) values was carried out on a DDS-307 instrument. Transmission electron microscopy investigations were carried out on a JEM-1200EX instrument. Dynamic light scattering was carried out on a Malvern Nanosizer S instrument at room temperature.

Synthesis of G-1



In a 250 mL round–bottom flask, 7-Hydroxycoumarin (3.24 g, 20.0 mmol), K_2CO_3 (11.0 g, 80 mmol), 1,10-Dibromodecane (12.0 g, 40.0 mmol) and acetonitrile (100 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 **G-1** (4.60 g, 60.0 %) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ (ppm): 7.65 (d, J = 8 Hz 1H), 7.37 (d, J = 8 Hz, 1H), 6.85–6.80 (m, 2H), 6.26 (d, J = 12 Hz 1H), 4.01 (t, J = 16 Hz 2H), 3.41 (t, J = 16 Hz 2H), 1.87–1.79 (m, 4H), 1.47–1.43 (m, 4H), 1.33–1.32 (m, 8H). The ^{13}C NMR (100 MHz, $CDCl_3$, 298K) δ (ppm): 162.43, 161.34, 155.93, 143.49, 128.71, 113.02, 112.91, 112.37, 101.31, 68.64, 34.08, 32.81, 29.41, 29.28, 28.96, 28.73, 28.15, 25.94.

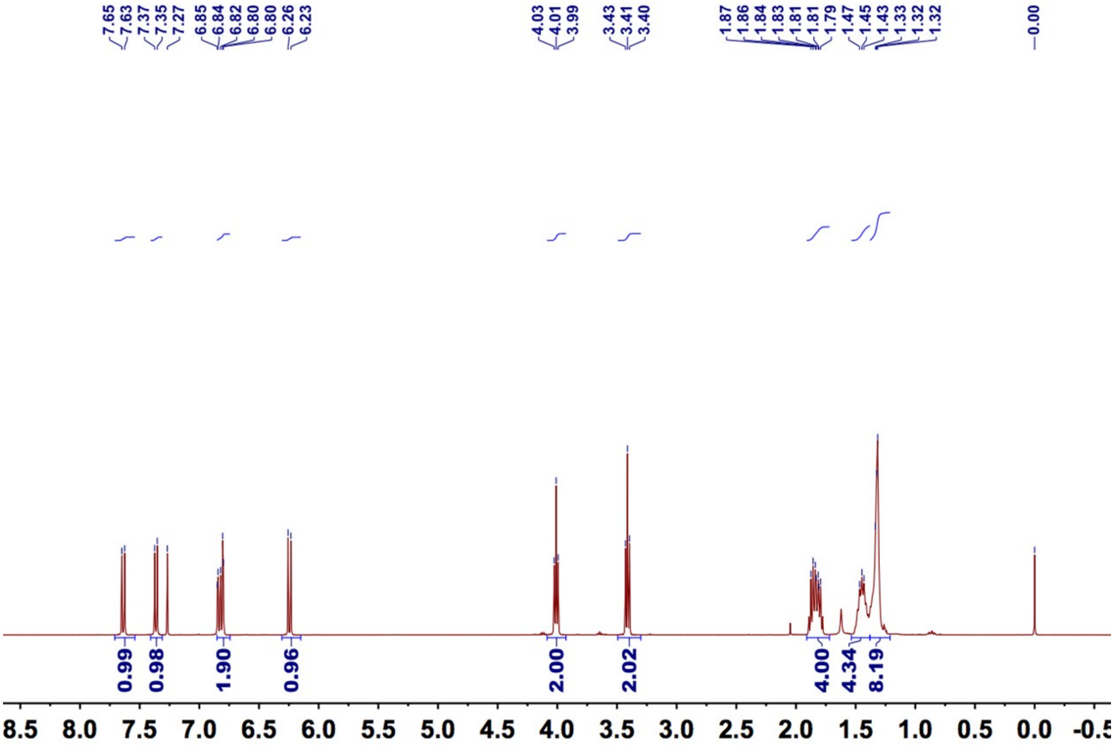


Fig. S1 ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of **G-1**.

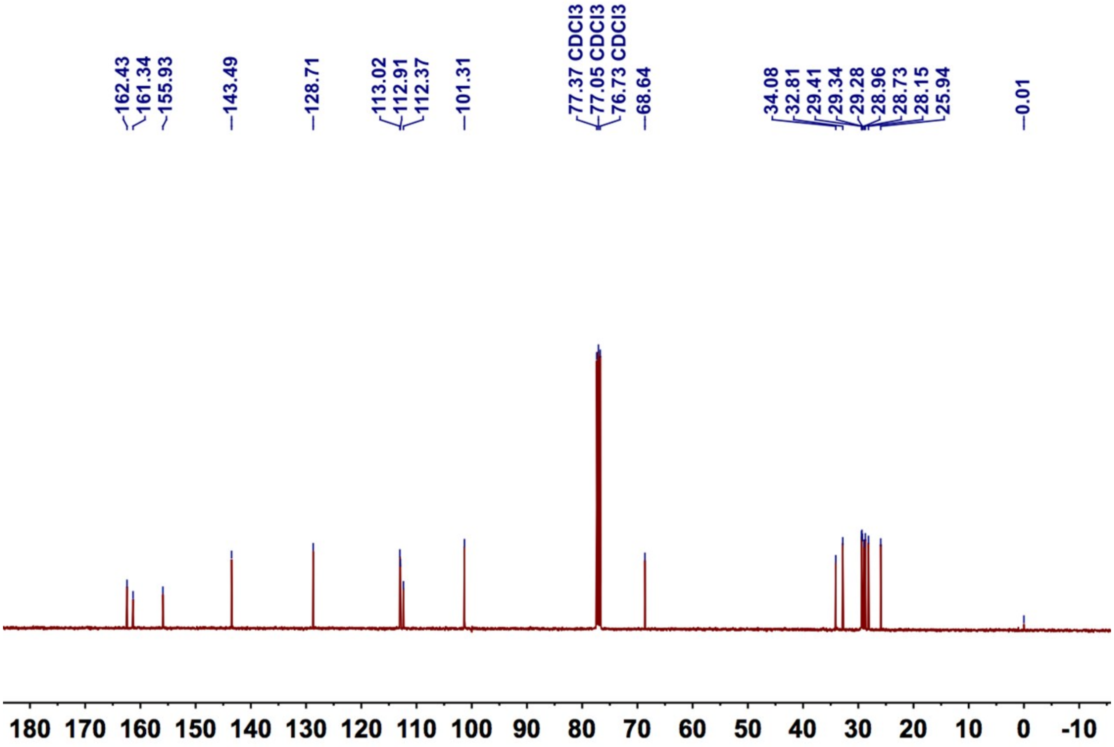
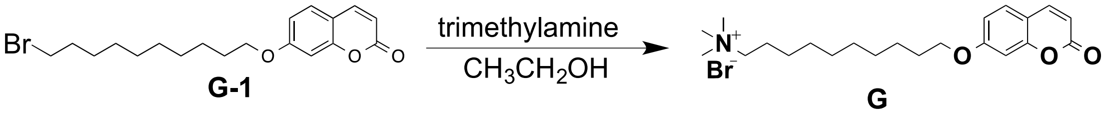


Fig. S2 ^{13}C NMR spectrum (100 MHz, $CDCl_3$, 298K) of **G-1**.

Synthesis of G



To a stirred solution of **G-1** (3.83 g, 10.0 mmol) in ethyl alcohol (40 mL) at room temperature was added trimethylamine (33.0% in ethyl alcohol, 4 mL). The resulting solution was refluxed for 24 h. The mixture was concentrated under reduced pressure to give compound **G** as a white solid (4.22 g, 96.0%). The proton NMR spectrum of **G** is shown in Fig. S3. ^{1}H NMR (400 MHz, $CDCl_3$, 298K) δ (ppm): 8.04 (d, *J* = 8 Hz, 1H), 7.66 (d, *J* = 8 Hz, 1H), 6.97–6.93 (m, 2H), 6.31 (t, *J* = 12 Hz, 1H), 4.07 (t, *J* = 16 Hz, 2H), 3.33 (m, 2H), 3.09 (m, 9H), 1.75–1.67 (m, 4H), 1.42–1.26 (m, 12H). The ^{13}C NMR spectrum of **G** is shown in Fig. S4. The ^{13}C NMR (125 MHz, $CDCl_3$, 298K) δ (ppm): 161.83, 160.29, 155.37, 144.36, 129.48, 112.66, 112.31, 112.21, 101.05, 68.24, 65.17, 52.09, 52.05, 28.83, 28.72, 28.64, 28.46, 28.38, 25.72, 25.38, 22.01. LRESIMS: m/z 360.2 $[1 - Br^-]^+$ (100%).

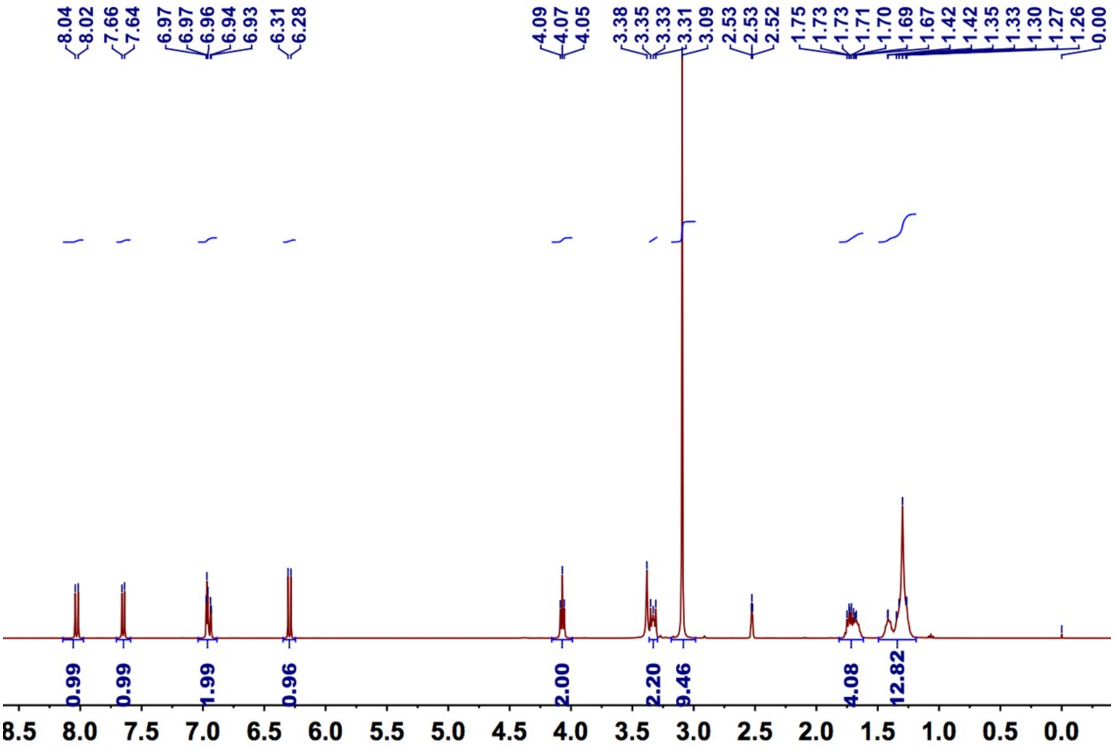


Fig. S3 ^{1}H NMR spectrum (400 MHz, DMSO-d_6, 298K) of **G**.

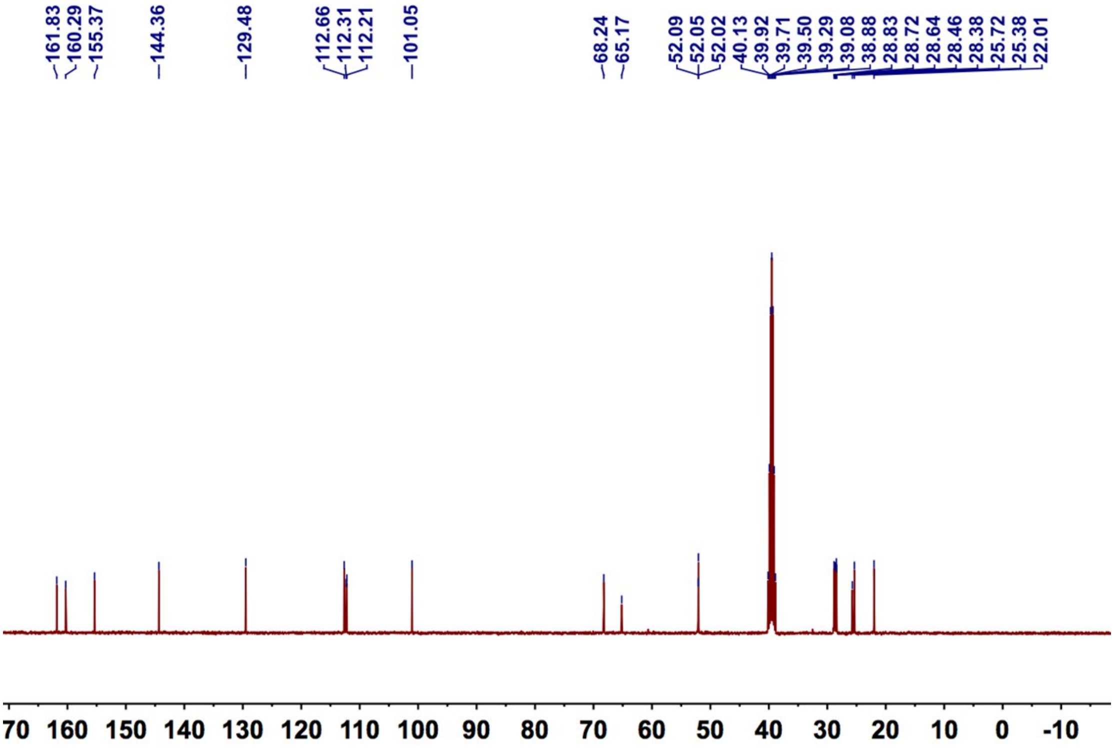


Fig. S4 ^{13}C NMR spectrum (100 MHz, DMSO-d_6, 298K) of **G**.

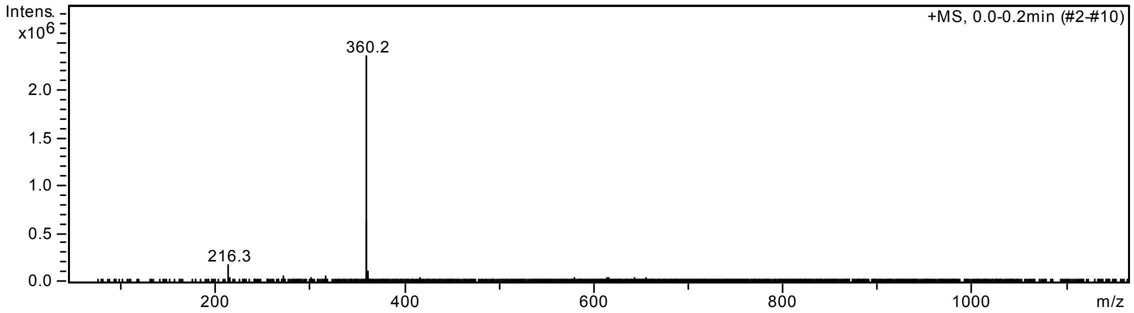


Fig. S5 Electrospray ionization mass spectrum of **G**. Assignment of the main peak: m/z 360.2 [**G** − Br⁻]⁺.

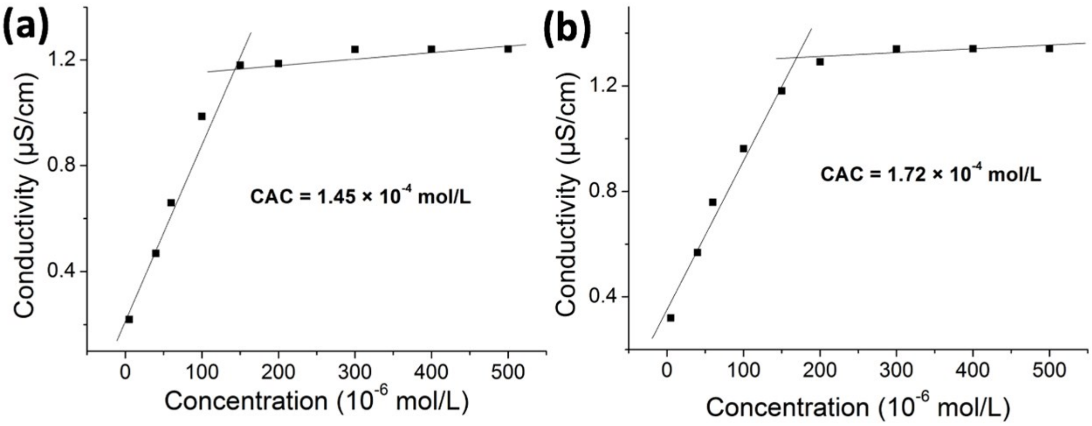


Fig. S6 (a) Conductivity as a function of the concentration of **G** before UV-irradiation. There are two linear segments in the curve and a sudden reduction of the slope, implying that the critical aggregation concentration (CAC) of **G** before UV-irradiation is approximately 1.45 × 10^{-4} M; (b) Conductivity as a function of the concentration of **G** after UV-irradiation. There are two linear segments in the curve and a sudden reduction of the slope, implying that the critical aggregation concentration (CAC) of **G** after UV-irradiation is approximately 1.72 × 10^{-4} M.

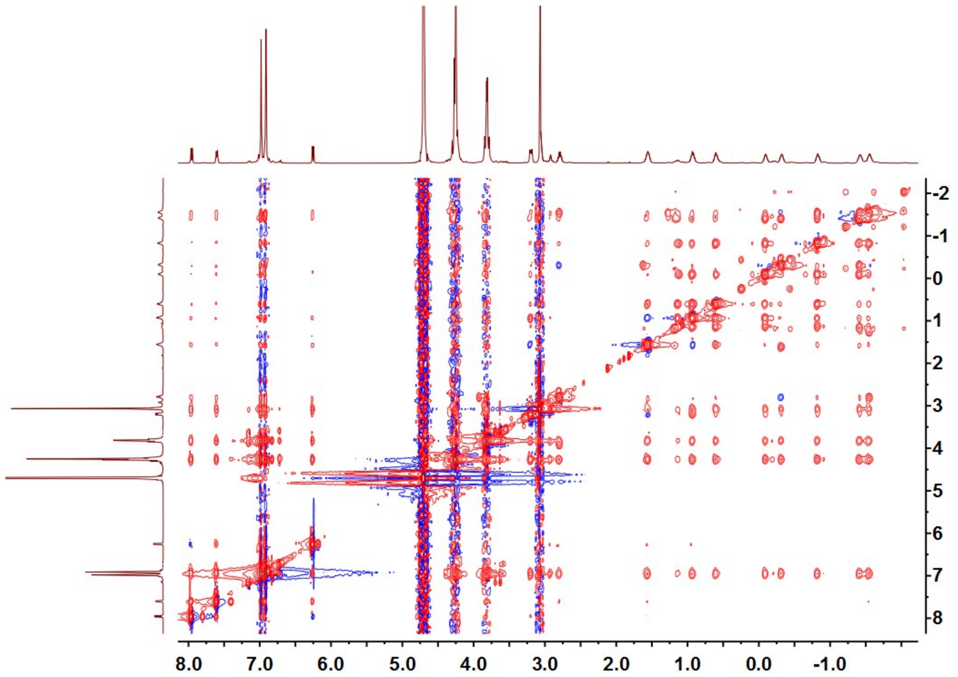


Fig. S7 2D NOESY NMR spectrum of spectrum of a solution of **WP5** (10.0 mM) and **G** (10.0 mM).

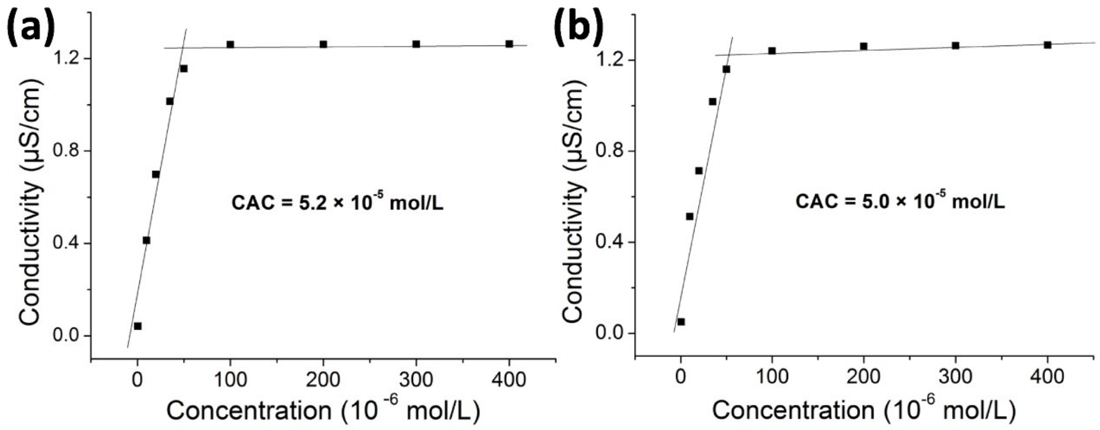


Fig. S8 (a) Conductivity as a function of the concentration of **WP5⊃G** before UV-irradiation. There are two linear segments in the curve and a sudden reduction of the slope, implying that the critical aggregation concentration (CAC) of **WP5⊃G** before UV-irradiation is approximately 5.2 × 10^{-5} M; (b) Conductivity as a function of the concentration of **WP5⊃G** after UV-irradiation. There are two linear segments in the curve and a sudden reduction of the slope, implying that the critical aggregation concentration (CAC) of **WP5⊃G** after UV-irradiation is approximately 5.0 × 10^{-5} M.

References

S1 (*a*) T. Ogoshi, S. Kanai, S. Fujinami, T. A. Yamagishi, Y. Nakamoto, *J. Am. Chem. Soc.* 2008, **130**, 5022; (*b*) G. Yu, M. Xue, Z. Zhang, J. Li, C. Han, F. Huang, *J. Am. Chem. Soc.* 2012, **134**, 13248.